International comparison CCQM-K112 Biogas

Final Report

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Field

Amount of substance

Subject

Composition of biogas (track C key comparison)

1 Introduction

Biogas is of increasing importance world wide as an energy vector. It presents an environmentally friendly alternative to natural gas and contributes to reduction of the emission of greenhouse gases from fossil fuels. The two mainstream approaches for producing biogas are fermentation and the gasification of biomass.

This key comparison is about the macro composition of biogas from fermentation. Such biogas is mainly composed of methane, nitrogen, and carbon dioxide, and also contains smaller fractions of oxygen and hydrogen. In some of these biogases, also ethane and propane are found, typically at an amount fraction levels in the 100s of ppm (parts-per-million).

The most commonly used methods for determining the calorific value of biogas involve the (gas chromatographic) determination of the composition, followed by the calculation of the calorific value. The same applies to the density of biogas, which plays a key role in the conversion of the volume of gas from actual (metering) conditions to reference conditions.

The key comparison aims to support calibration and measurement capabilities (CMCs) for the composition of biogas obtained by fermentation and from landfills.

The evaluation of the results of this key comparison was done using a consensus value. For the different measurands (i.e., the amount fractions of methane, carbon dioxide, nitrogen, hydrogen, oxygen, ethane and propane), different statistical approaches to obtain a consensus value were used. In the calculation of the consensus value, effects of the (small) differences in properties of the transfer standards were taken into account.

2 Design and organisation of the key comparison

2.1 Participants

Table 1 lists the participants in this key comparison.

Table 1: Participating national metrology institutes in CCQM-K112

Acronym	Country	Institute
CEM	ES	Centro Español de Metrología, Madrid, Spain
CMI	CZ	Český Metrologický Institut, Praha, Czech Republik
INMETRO	BR	Instituto Nacional de Metrologia, Qualidade e Technologia, Xerém RJ, Brasil
BFKH[a]	HU	Government Office of the Capital City Budapest, Budapest, Hungary
NPL	GB	National Physical Laboratory, Teddington, United Kingdom
SMU	SK	Slovak Institute of Metrology, Bratislava, Slovak Republic
RISE	SE	RISE Research Institutes of Sweden, Borås, Sweden
UME	TR	TÜBİTAK Ulusal Metroloji Enstitüsü, Gebze/KOCAELİ, Turkey
VNIIIM	RU	D.I. Mendeleyev Institute for Metrology, St Petersburg, Russia
VSL	NL	Van Swinden Laboratorium, Delft, The Netherlands

[a] During the comparison the name of Hungarian institute changed from MKEH (Hungurian Trade Licencing Office) to BFKH (Government Office of the Capital City Budapest).

2.2 Measurement standards

A set of gravimetrically prepared mixtures was obtained from an external party. The nominal composition of the mixtures is within the following ranges (see table 2). The pressure in the cylinders was approximately 70 bar; aluminium cylinders having a 5 L water volume were used. These gas mixtures were assessed for homogeneity and stability by the coordinating laboratory.

The assessment involved two measurements before dispatch and four measurements after return of the cylinders to the coordinating laboratory. for methane, carbon dioxide, nitrogen and hydrogen. For ethane and propane, only three measurements were taken after return of the cylinders to the coordinating laboratory. An overview of the dates of measurements is given in table 3. The measurements performed by the participating national metrology institute were performed between measurements 2 and 3. The link between cylinder code and participant is presented in annex A, tables 16–22.

Table 2: Specifications for the transfer standards

Component	Amount fraction x ($\mathrm{cmol\,mol^{-1}}$)
Methane	40 – 56
Carbon dioxide	36 – 42
Nitrogen	12 – 16
Hydrogen	0.8 – 1.2
Oxygen	0.3 – 0.6
Ethane	0.02 – 0.08
Propane	0.005 – 0.020

Table 3: Dates of measurement of the suite of measurement standards

Measurement number	Major components	Ethane and propane
1	2014-12-05	2014-12-11
2	2014-12-16	2014-12-18
Measurements by participants		
3	2015-11-16	2015-11-24
4	2015-11-27	2015-11-30
5	2015-12-02	2015-12-04
6	2016-06-13	—

2.3 Measurement protocol

The measurement protocol requested the participating national metrology institutes to perform at least 3 measurements, each with its own calibration. The 5 replicates, leading to a measurement, were to be carried out under repeatability conditions. The protocol informed the participants also about the nominal concentration 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 estimating the uncertainty of their result.

2.4 Schedule

The schedule of this key comparison was as follows (table 4).

Table 4: Schedule for CCQM-K112

Date	Event
December 2013	Agreement of draft protocol
February 2014	Registration of participants
April 2014	Preparation of mixtures
May 2014-February 2015	Characterisation of mixture compositions
March 2015	Dispatch of mixtures
June 2015	Reports and cylinder arrived at VSL
September 2015	Re-characterisation of the mixtures
March 2017	Draft A report available
March 2019	Draft B report available

2.5 Assessment of the transfer standards

The transfer standards have been analysed as detailed in table 3. These data have been 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).

The measurements have been performed on two instruments:

1. GC/FID for propane and ethane; Agilent 7980A with $10' \times 1/8''$ Sulfinert Molsieve 5A column and a flame ionization detector (FID);
2. GC/TCD for methane, carbon dioxide, nitrogen, hydrogen and oxygen; Agilent 7980A with pre-column HayeSep Q and HayeSep T and a thermal conductivity detector (TCD). Helium as carrier, carbon dioxide and methane are determined. Hayesep/Molsieve column equipped with TCD and argon as carrier gas was used to determine hydrogen, oxygen and nitrogen.

The GCs have been calibrated with a suite of 5 Primary Standard gas Mixtures (PSMs), prepared in accordance with ISO 6142-1 [1]. The purity analysis of the materials used was done in accordance with ISO 19229 [2]. For the measurements before shipment and those after return of the transfer standards, the same calibration function has been used. The sixth measurement on the GC/TCD has been done using a new calibration function, using the same suite of PSMs. The errors-in-variables regression has been performed in accordance with ISO 6143 [3]. A calibration function was only accepted if the goodness-of-fit, as required by ISO 6143, did not exceed a value of 2. For all components, a quadratic polynomial has been used, satisfying the goodness-of-fit criterion.

The values of the amount fractions have been obtained using the calibration function. The assigned value for the amount fraction of a component is obtained by using the calibration function and using the bisection algorithm [4] to find for a response A_0 the corresponding amount fraction x_0

$$A_0 = f(x_0; \boldsymbol{a}) \tag{1}$$

where f denotes the calibration function, $\boldsymbol{a}$ the vector holding the coefficients of the calibration function, and A_0 the instrument response, calculated as peak area ratio.

Using the law of propagation of uncertainty of GUM Supplement 2 (GUM-S2) [5], the standard uncertainty associated with x_0 can be computed as [6]

$$u(x_0) = \left(\left[\frac{\partial f(x; \boldsymbol{a})}{\partial x} \right]^{-2} \left[u^2(A_0) + \boldsymbol{C} \boldsymbol{U_a} \boldsymbol{C}^{\mathsf{T}} \right] \right)^{\frac{1}{2}} \tag{2}$$

where $\boldsymbol{U_a}$ denotes the covariance matrix associated with the vector of the coefficients of the calibration function, and $\boldsymbol{C} = (1, x, x^2)$, evaluated at $x = x_0$. These calculations have been performed using VSL's own software [7].

Based on the data thus obtained, it was concluded that there were no stability issues (see for a discussion section 3.1). Hence, to obtain a representative for the amount fraction of the components in each transfer standard, the six (five for ethane and propane) amount fractions were converted into a mean value using meta-analysis. This method would also include in the uncertainty evaluation a reproducibility effect. The amount fraction ξ is obtained by fitting the data to the following equation

$$x_i = \xi + B_i + \epsilon_i \tag{3}$$

where x_i denotes the amount fraction of a component in a transfer standard of measurement i, ξ the mean value, B_i a bias term modelling the reproducibility effect and ϵ_i a random error term. The calculation of the amount fractions in the transfer standards has been performed using equation (3). As model, the DerSimonian-Liard model (DL) [8] was chosen. The calculations were performed using R [9] and the metafor package [10] that implements many models from meta-analysis under which the DL.

The results obtained from this calculation are shown in figures 8 and 9 in section 3.3. Based on these results, it was decided to establish the key comparison reference value (KCRV) as the consensus value of the laboratory results, and to use the results from the homogeneity and stability study to establish corrections to the amount fractions due to the differences in the composition of these mixtures. A fixed effects model was used [11, 12] to obtain the corrections as

$$\Delta x_j = x_j - \bar{x}$$

where $\bar{x}$ denotes the arithmetic mean. The standard uncertainty of the correction to the amount fraction Δx_j was taken to be the amount fraction computed for x_j from the DL in the previous step (in that model, see equation 3, x_j appears as ξ).

2.6 Measurement equation

The calculation of the KCRV for the amount fractions of the seven components was performed as follows. A priori three alternatives were considered

1. the weighted mean, if the dataset was homogeneous (also known as "procedure A" [13]);
2. the median, if the dataset was heterogeneous (also known as "procedure B" [13]
3. the largest consistent subset (LCS) in combination with the weighted mean, if the dataset was heterogeneous [14]

As a component-by-component approach was chosen, it was decided that the evaluation procedure could differ from component to component. The datasets were generally not homogeneous (see for a discussion section 3.1). The root cause of the heterogeneity was deemed to be different for the various components. As the amount fractions of nitrogen, carbon dioxide and methane had also been subject of several key comparisons on natural gas [15–18] already, it was deemed appropriate to consider the discrepant results as being caused by a flaw in the measurement. For these components, the LCS was used. For the other component fractions, such experience did not exist, and it was assumed that discrepancies would arise from, among others, understating the measurement uncertainty. For these components, procedure B using the median as KCRV was used.

The LCS for nitrogen, carbon dioxide, and methane were formed manually, after applying the correction to the amount fraction as reported by the participant as discussed previously. Applying this correction precludes eliminating results because of differences in the composition of the transfer standards. The largest consistent subset (LCS) [14] was formed by removing one by one the most discrepant result, i.e., the result that contributed most to the value of χ^2 as defined in procedure A [13]. This process was repeated until a dataset was obtained satisfying the χ^2 criterion as described in procedure A. In none of the datasets there was any ambiguity concerning the set of results that formed the largest consistent subset.

When applying procedure B, also first the correction due to batch inhomogeneity was applied to the measurement results stated by the participants. Using the Monte Carlo method of GUM Supplement 1 (GUM-S1) [19]. The Monte Carlo method was implemented in R [9] using 1 000 000 Monte Carlo trials. The amount fractions of the participants were assigned normal distributions with as mean the amount fraction after correction and as standard deviation the standard uncertainty as reported by the NMI, combined with the standard uncertainty from the correction for batch inhomogeneity.

2.7 Measurement methods used by the participants

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

Table 5: Overview of calibration methods and metrological traceability

Laboratory	Measurement dates	Calibration method	Traceability	Matrix	Measurement technique
CEM	24/29/30 July 2015 and 07/10/11/12 August 2015	Multipoint calibration (3 standards)	Own standards (ISO 6142)	Methane	GC/TCD/FID Paramagnetic
CMI	27 August 2015 and 12/14 October 2015	Multipoint calibration (3 standards)	Own standard	Methane	GC/TCD/FID
INMETRO	13/15 May 2015 and 17/19 May 2015 and 09/23 June 2015 and 16/24 June 2015 and 24/25 June 2015	ISO 6143	Own standards (ISO 6142) and 3 NPL standards	Methane	GC/TCD/FID
BFKH	29/30/31 July 2015	Matching standard	Own standard	Methane	GC/TCD/FID
NPL	22/23 July 2015 and 03/04/05 August 2015	Bracketing	Own standard	Methane	GC/TCD/FID
SMU	04/11/18/23/24/25 March 2015 and 02/09/10 April 2015	ISO 6143	Own standards	Nitrogen, methane and helium	GC/TCD/FID
RISE	05/11/12 March 2015	Bracketing	NPL standards	Unknown	GC/TCD/FID
UME	27 May 2015 and 02/03/20/21 June 2015	Multipoint calibration (3 standards)	Own standards	Methane	GC/TCD/FID
VNIIIM	01/02/03 July 2015	Matching standard	Own standards	Methane	GC/TCD/FID
VSL	24/25/27/31 August 2015 and 04/08 September 2015	ISO 6143	Own standards (ISO 6142)	Methane	GC/TCD/FID

2.8 Degrees of equivalence

The unilateral degree-of-equivalence for laboratory i is defined as

$$d_i = x_{\mathrm{lab},i} - x_{\mathrm{KCRV},i} \tag{4}$$

and its associated expanded uncertainty. In case of applying the LCS, the uncertainty calculation was performed in accordance with procedure A [13].

The KCRV for transfer standard i is obtained as $x_{\mathrm{KCRV},i} = x_{\mathrm{KCRV}} + \Delta x_i$, where the correction Δx_i is made for the difference in amount fraction between the transfer standards.

In case of procedure B, the uncertainty calculation was embedded in the implementation of the Monte Carlo method. The expanded uncertainty was computed as the half-width of the 95 % coverage interval. The coverage factor was computed as the ratio of the expanded and standard uncertainty.

3 Results

3.1 Stability assessment

The results from the analysis of the transfer standards before shipment and after their return are given in figures 1 through 7. The relationship between the identifications of the gas mixtures and the participants is given in annex A, tables 16–22. The values and standard uncertainties used in these calculations are also given in annex A, tables 23–29.

Based on these results, the amount fraction was considered to be stable. The mean value as obtained from fitting the DL is denoted in the figures by the solid line; the dotted lines are giving the boundaries of the 95 % coverage interval.

From the figures 1 through 7, it is readily seen that the batch homogeneity for methane (figure 1) and hydrogen (figure 4) for instance is rather good, but that for other components, such as nitrogen (figure 2), carbon dioxide (figure 3) and oxygen (figure 5) there are substantial differences to the mean value assigned to the amount fraction of these components.

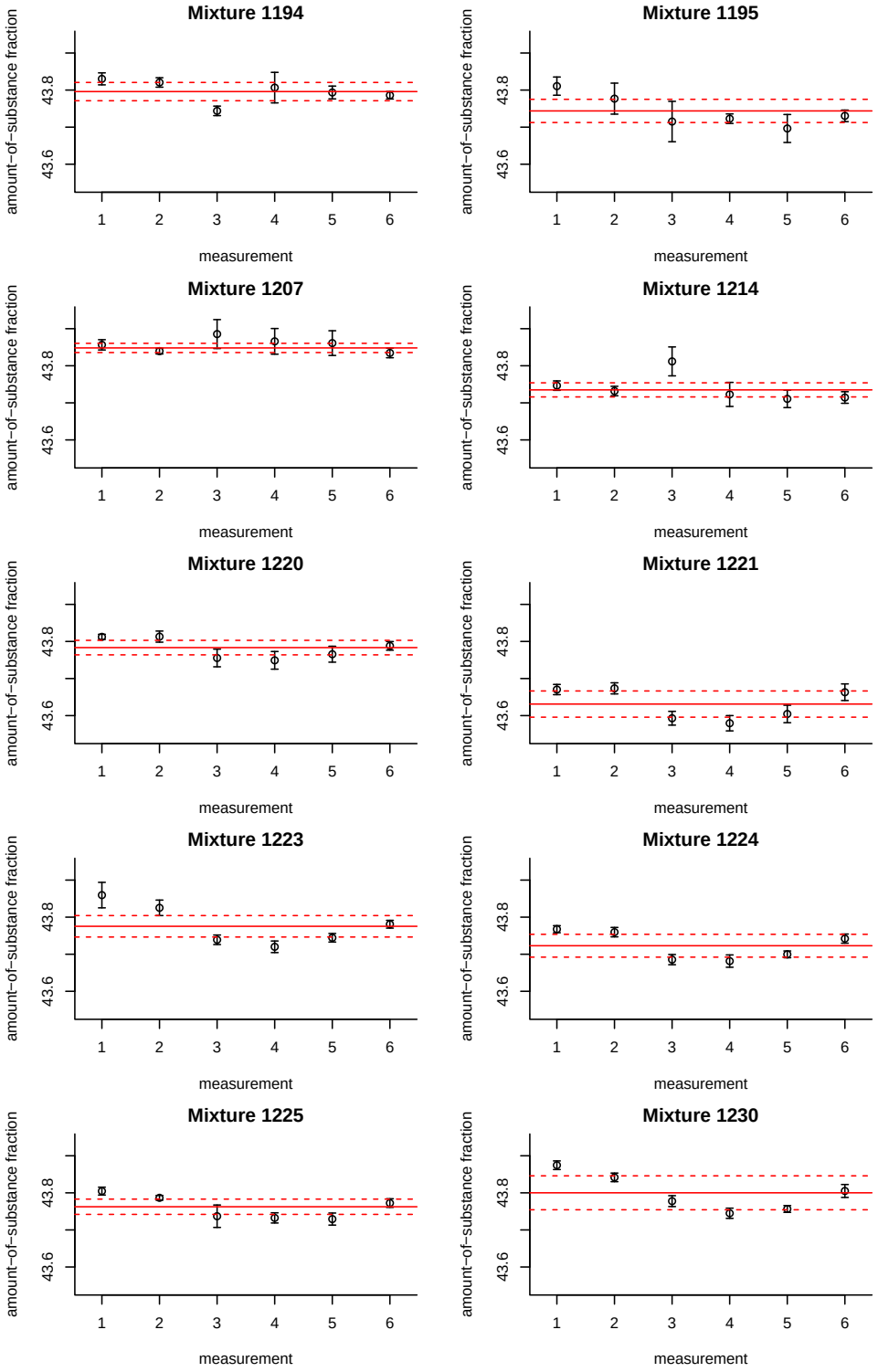


Figure 1: Results of the analysis of the transfer standards before shipment to the participants and after return to the coordinating laboratory for methane

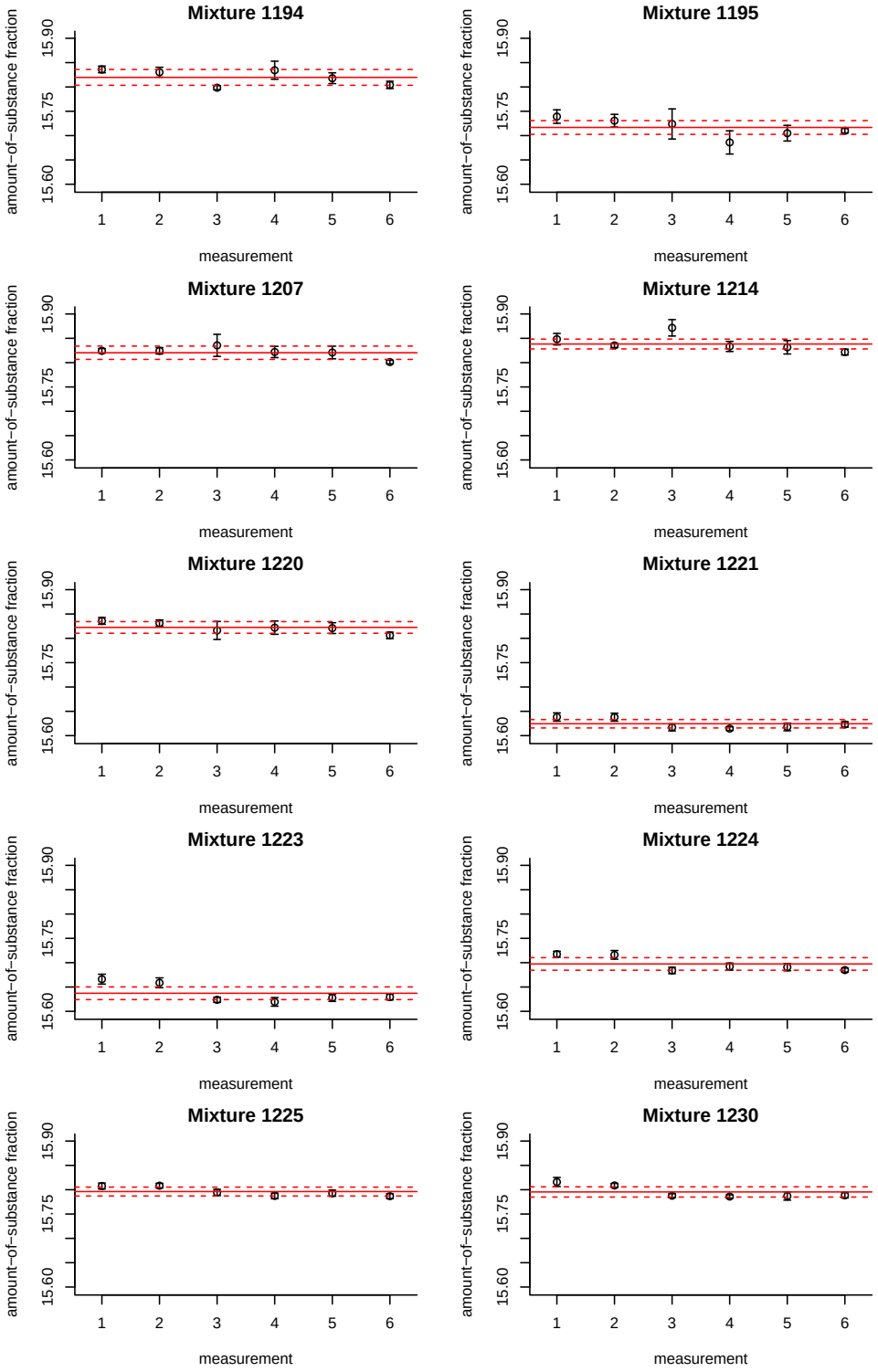


Figure 2: Results of the analysis of the transfer standards before shipment to the participants and after return to the coordinating laboratory for nitrogen

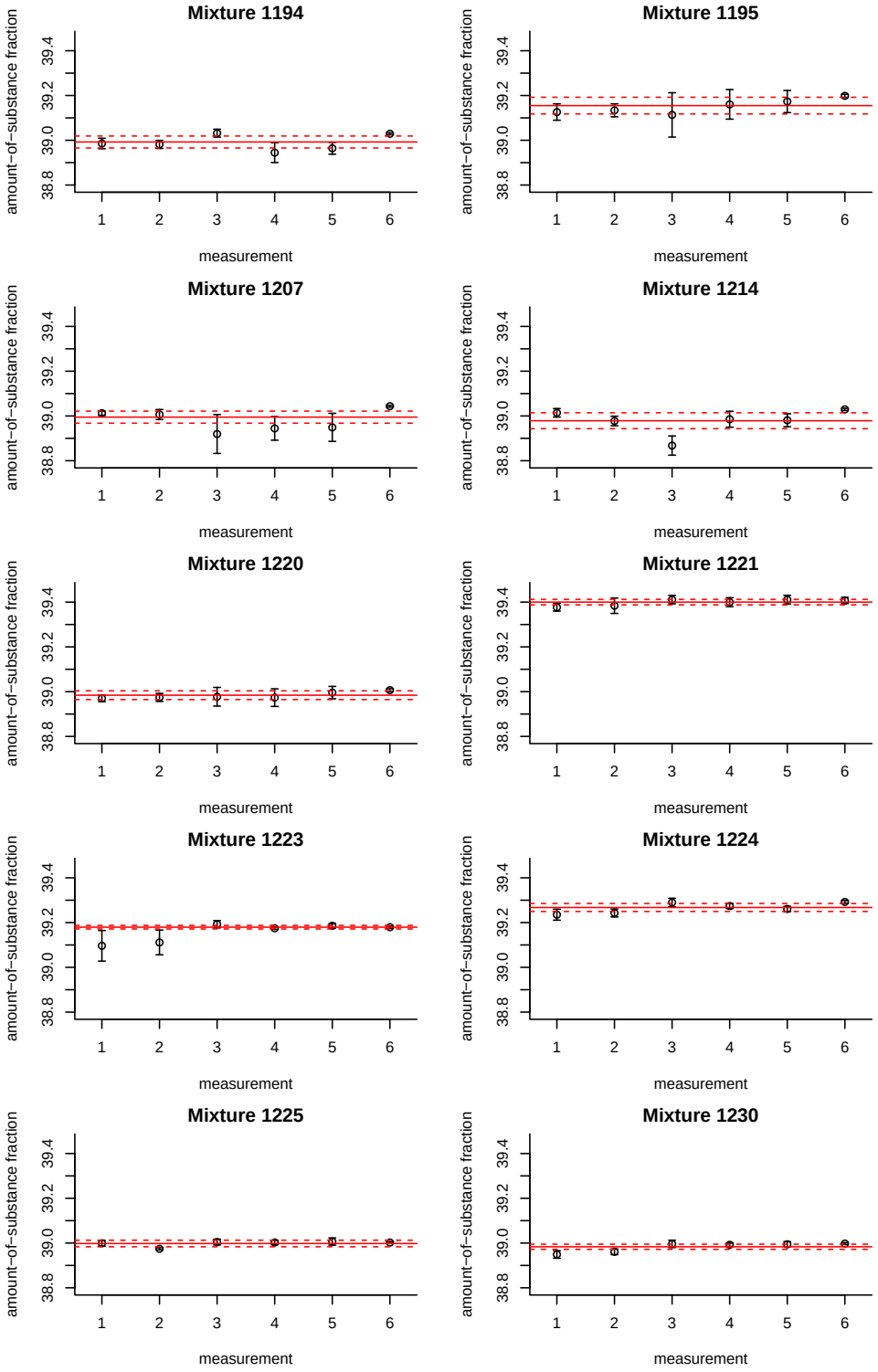


Figure 3: Results of the analysis of the transfer standards before shipment to the participants and after return to the coordinating laboratory for carbon dioxide

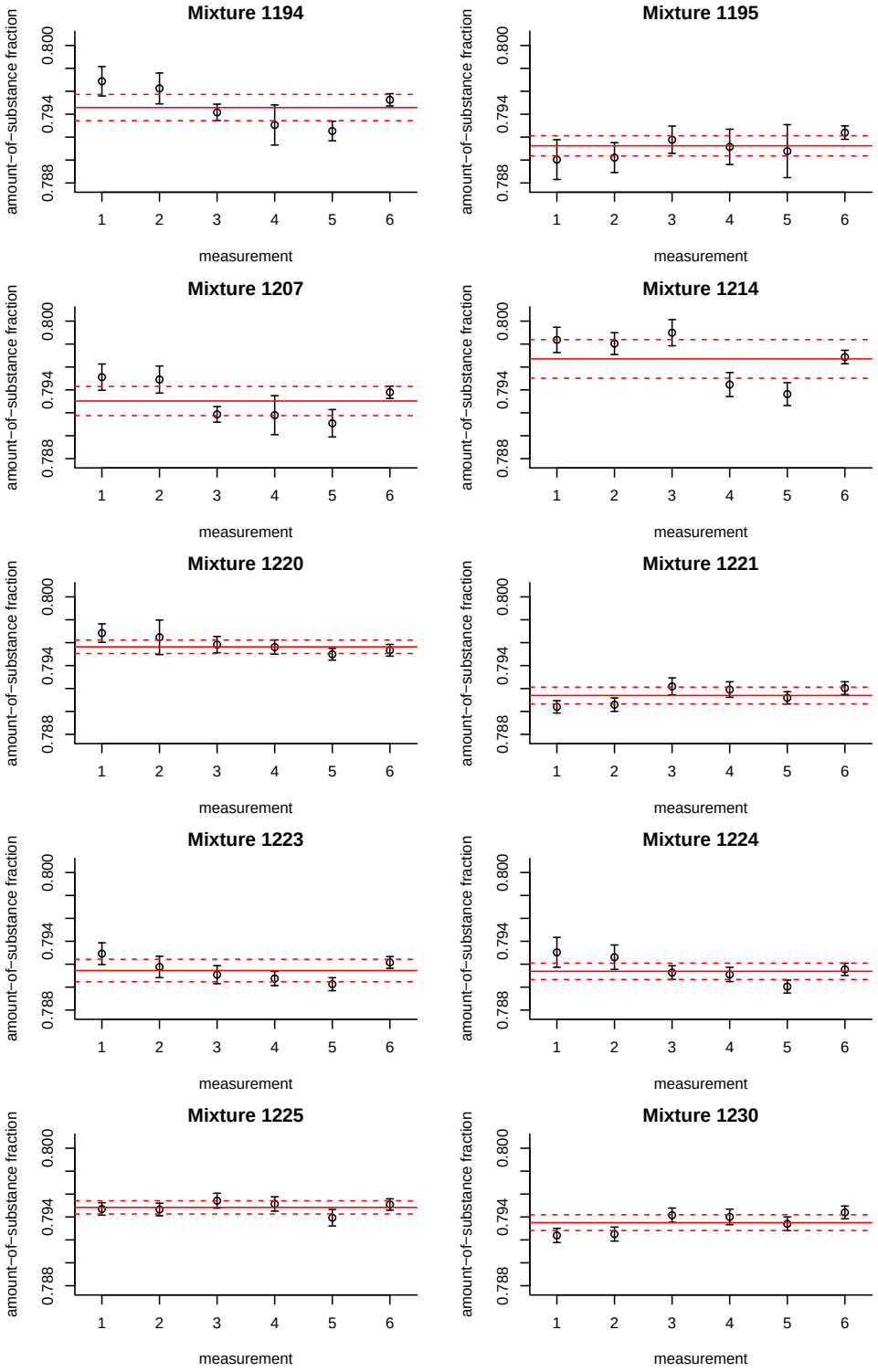


Figure 4: Results of the analysis of the transfer standards before shipment to the participants and after return to the coordinating laboratory for hydrogen

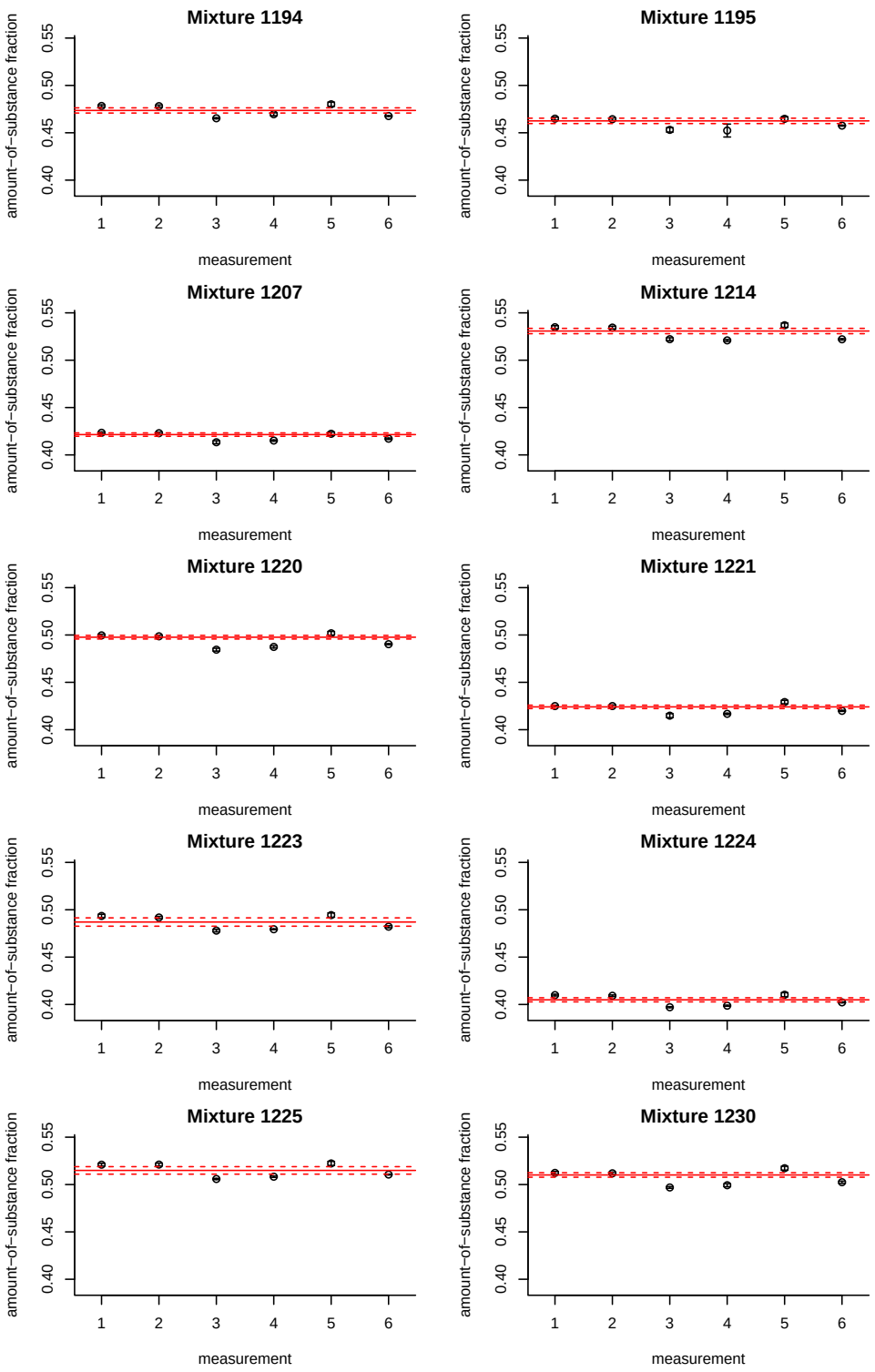


Figure 5: Results of the analysis of the transfer standards before shipment to the participants and after return to the coordinating laboratory for oxygen

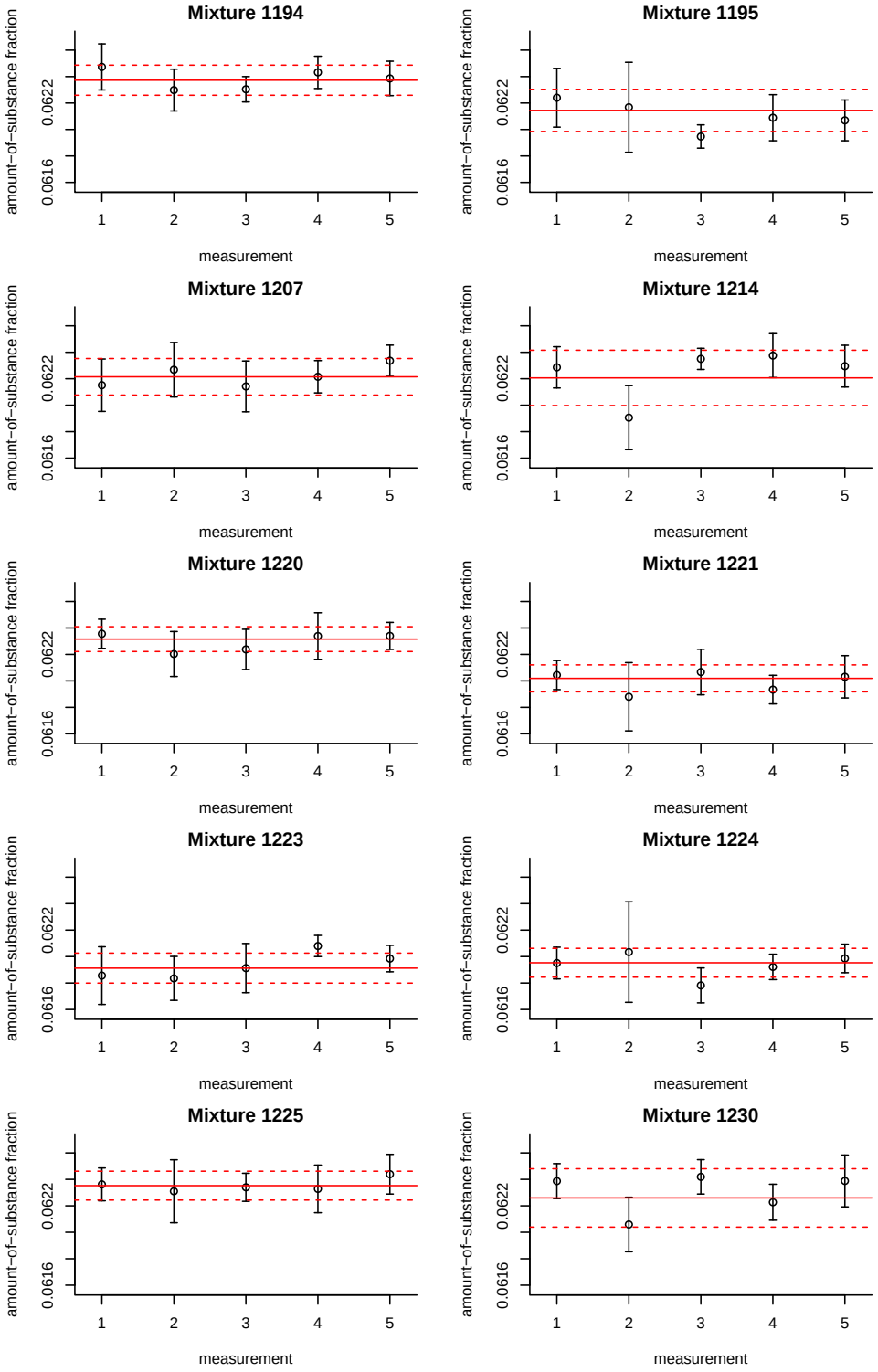


Figure 6: Results of the analysis of the transfer standards before shipment to the participants and after return to the coordinating laboratory for ethane

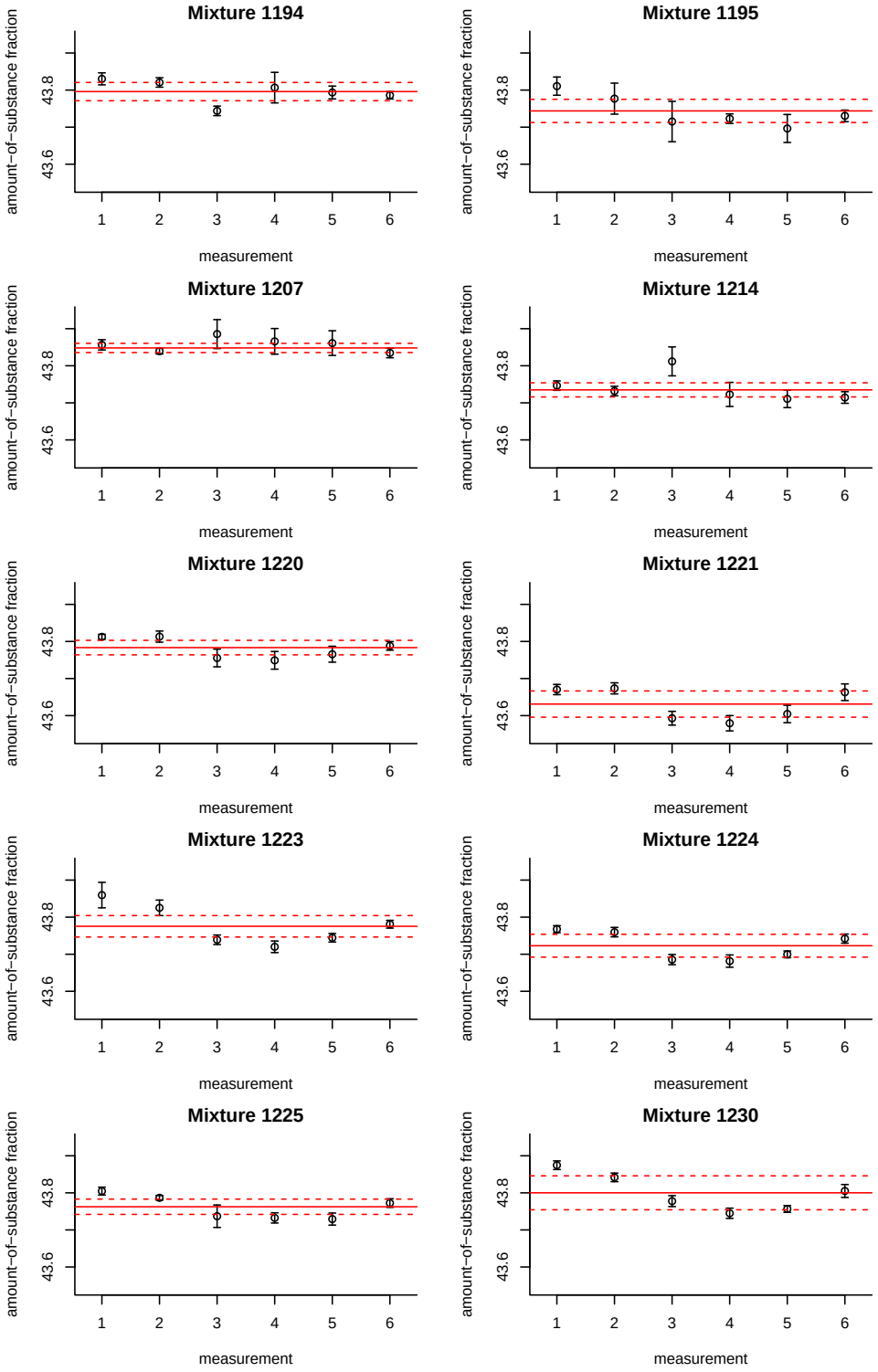


Figure 7: Results of the analysis of the transfer standards before shipment to the participants and after return to the coordinating laboratory for propane

3.2 Comparison of the results on the transfer standards

In figures 8 and 9, the results from the analyses discussed in section 3.1 have been plotted alongside the results reported by the participants. The latter are given in annex B and summarised in annex A, tables 16-14. The error bars show expanded uncertainties. The solid lines indicate the KCRV obtained using procedure B (see also table 7); the dotted lines indicate the 95 % coverage interval of the KCRV.

For oxygen (figure 8e) and to a lesser extent carbon dioxide (figure 8c), there seems to be a systematic difference between the results from the assessment of the transfer standards and the results of the participants (that is, leaving aside some incidental discrepant results). At the same time, it should be noted that these deviations are substantially smaller than the discrepancies in the datasets from the participants.

For the other components, the results generally agree well. In those instances, it is readily seen that there is a strong correlation between the results.

3.3 Calculation of corrections due to between-bottle inhomogeneity

From the results shown in figures 8 and 9, corrections have been calculated to the amount fractions due to batch inhomogeneity, using a fixed effects model. The corrections are shown in figures 10 and 11. The error bars represent standard uncertainties. These values have been summarised in annex A, tables 16 to 22. For many of the components and mixtures, these corrections are significant. These corrections have been applied to the laboratory results before applying procedure B to compute the KCRV and the degrees-of-equivalence.

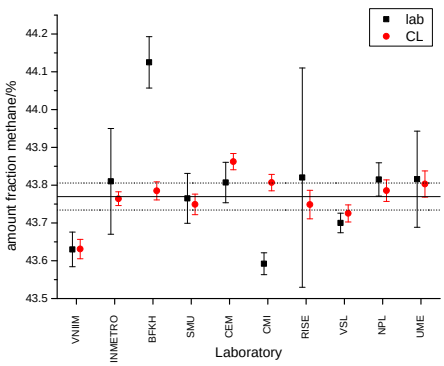
3.4 Degrees-of-equivalence

An overview of the largest consistent subsets is given in table 6. From this table, it is readily seen that applying this approach to all datasets leads to a strong reduction in size of some of the datasets, especially those of oxygen (only 5 results left) and propane (only 6 results left).

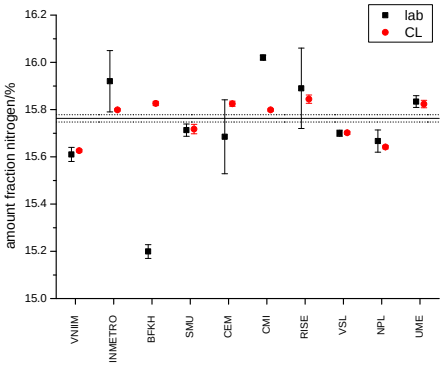
Table 6: Largest consistent subsets for the components in the mixtures; "X" denotes included in the subset, "–" denotes excluded from the subset

	CH_4	CO_2	N_2	H_2	O_2	C_2H_6	C_3H_8	Total
VNIIM	X	X	X	X	X	X	–	6
INMETRO	X	X	X	–	–	X	X	5
BFKH	–	–	–	–	–	X	X	2
SMU	X	X	X	X	X	X	X	7
CEM	X	X	X	X	–	X	–	5
CMI	–	X	–	X	X	X	X	5
RISE	X	X	X	X	–	X	X	6
VSL	X	X	X	X	X	X	X	7
NPL	X	X	X	–	X	X	–	5
UME	X	X	X	X	–	X	–	5
Total	8	9	8	7	5	10	6	

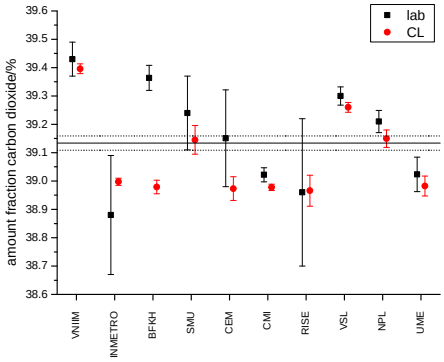
For comparison purposes, the LCS have been used to compute consensus values for the amount fractions methane, carbon dioxide, nitrogen, and ethane. For the other components, datasets larger than the LCS were used, as the LCS was considered to be unrepresentative for the data reported in this key comparison. For hydrogen, INMETRO and BFKH were removed from the dataset. For oxygen, BFKH, CEM, and UME were removed from the dataset. In the case of propane, VNIIM and UME were removed. For those (reduced) datasets that were not consistent, the DL has been used to compute the consensus value,



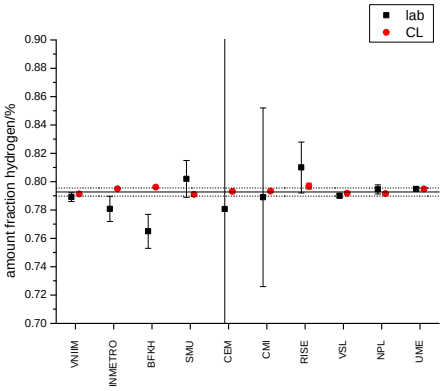
(a) Methane



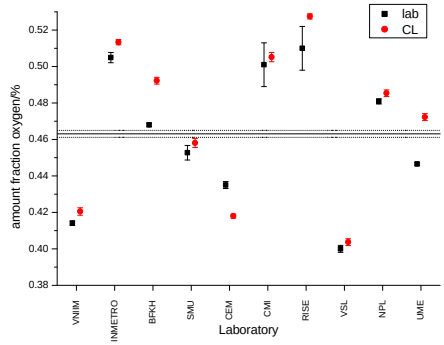
(b) Nitrogen



(c) Carbon dioxide

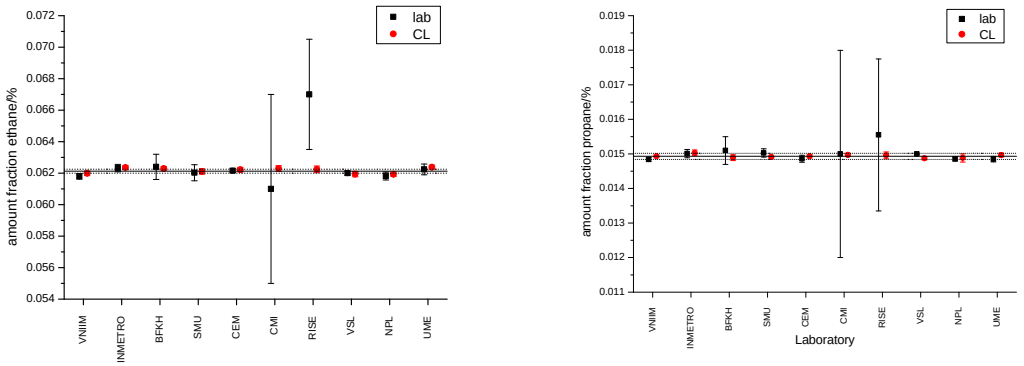


(d) Hydrogen



(e) Oxygen

Figure 8: Comparison between the results obtained from the homogeneity and stability study of the transfer standards and the participants for methane, carbon dioxide, nitrogen, hydrogen and oxygen. The solid line represents the KCRV and the dotted lines its 95 % coverage interval



(a) Ethane

(b) Propane

Figure 9: Comparison between the results obtained from the homogeneity and stability study of the transfer standards and the participants for ethane and propane. The solid line represents the KCRV and the dotted lines its 95 % coverage interval

including an uncertainty contribution for the excess dispersion of the data. The values $\bar{x}$ and associated standard uncertainties $u(\bar{x})$ are given in table 7 in the second and third columns.

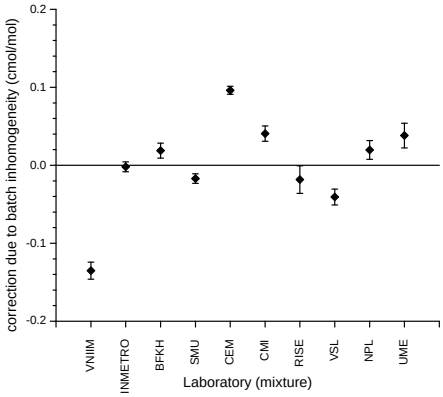
The key comparison has eventually been evaluated using procedure B [13] with the median as KCRV. The KCRV x_{KCRV} and its associated standard uncertainty $u(x_{\mathrm{KCRV}})$ are given in table 7 in the fourth and fifth columns. In figures 8 and 9, the KCRVs and their 95 % coverage intervals are shown alongside the reported results by the participants.

Table 7: Consensus values based on selected results from participants and the key comparison reference values as computed using procedure B using the median, expressed as amount fractions ($\mathrm{cmol\,mol^{-1}}$)

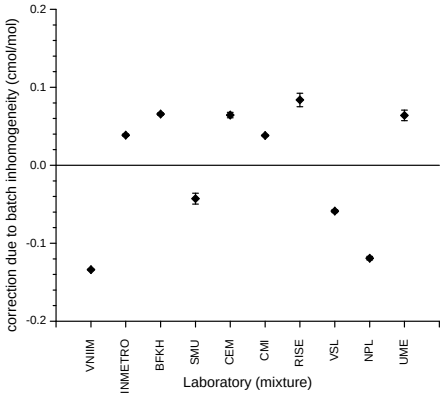
Lab	LCS/Excess		Procedure B	
Component	$\bar{x}$	$u(\bar{x})$	x_{KCRV}	$u(x_{\mathrm{KCRV}})$
Methane	43.75521	0.00888	43.76990	0.01780
Carbon dioxide	39.12853	0.00799	39.13397	0.01247
Nitrogen	15.75998	0.00483	15.76297	0.00776
Hydrogen	0.79630	0.00310	0.79270	0.00141
Oxygen	0.46270	0.00200	0.46308	0.00095
Ethane	0.06213	0.00012	0.06213	0.00006
Propane	0.01495	0.00005	0.01493	0.00004

In figures 12-18 the degrees of equivalence for all participating laboratories are given relative to the KCRV as obtained from procedure B. These degrees-of-equivalence are calculated from the amount fractions reported by the laboratories, after correction for batch inhomogeneity. The corrected results (x'_{lab} and $u(x'_{\mathrm{lab}})$) are given in tables 8–14. The reported results from which these have been calculated are given in annex A, tables 16–22. These corrections are necessary as each NMI received its own transfer standards, and for most components, a part of the dispersion of the results can be explained from differences in the composition of the transfer standards. After applying this correction, the results can be used for calculating the KCRV.

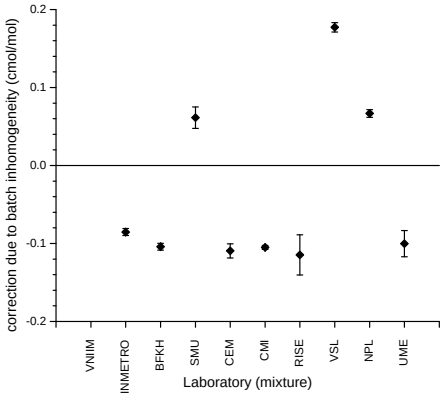
Another way of putting it is to say that each transfer standard has for each component its own KCRV, just as in other key comparisons in this area [15–18]. The only difference is that in the natural gas key comparisons so far an independent value, calculated from gravimetric gas mixture preparation has been



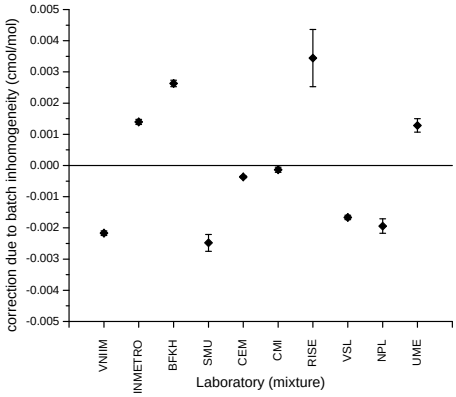
(a) Methane



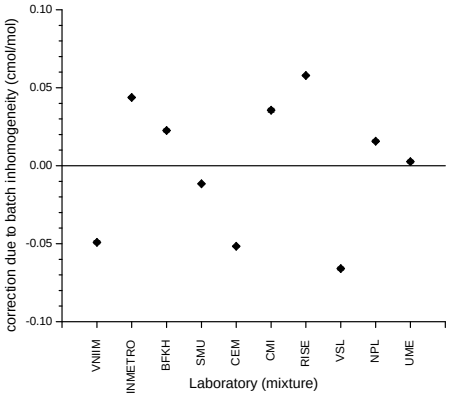
(b) Nitrogen



(c) Carbon dioxide

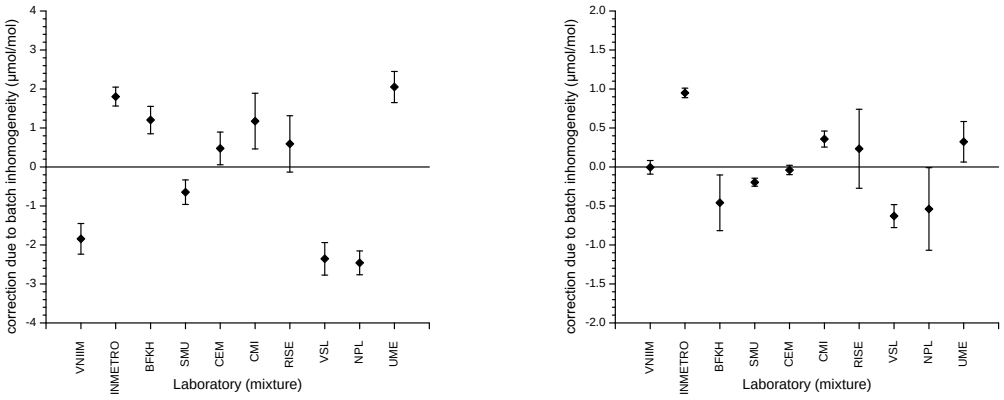


(d) Hydrogen



(e) Oxygen

Figure 10: Corrections due to batch inhomogeneity for the amount fractions for methane, carbon dioxide, nitrogen, hydrogen and oxygen



(a) Ethane (b) Propane

Figure 11: Corrections due to batch inhomogeneity for the amount fractions ethane and propane

used, whereas in this key comparison a consensus value is used as KCRV, with for each transfer standard and component an individual correction due to the observed differences in the amount fraction of the components (see sections 3.1 and 3.3).

The uncertainties of the degrees-of-equivalence are, as required by the MRA [20], given as 95 % coverage intervals. These intervals have been computed as probabilistically-symmetric coverage intervals from the output of the Monte Carlo method applied in procedure B [13]. The standard uncertainty of the corrected laboratory results was obtained by combining the standard uncertainty of the laboratory result with the standard uncertainty of the correction for the amount fraction of the component and the transfer standard used. For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty (stated at a confidence level of 95 %) from the laboratory was divided by the reported coverage factor, which in all cases was $k = 2$.

For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor $k = 2$ was used throughout. For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty (stated at a confidence level of 95 %) from the laboratory was divided by the reported coverage factor, which in all cases was $k = 2$ (see also tables 8-14).

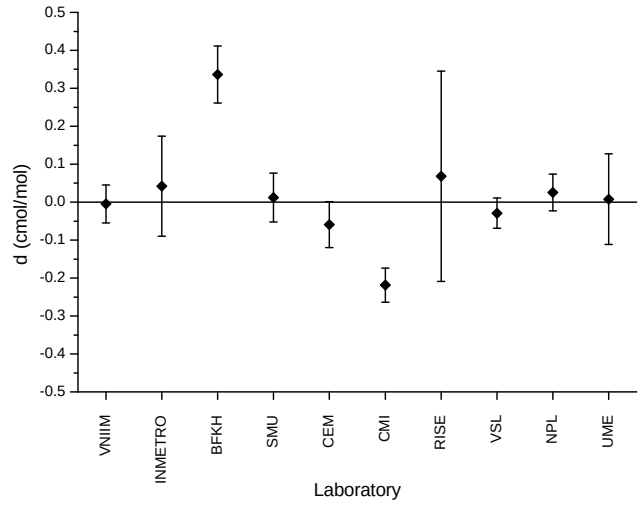


Figure 12: Degrees-of-equivalence for methane

Most of the results reported by the participants agree with the reference value (see figure 12). The data reported by the participants are not completely internally consistent. The results of the degrees-of-equivalence calculation are summarised in table 8.

Table 8: Corrected amount fraction of methane from the participants (x'_{lab}), the associated standard uncertainty ($u(x'_{\mathrm{lab}})$), and the degree-of-equivalence (difference d, standard uncertainty $u(d)$, and expanded uncertainty ($U(d)$)) ($\mathrm{cmol\,mol^{-1}}$)

Lab	x'_{lab}	$u(x'_{\mathrm{lab}})$	d	$u(d)$	$U(d)$
VNIIM	43.765	0.023	-0.005	0.024	0.050
INMETRO	43.812	0.070	0.042	0.066	0.132
BFKH	44.106	0.034	0.336	0.038	0.075
SMU	43.782	0.033	0.012	0.031	0.064
CEM	43.711	0.027	-0.059	0.031	0.060
CMI	43.551	0.015	-0.219	0.023	0.045
RISE	43.838	0.145	0.068	0.140	0.277
VSL	43.741	0.013	-0.029	0.021	0.040
NPL	43.795	0.022	0.025	0.025	0.048
UME	43.778	0.064	0.008	0.059	0.119

In the data for carbon dioxide (see figure 13), there is only one result not agreeing with the reference value. The results of the degrees-of-equivalence calculation are summarised in table 9.

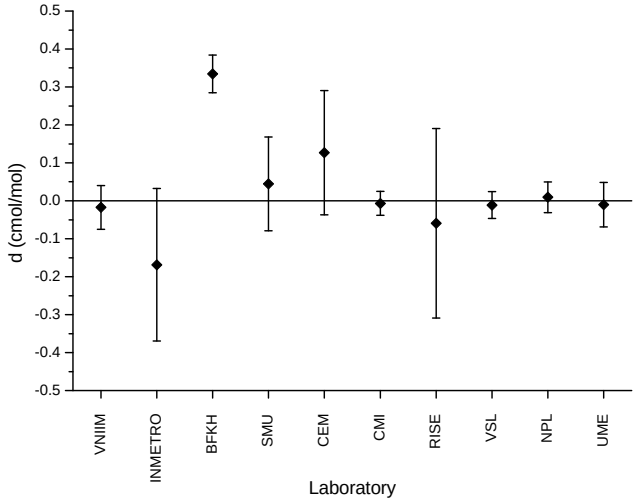


Figure 13: Degrees-of-equivalence for carbon dioxide

Table 9: Corrected amount fraction of carbon dioxide from the participants (x'_{lab}), the associated standard uncertainty ($u(x'_{\mathrm{lab}})$), and the degree-of-equivalence (difference d, standard uncertainty $u(d)$, and expanded uncertainty ($U(d)$)) (cmol mol^{-1})

Lab	x'_{lab}	$u(x'_{\mathrm{lab}})$	d	$u(d)$	$U(d)$
VNIIM	39.117	0.030	-0.017	0.029	0.058
INMETRO	38.965	0.105	-0.168	0.104	0.201
BFKH	39.468	0.022	0.334	0.025	0.050
SMU	39.179	0.065	0.045	0.063	0.124
CEM	39.260	0.085	0.126	0.085	0.164
CMI	39.127	0.013	-0.007	0.015	0.032
RISE	39.075	0.130	-0.059	0.126	0.249
VSL	39.123	0.016	-0.011	0.018	0.036
NPL	39.143	0.020	0.009	0.020	0.040
UME	39.124	0.031	-0.010	0.029	0.059

The dataset for nitrogen is not entirely consistent. Most of the laboratories report a result that is consistent with the reference value (see figure 14). The degrees-of-equivalence are shown in table 10.

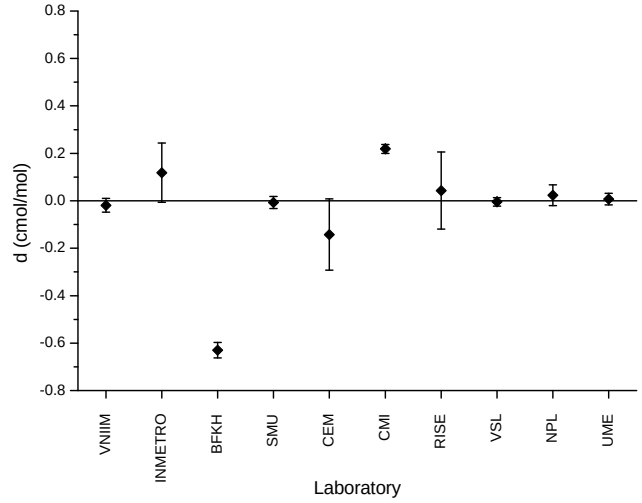


Figure 14: Degrees-of-equivalence for nitrogen

Table 10: Corrected amount fraction of nitrogen from the participants (x'_{lab}), the associated standard uncertainty ($u(x'_{\mathrm{lab}})$), and the degree-of-equivalence (difference d, standard uncertainty $u(d)$, and expanded uncertainty ($U(d)$)) (cmol mol^{-1})

Lab	x'_{lab}	$u(x'_{\mathrm{lab}})$	d	$u(d)$	$U(d)$
VNIIM	15.744	0.015	-0.019	0.016	0.029
INMETRO	15.881	0.065	0.118	0.065	0.125
BFKH	15.133	0.015	-0.630	0.016	0.032
SMU	15.756	0.013	-0.007	0.013	0.025
CEM	15.621	0.078	-0.142	0.078	0.151
CMI	15.982	0.006	0.219	0.010	0.019
RISE	15.806	0.085	0.043	0.082	0.163
VSL	15.759	0.007	-0.004	0.009	0.018
NPL	15.786	0.024	0.023	0.023	0.044
UME	15.770	0.012	0.007	0.012	0.024

The results for hydrogen (see figure 15) are more homogeneous than those for nitrogen and methane. All but two results are consistent with the reference value.

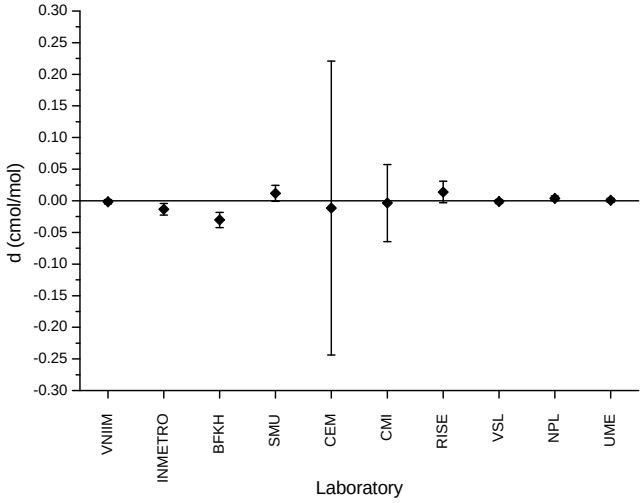


Figure 15: Degrees-of-equivalence for hydrogen

Table 11: Corrected amount fraction of hydrogen from the participants (x'_{lab}), the associated standard uncertainty ($u(x'_{\mathrm{lab}})$), and the degree-of-equivalence (difference d, standard uncertainty $u(d)$, and expanded uncertainty ($U(d)$)) ($\mathrm{cmol\,mol^{-1}}$)

Lab	x'_{lab}	$u(x'_{\mathrm{lab}})$	d	$u(d)$	$U(d)$
VNIIM	0.7913	0.0016	-0.0014	0.0018	0.0035
INMETRO	0.7794	0.0045	-0.0133	0.0047	0.0092
BFKH	0.7624	0.0060	-0.0303	0.0062	0.0121
SMU	0.8045	0.0065	0.0118	0.0065	0.0125
CEM	0.7811	0.1188	-0.0117	0.1181	0.2317
CMI	0.7891	0.0315	-0.0036	0.0309	0.0609
RISE	0.8066	0.0090	0.0138	0.0089	0.0170
VSL	0.7917	0.0007	-0.0010	0.0015	0.0030
NPL	0.7965	0.0016	0.0038	0.0020	0.0038
UME	0.7935	0.0007	0.0008	0.0015	0.0030

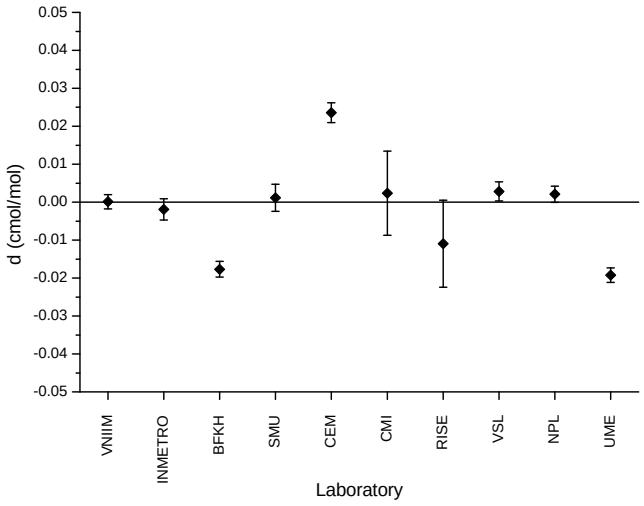


Figure 16: Degrees-of-equivalence for oxygen

The dataset for oxygen (see figure 16) is not very homogeneous. Furthermore, the reference value seems to be biased with respect to the majority of the reported results. The results of SMU, RISE, VNIIM, NPL, VSL, INMETRO and CMI form the largest consistent subset. The difference between the KCRVs and the consensus value is smaller than the dispersion of the results provided for the oxygen fraction.

Table 12: Corrected amount fraction of oxygen from the participants (x'_{lab}), the associated standard uncertainty ($u(x'_{\mathrm{lab}})$), and the degree-of-equivalence (difference d, standard uncertainty $u(d)$, and expanded uncertainty ($U(d)$)) ($\mathrm{cmol\,mol^{-1}}$)

Lab	x'_{lab}	$u(x'_{\mathrm{lab}})$	d	$u(d)$	$U(d)$
VNIIM	0.46320	0.00060	0.00013	0.00098	0.00188
INMETRO	0.46116	0.00140	-0.00192	0.00149	0.00280
BFKH	0.44539	0.00050	-0.01769	0.00107	0.00206
SMU	0.46422	0.00200	0.00114	0.00178	0.00355
CEM	0.48667	0.00095	0.02359	0.00134	0.00262
CMI	0.46543	0.00600	0.00236	0.00553	0.01109
RISE	0.45212	0.00600	-0.01096	0.00598	0.01149
VSL	0.46591	0.00095	0.00283	0.00132	0.00254
NPL	0.46516	0.00070	0.00208	0.00114	0.00215
UME	0.44385	0.00034	-0.01923	0.00100	0.00192

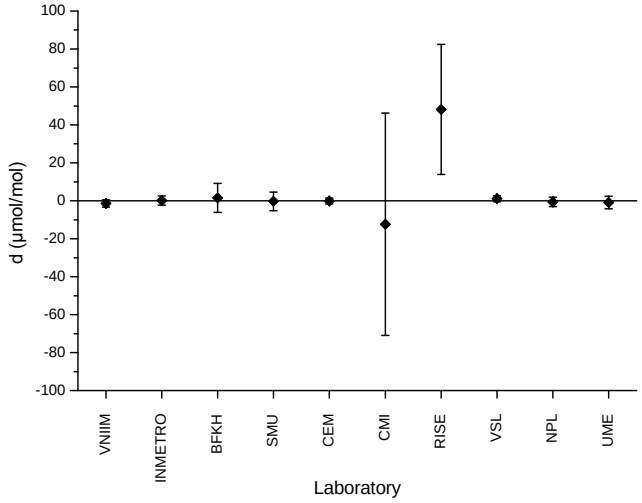


Figure 17: Degrees-of-equivalence for ethane

The results for ethane (see figure 17) are homogeneous and consistent, except for the result of RISE.

Table 13: Corrected amount fraction of ethane from the participants (x'_{lab}), the associated standard uncertainty ($u(x'_{\mathrm{lab}})$), and the degree-of-equivalence (difference d, standard uncertainty $u(d)$, and expanded uncertainty ($U(d)$)) (µmol mol^{-1})

Lab	x'_{lab}	$u(x'_{\mathrm{lab}})$	d	$u(d)$	$U(d)$
VNIIM	619.8	0.9	-1.4	1.0	1.9
INMETRO	621.4	1.2	0.1	1.2	2.4
BFKH	622.8	4.0	1.5	3.9	7.7
SMU	620.9	2.6	-0.3	2.4	4.9
CEM	621.1	0.6	-0.1	0.7	1.5
CMI	608.8	30.0	-12.4	29.8	58.6
RISE	669.4	17.5	48.2	17.5	34.4
VSL	622.4	0.7	1.1	0.9	1.6
NPL	620.7	1.3	-0.6	1.2	2.5
UME	620.3	1.7	-0.9	1.6	3.3

The data for propane (see figure 18) are quite homogeneous. The result of VSL is not consistent with the reference value.

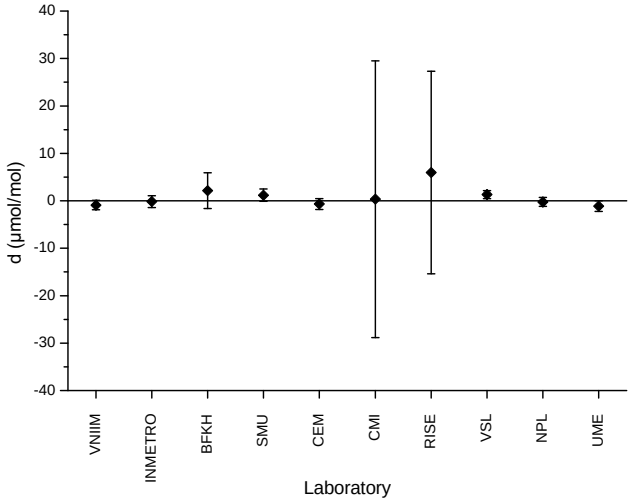


Figure 18: Degrees-of-equivalence for propane

Table 14: Corrected amount fraction of propane from the participants (x'_{lab}), the associated standard uncertainty ($u(x'_{\mathrm{lab}})$), and the degree-of-equivalence (difference d, standard uncertainty $u(d)$, and expanded uncertainty ($U(d)$)) (µmol mol^{-1})

Lab	x'_{lab}	$u(x'_{\mathrm{lab}})$	d	$u(d)$	$U(d)$
VNIIM	148.4	0.3	-0.9	0.5	1.0
INMETRO	149.1	0.6	-0.2	0.6	1.3
BFKH	151.5	2.0	2.1	1.9	3.8
SMU	150.5	0.6	1.2	0.7	1.3
CEM	148.6	0.5	-0.7	0.6	1.2
CMI	149.6	15.0	0.4	14.8	29.1
RISE	155.3	11.0	6.0	10.8	21.3
VSL	150.6	0.1	1.3	0.5	0.8
NPL	149.1	0.3	-0.2	0.5	0.9
UME	148.2	0.4	-1.1	0.6	1.1

4 Support to CMC claims

The support of CMC claims is described in more detail in the ”GAWG strategy for comparisons and CMC claims” [21]. The results of this key comparison can be used to support CMC claims for the composition of biogas in the following ranges (see table 15). CMCs outsite the listed ranges are not supported by the results of this key comparison without further evidence.

Table 15: Supported component ranges

Component	Amount fraction x (cmol mol^{-1})
Methane	35 – 95
Carbon dioxide	4 – 45
Nitrogen	4 – 25
Hydrogen	0.2 – 3.0
Oxygen	0.2 – 1.5
Ethane	0.002 – 0.5
Propane	0.002 – 0.5

5 Discussion and conclusions

The results in this Track C key comparison on the composition of biogas are generally good. Some of the datasets, especially that of oxygen, showed substantial extra dispersion, that could not be explained by the stated uncertainties.

This is the first key comparison of the CCQM-GAWG that has been evaluated using procedure B and the median as key comparison reference value. Corrections had to be made to the laboratory results to account for differences in the amount fractions of the components in the gas mixtures used as transfer standards. The calculation of the degrees-of-equivalence using this procedure B shows that it can also be applied in key comparisons with multiple transfer standards.

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A Measurement data used for calculating the reference values

A.1 Measurement data

Tables 16–22 summarise the reported results by the participating NMIs (see also the measurement reports contained in annex B). In these tables, also the corrections due to batch inhomogeneity, as calculated using a fixed effects model, are provided.

Table 16: Reported laboratory results and corrections due to batch inhomogeneity for methane. All data are given as amount fractions in cmol mol^{-1}

Laboratory	Mixture	x_{lab}	$u(x_{\mathrm{lab}})$	k	Δx_{hom}	$u(\Delta x_{\mathrm{hom}})$
UME	TS1194	43.8159	0.1271	2	0.0381	0.0157
SMU	TS1195	43.765	0.066	2	−0.0171	0.0061
CEM	TS1207	43.8070	0.0535	2	0.0962	0.0051
RISE	TS1214	43.82	0.29	2	0.0183	0.0177
BFKH	TS1220	44.125	0.068	2	0.0188	0.0095
VNIIM	TS1221	43.630	0.046	2	−0.1352	0.0109
NPL	TS1223	43.815	0.044	2	0.0196	0.0120
VSL	TS1224	43.700	0.026	2	−0.0407	0.0102
INMETRO	TS1225	43.81	0.14	2	−0.0020	0.0064
CMI	TS1230	43.592	0.029	2	0.0407	0.0098

Table 17: Reported laboratory results and corrections due to batch inhomogeneity for carbon dioxide. All data are given as amount fractions in cmol mol^{-1}

Laboratory	Mixture	x_{lab}	$u(x_{\mathrm{lab}})$	k	Δx_{hom}	$u(\Delta x_{\mathrm{hom}})$
UME	TS1194	39.0234	0.0610	2	−0.1002	0.0168
SMU	TS1195	39.24	0.13	2	0.0613	0.0137
CEM	TS1207	39.1510	0.1706	2	−0.1094	0.0091
RISE	TS1214	38.96	0.26	2	−0.1147	0.0257
BFKH	TS1220	39.364	0.044	2	−0.1042	0.0044
VNIIM	TS1221	39.43	0.06	2	0.3135	0.0029
NPL	TS1223	39.210	0.039	2	0.0667	0.0050
VSL	TS1224	39.300	0.032	2	0.1772	0.0060
INMETRO	TS1225	38.88	0.21	2	−0.0853	0.0045
CMI	TS1230	39.022	0.025	2	−0.1050	0.0026

Table 18: Reported laboratory results and corrections due to batch inhomogeneity for nitrogen. All data are given as amount fractions in cmol mol^{-1}

Laboratory	Mixture	x_{lab}	$u(x_{lab})$	k	Δx_{hom}	$u(\Delta x_{hom})$
UME	TS1194	15.834	0.0248	2	0.0639	0.0067
SMU	TS1195	15.713	0.026	2	−0.0428	0.0070
CEM	TS1207	15.6850	0.1565	2	0.0644	0.0035
RISE	TS1214	15.89	0.17	2	0.0837	0.0086
BFKH	TS1220	15.199	0.029	2	0.0657	0.0015
VNIIM	TS1221	15.61	0.03	2	−0.1339	0.0009
NPL	TS1223	15.667	0.047	2	−0.1192	0.0023
VSL	TS1224	15.700	0.013	2	−0.0588	0.0019
INMETRO	TS1225	15.92	0.13	2	0.0387	0.0014
CMI	TS1230	16.020	0.011	2	0.0381	0.0012

Table 19: Reported laboratory results and corrections due to batch inhomogeneity for hydrogen. All data are given as amount fractions in cmol mol^{-1}

Laboratory	Mixture	x_{lab}	$u(x_{lab})$	k	Δx_{hom}	$u(\Delta x_{hom})$
UME	TS1194	0.794 81	0.001 33	2	0.001 28	0.000 22
SMU	TS1195	0.802	0.013	2	−0.002 48	0.000 27
CEM	TS1207	0.7807	0.2376	2	−0.000 36	0.000 03
RISE	TS1214	0.810	0.018	2	0.003 45	0.000 92
BFKH	TS1220	0.765	0.012	2	0.002 63	0.000 11
VNIIM	TS1221	0.7891	0.0031	2	−0.002 17	0.000 07
NPL	TS1223	0.7946	0.0032	2	−0.001 94	0.000 23
VSL	TS1224	0.7900	0.0014	2	−0.001 67	0.000 07
INMETRO	TS1225	0.7808	0.0089	2	0.001 40	0.000 08
CMI	TS1230	0.789	0.063	2	−0.000 14	0.000 08

Table 20: Reported laboratory results and corrections due to batch inhomogeneity for oxygen. All data are given as amount fractions in cmol mol^{-1}

Laboratory	Mixture	x_{lab}	$u(x_{lab})$	k	Δx_{hom}	$u(\Delta x_{hom})$
UME	TS1194	0.446 51	0.000 68	2	0.002 66	0.000 85
SMU	TS1195	0.4527	0.0040	2	−0.011 52	0.000 20
CEM	TS1207	0.4350	0.0019	2	−0.051 67	0.000 45
RISE	TS1214	0.510	0.012	2	0.057 88	0.000 30
BFKH	TS1220	0.468	0.001	2	0.022 61	0.000 85
VNIIM	TS1221	0.4141	0.0012	2	−0.049 10	0.000 91
NPL	TS1223	0.4809	0.0014	2	0.015 74	0.000 76
VSL	TS1224	0.4000	0.0019	2	−0.065 91	0.000 88
INMETRO	TS1225	0.5049	0.0028	2	0.043 74	0.000 58
CMI	TS1230	0.501	0.012	2	0.035 57	0.001 21

Table 21: Reported laboratory results and corrections due to batch inhomogeneity for ethane. All data are given as amount fractions in cmol mol^{-1}

Laboratory	Mixture	x_{lab}	$u(x_{lab})$	k	Δx_{hom}	$u(\Delta x_{hom})$
UME	TS1194	0.062 24	0.000 34	2	0.000 205	0.000 040
SMU	TS1195	0.062 03	0.000 51	2	−0.000 065	0.000 031
CEM	TS1207	0.062 16	0.000 11	2	0.000 048	0.000 042
RISE	TS1214	0.0670	0.0035	2	0.000 059	0.000 072
BFKH	TS1220	0.0624	0.0008	2	0.000 120	0.000 035
VNIIM	TS1221	0.061 80	0.000 18	2	−0.000 184	0.000 039
NPL	TS1223	0.061 82	0.000 25	2	−0.000 246	0.000 031
VSL	TS1224	0.062 00	0.000 13	2	−0.000 236	0.000 042
INMETRO	TS1225	0.062 32	0.000 24	2	0.000 180	0.000 024
CMI	TS1230	0.061	0.006	2	0.000 118	0.000 072

Table 22: Reported laboratory results and corrections due to batch inhomogeneity for propane. All data are given as amount fractions in cmol mol^{-1}

Laboratory	Mixture	x_{lab}	$u(x_{lab})$	k	Δx_{hom}	$u(\Delta x_{hom})$
UME	1194	0.014 85	0.000 08	2	0.000 032 3	0.000 025 9
SMU	1195	0.015 03	0.000 12	2	−0.000 019 6	0.000 005 1
CEM	1207	0.014 86	0.000 10	2	−0.000 003 9	0.000 006 0
RISE	1214	0.015 55	0.002 20	2	0.000 023 4	0.000 050 7
BFKH	1220	0.0151	0.0004	2	−0.000 045 9	0.000 035 7
VNIIM	1221	0.014 84	0.000 06	2	−0.000 000 4	0.000 008 7
NPL	1223	0.014 854	0.000 059	2	−0.000 053 8	0.000 052 9
VSL	1224	0.015 000	0.000 021	2	−0.000 063 0	0.000 014 7
INMETRO	1225	0.015 01	0.000 12	2	0.000 095 0	0.000 006 2
CMI	1230	0.015	0.003	2	0.000 035 9	0.000 010 3

A.2 Calculation of reference values

Table 23: Measurement data for methane. All data are given as amount fractions in 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	$u(x_6)$
TS1194	43.8302	0.0081	43.8206	0.0064	43.7439	0.0064	43.8066	0.0206	43.8022	0.0088	43.7860	0.0050
TS1195	43.8107	0.0123	43.7769	0.0209	43.7152	0.0272	43.7229	0.0064	43.6921	0.0064	43.7304	0.0078
TS1207	43.8565	0.0069	43.8396	0.0039	43.8855	0.0195	43.8659	0.0173	43.8598	0.0103	43.8347	0.0065
TS1214	43.7465	0.0064	43.7319	0.0064	43.8118	0.0195	43.7227	0.0162	43.7193	0.0119	43.7144	0.0078
TS1220	43.8124	0.0035	43.8131	0.0075	43.7554	0.0119	43.7491	0.0119	43.7742	0.0109	43.7881	0.0058
TS1221	43.6703	0.0069	43.6735	0.0075	43.5929	0.0093	43.5795	0.0103	43.6129	0.0119	43.6631	0.0112
TS1223	43.8595	0.0172	43.8252	0.0105	43.7390	0.0064	43.7201	0.0078	43.7530	0.0060	43.7809	0.0052
TS1224	43.7676	0.0048	43.7596	0.0064	43.6855	0.0069	43.6815	0.0083	43.7083	0.0048	43.7421	0.0062
TS1225	43.8047	0.0053	43.7866	0.0032	43.7370	0.0151	43.7324	0.0069	43.7379	0.0083	43.7725	0.0058
TS1230	43.8746	0.0058	43.8417	0.0058	43.7777	0.0073	43.7449	0.0069	43.7652	0.0049	43.8051	0.0087

Table 24: Measurement data for carbon dioxide. All data are given as amount fractions in 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	$u(x_6)$
TS1194	38.9856	0.0117	38.9814	0.0090	39.0318	0.0088	38.9448	0.0221	38.9726	0.0131	39.0291	0.0021
TS1195	39.1261	0.0183	39.1338	0.0144	39.1133	0.0495	39.1605	0.0330	39.1966	0.0155	39.1984	0.0035
TS1207	39.0125	0.0047	39.0064	0.0112	38.9194	0.0434	38.9444	0.0263	38.9739	0.0264	39.0438	0.0021
TS1214	39.0141	0.0095	38.9776	0.0106	38.8677	0.0215	38.9854	0.0178	38.9892	0.0143	39.0294	0.0025
TS1220	38.9700	0.0074	38.9744	0.0090	38.9773	0.0209	38.9732	0.0196	39.0042	0.0137	39.0069	0.0030
TS1221	39.3767	0.0085	39.3840	0.0172	39.4114	0.0094	39.3999	0.0100	39.4192	0.0096	39.4077	0.0069
TS1223	39.0963	0.0342	39.1113	0.0276	39.1927	0.0082	39.1747	0.0026	39.1939	0.0047	39.1795	0.0025
TS1224	39.2354	0.0122	39.2430	0.0090	39.2900	0.0094	39.2741	0.0058	39.2691	0.0057	39.2924	0.0030
TS1225	38.9991	0.0063	38.9743	0.0024	39.0045	0.0064	39.0024	0.0047	39.0151	0.0079	39.0024	0.0021
TS1230	38.9492	0.0084	38.9609	0.0063	38.9963	0.0082	38.9922	0.0036	39.0028	0.0057	38.9976	0.0021

Table 25: Measurement data for nitrogen. All data are given as amount fractions in 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	$u(x_6)$
TS1194	15.8360	0.0035	15.8303	0.0051	15.7984	0.0022	15.8343	0.0093	15.8187	0.0052	15.8042	0.0037
TS1195	15.7391	0.0069	15.7307	0.0065	15.7239	0.0155	15.6860	0.0120	15.7007	0.0031	15.7099	0.0024
TS1207	15.8242	0.0024	15.8244	0.0033	15.8355	0.0113	15.8219	0.0058	15.8174	0.0024	15.8012	0.0019
TS1214	15.8482	0.0059	15.8352	0.0021	15.8716	0.0084	15.8333	0.0052	15.8323	0.0066	15.8217	0.0030
TS1220	15.8359	0.0035	15.8311	0.0033	15.8162	0.0093	15.8219	0.0068	15.8218	0.0052	15.8060	0.0034
TS1221	15.6383	0.0042	15.6379	0.0040	15.6170	0.0036	15.6145	0.0019	15.6193	0.0034	15.6230	0.0028
TS1223	15.6661	0.0051	15.6587	0.0051	15.6237	0.0027	15.6194	0.0044	15.6293	0.0032	15.6294	0.0030
TS1224	15.7174	0.0031	15.7161	0.0045	15.6839	0.0032	15.6920	0.0036	15.6920	0.0032	15.6848	0.0021
TS1225	15.8076	0.0031	15.8083	0.0024	15.7944	0.0032	15.7873	0.0029	15.7937	0.0025	15.7867	0.0025
TS1230	15.8158	0.0047	15.8088	0.0021	15.7877	0.0020	15.7860	0.0018	15.7879	0.0038	15.7886	0.0027

Table 26: Measurement data for hydrogen. All data are given as amount fractions in 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	$u(x_6)$
TS1194	0.79688	0.00064	0.79625	0.00067	0.79416	0.00036	0.79306	0.00088	0.79325	0.00064	0.79526	0.00027
TS1195	0.79004	0.00087	0.79022	0.00065	0.79177	0.00059	0.79115	0.00077	0.79264	0.00052	0.79240	0.00029
TS1207	0.79512	0.00057	0.79490	0.00059	0.79186	0.00034	0.79180	0.00085	0.79164	0.00090	0.79379	0.00027
TS1214	0.79836	0.00055	0.79804	0.00048	0.79899	0.00057	0.79447	0.00052	0.79471	0.00052	0.79687	0.00029
TS1220	0.79684	0.00040	0.79647	0.00075	0.79583	0.00036	0.79562	0.00031	0.79607	0.00030	0.79534	0.00026
TS1221	0.79040	0.00027	0.79059	0.00029	0.79218	0.00037	0.79191	0.00034	0.79226	0.00031	0.79204	0.00028
TS1223	0.79292	0.00048	0.79176	0.00047	0.79109	0.00039	0.79075	0.00031	0.79134	0.00032	0.79215	0.00026
TS1224	0.79304	0.00065	0.79261	0.00053	0.79127	0.00030	0.79111	0.00031	0.79113	0.00032	0.79155	0.00027
TS1225	0.79470	0.00027	0.79466	0.00027	0.79542	0.00032	0.79514	0.00031	0.79501	0.00039	0.79509	0.00025
TS1230	0.79239	0.00031	0.79251	0.00031	0.79416	0.00031	0.79401	0.00034	0.79448	0.00034	0.79440	0.00028

Table 27: Measurement data for oxygen. All data are given as amount fractions in 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	$u(x_6)$
TS1194	0.47832	0.00057	0.47814	0.00058	0.46531	0.00032	0.46957	0.00077	0.46781	0.00068	0.46766	0.00023
TS1195	0.46490	0.00080	0.46437	0.00067	0.45309	0.00116	0.45237	0.00341	0.45326	0.00056	0.45758	0.00024
TS1207	0.42338	0.00045	0.42295	0.00057	0.41340	0.00078	0.41517	0.00035	0.41286	0.00027	0.41714	0.00037
TS1214	0.53484	0.00079	0.53443	0.00072	0.52217	0.00073	0.52093	0.00049	0.52241	0.00130	0.52207	0.00038
TS1220	0.49961	0.00060	0.49863	0.00060	0.48449	0.00075	0.48740	0.00058	0.48839	0.00035	0.49029	0.00032
TS1221	0.42495	0.00043	0.42497	0.00056	0.41483	0.00106	0.41675	0.00037	0.41940	0.00026	0.41991	0.00028
TS1223	0.49348	0.00089	0.49184	0.00058	0.47795	0.00065	0.47943	0.00025	0.48134	0.00065	0.48216	0.00054
TS1224	0.40990	0.00045	0.40921	0.00041	0.39710	0.00030	0.39872	0.00029	0.40136	0.00062	0.40223	0.00026
TS1225	0.52095	0.00073	0.52108	0.00077	0.50585	0.00035	0.50827	0.00037	0.50774	0.00052	0.51055	0.00023
TS1230	0.51231	0.00071	0.51188	0.00062	0.49692	0.00044	0.49928	0.00079	0.50296	0.00040	0.50245	0.00057

Table 28: Measurement data for ethane. All data are given as amount fractions in 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	$u(x_5)$
TS1194	0.062473	0.000087	0.062298	0.000079	0.062304	0.000048	0.062432	0.000061	0.062386	0.000065
TS1195	0.062240	0.000111	0.062168	0.000170	0.061947	0.000044	0.062089	0.000087	0.062069	0.000077
TS1207	0.062151	0.000099	0.062268	0.000103	0.062142	0.000096	0.062215	0.000061	0.062336	0.000059
TS1214	0.062286	0.000078	0.061906	0.000121	0.062350	0.000040	0.062375	0.000083	0.062295	0.000079
TS1220	0.062356	0.000055	0.062203	0.000085	0.062238	0.000076	0.062339	0.000088	0.062340	0.000051
TS1221	0.062044	0.000055	0.061880	0.000129	0.062067	0.000086	0.061934	0.000054	0.062031	0.000080
TS1223	0.061856	0.000109	0.061835	0.000083	0.061913	0.000093	0.062080	0.000040	0.061985	0.000050
TS1224	0.061951	0.000060	0.062034	0.000190	0.061782	0.000066	0.061922	0.000048	0.061986	0.000054
TS1225	0.062362	0.000062	0.062310	0.000119	0.062340	0.000053	0.062328	0.000090	0.062439	0.000075
TS1230	0.062387	0.000066	0.062059	0.000103	0.062419	0.000065	0.062227	0.000068	0.062388	0.000098

Table 29: Measurement data for propane. All data are given as amount fractions in 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	$u(x_5)$
TS1194	0.014898	0.000038	0.015038	0.000018	0.014953	0.000014	0.014975	0.000013	0.014974	0.000017
TS1195	0.014903	0.000023	0.014920	0.000052	0.014910	0.000014	0.014914	0.000018	0.014931	0.000019
TS1207	0.014897	0.000012	0.014957	0.000075	0.014912	0.000024	0.014926	0.000017	0.014940	0.000013
TS1214	0.014808	0.000044	0.015084	0.000030	0.014977	0.000012	0.014953	0.000013	0.014975	0.000018
TS1220	0.014934	0.000012	0.014743	0.000048	0.014925	0.000025	0.014914	0.000021	0.014948	0.000012
TS1221	0.014948	0.000015	0.014983	0.000047	0.014925	0.000021	0.014894	0.000013	0.014912	0.000019
TS1223	0.014716	0.000067	0.015005	0.000076	0.014885	0.000023	0.014899	0.000011	0.014909	0.000013
TS1224	0.014884	0.000019	0.014812	0.000042	0.014880	0.000016	0.014881	0.000014	0.014911	0.000014
TS1225	0.015137	0.000057	0.015118	0.000112	0.014957	0.000011	0.014939	0.000021	0.014967	0.000018
TS1230	0.014983	0.000028	0.015017	0.000047	0.014973	0.000016	0.014929	0.000019	0.014944	0.000021

Table 30: Results of the meta analysis of the measurement data for methane. All data are given as amount fractions in cmol mol^{-1}

Mixture	μ	$s(\mu)$	τ	u_{cal}	$u(\mu)$
TS1194	43.7959	0.0120	0.0277	0.0029	0.0123
TS1195	43.7438	0.0154	0.0338	0.0029	0.0156
TS1207	43.8481	0.0055	0.0095	0.0029	0.0062
TS1214	43.7350	0.0090	0.0190	0.0029	0.0095
TS1220	43.7835	0.0093	0.0211	0.0029	0.0098
TS1221	43.6311	0.0174	0.0416	0.0029	0.0177
TS1223	43.7754	0.0142	0.0335	0.0029	0.0145
TS1224	43.7229	0.0151	0.0366	0.0029	0.0154
TS1225	43.7625	0.0099	0.0229	0.0029	0.0103
TS1230	43.8001	0.0227	0.0553	0.0029	0.0229

Table 31: Results of the meta analysis of the measurement data for carbon dioxide. All data are given as amount fractions in cmol mol^{-1}

Mixture	μ	$s(\mu)$	τ	u_{cal}	$u(\mu)$
TS1194	38.9923	0.0133	0.0306	0.0018	0.0134
TS1195	39.1549	0.0186	0.0397	0.0018	0.0187
TS1207	38.9948	0.0134	0.0275	0.0018	0.0135
TS1214	38.9787	0.0177	0.0415	0.0018	0.0178
TS1220	38.9842	0.0096	0.0207	0.0018	0.0098
TS1221	39.4001	0.0059	0.0113	0.0018	0.0062
TS1223	39.1795	0.0036	0.0064	0.0018	0.0040
TS1224	39.2674	0.0088	0.0202	0.0018	0.0089
TS1225	38.9979	0.0071	0.0169	0.0018	0.0073
TS1230	38.9834	0.0055	0.0125	0.0018	0.0058

Table 32: Results of the meta analysis of the measurement data for nitrogen. All data are given as amount fractions in cmol mol^{-1}

Mixture	μ	$s(\mu)$	τ	u_{cal}	$u(\mu)$
TS1194	15.8196	0.0080	0.0188	0.0017	0.0081
TS1195	15.7167	0.0069	0.0145	0.0017	0.0071
TS1207	15.8203	0.0066	0.0153	0.0017	0.0068
TS1214	15.8383	0.0048	0.0105	0.0017	0.0051
TS1220	15.8224	0.0058	0.0131	0.0017	0.0060
TS1221	15.6244	0.0040	0.0093	0.0017	0.0043
TS1223	15.6371	0.0063	0.0150	0.0017	0.0065
TS1224	15.6974	0.0062	0.0149	0.0017	0.0064
TS1225	15.7962	0.0042	0.0101	0.0017	0.0046
TS1230	15.7954	0.0050	0.0119	0.0017	0.0053

Table 33: Results of the meta analysis of the measurement data for hydrogen. All data are given as amount fractions in cmol mol^{-1}

Mixture	μ	$s(\mu)$	τ	u_{cal}	$u(\mu)$
TS1194	0.7946	0.0005	0.0012	0.0002	0.0006
TS1195	0.7912	0.0004	0.0008	0.0002	0.0004
TS1207	0.7930	0.0006	0.0014	0.0002	0.0006
TS1214	0.7967	0.0008	0.0019	0.0002	0.0008
TS1220	0.7956	0.0002	0.0003	0.0002	0.0003
TS1221	0.7914	0.0003	0.0007	0.0002	0.0004
TS1223	0.7914	0.0004	0.0010	0.0002	0.0005
TS1224	0.7914	0.0003	0.0006	0.0002	0.0004
TS1225	0.7948	0.0001	0.0003	0.0002	0.0003
TS1230	0.7935	0.0002	0.0006	0.0002	0.0003

Table 34: Results of the meta analysis of the measurement data for oxygen. All data are given as amount fractions in cmol mol^{-1}

Mixture	μ	$s(\mu)$	τ	u_{cal}	$u(\mu)$
TS1194	0.4736	0.0013	0.0025	0.0005	0.0014
TS1195	0.4625	0.0013	0.0023	0.0005	0.0014
TS1207	0.4215	0.0008	0.0014	0.0004	0.0009
TS1214	0.5308	0.0012	0.0022	0.0007	0.0014
TS1220	0.4976	0.0008	0.0013	0.0006	0.0010
TS1221	0.4241	0.0008	0.0014	0.0004	0.0009
TS1223	0.4870	0.0021	0.0046	0.0005	0.0022
TS1224	0.4049	0.0010	0.0020	0.0004	0.0011
TS1225	0.5149	0.0019	0.0043	0.0006	0.0020
TS1230	0.5101	0.0010	0.0017	0.0006	0.0012

Table 35: Results of the meta analysis of the measurement data for ethane. All data are given as amount fractions in µmol mol^{-1}

Mixture	μ	$s(\mu)$	τ	u_{cal}	$u(\mu)$
TS1194	623.727	0.523	0	0.227	0.570
TS1195	621.444	0.763	0	0.225	0.796
TS1207	622.146	0.652	0	0.226	0.691
TS1214	622.064	1.020	1.565	0.226	1.045
TS1220	623.157	0.411	0	0.227	0.469
TS1221	620.191	0.456	0	0.225	0.509
TS1223	619.128	0.521	0	0.224	0.567
TS1224	619.533	0.496	0	0.224	0.545
TS1225	623.525	0.496	0	0.227	0.546
TS1230	622.597	1.079	1.499	0.227	1.103

Table 36: Results of the meta analysis of the measurement data for propane. All data are given as amount fractions in µmol mol^{-1}

Mixture	μ	$s(\mu)$	τ	u_{cal}	$u(\mu)$
TS1194	149.722	0.369	0.638	0.068	0.375
TS1195	149.069	0.187	0	0.068	0.199
TS1207	148.995	0.099	0	0.068	0.120
TS1214	149.606	0.538	1.078	0.068	0.542
TS1220	148.899	0.411	0.688	0.067	0.417
TS1221	149.469	0.120	0	0.068	0.137
TS1223	148.819	0.441	0.712	0.067	0.446
TS1224	148.752	0.155	0	0.067	0.169
TS1225	150.253	0.511	0.823	0.069	0.515
TS1230	149.871	0.220	0	0.068	0.230

B Measurement reports of the participating institutes

Measurement report CEM

Cylinder number: 2031207 (029524)

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Methane	07/08/15	437820	0.011	6
Carbon dioxide	24/07/15	390830	0.082	6
Nitrogen	24/07/15	157590	0.22	6
Hydrogen				
Oxygen	07/08/15	4339	0.30	90
Ethane	07/08/15	621.3	0.018	6
Propane	07/08/15	148.6	0.025	6

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Methane	11/08/15	438400	0.018	6
Carbon dioxide	29/07/15	392130	0.13	6
Nitrogen	29/07/15	158040	0.24	6
Hydrogen				
Oxygen	10/08/15	4356	0.30	90
Ethane	11/08/15	622.1	0.032	6
Propane	11/08/15	148.37	0.014	6

Measurement #3[1]

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Methane	12/08/15	437990	0.021	6
Carbon dioxide	30/07/15	391570	0.055	6
Nitrogen	30/07/15	156850	0.10	6
Hydrogen				
Oxygen	11/08/15	4355	0.25	90
Ethane	12/08/15	621.28	0.024	6
Propane	10/08/15	148.78	0.26	6

[1] If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Methane		438070	535	2
Carbon dioxide		391510	1706	2
Nitrogen		156850	1565	2
Hydrogen*		7807	2376	2
Oxygen		4350	19	2
Ethane		621.6	1.1	2
Propane		148.6	1.0	2

*Hydrogen obtained by difference

Calibration standards

- Method of preparation: A set of primary standard gas mixtures (PSMs) were prepared according the gravimetric method described in ISO 6142. All PSMs are multicomponent mixtures for the comparison (excepting hydrogen) in methane balance and the three calibration standards were prepared both in several stage dilution process and by direct weighing depending on the component.

PSM 1 MRP492362	x_i assigned value (µmol/mol)	Relative U_i (%)
Methane	503272	0.1
Carbon dioxide	374233	0.3
Nitrogen	119333	0.9
Oxygen	2912	0.5
Ethane	199	0.4
Propane	50	0.5

PSM 2 MRP292363	x_i assigned value (µmol/mol)	Relative U_i (%)
Methane	434156	0.1
Carbon dioxide	398110	0.3
Nitrogen	162733	0.6
Oxygen	4379.2	0.3
Ethane	502.7	0.1
Propane	118.5	0.2

PSM 3 MRP292364	x_i assigned value (μmol/mol)	Relative U_i (%)
Methane	390937	0.1
Carbon dioxide	422486	0.3
Nitrogen	179663	0.6
Oxygen	5901.8	0.2
Ethane	809.7	0.1
Propane	201.6	0.2

- Weighing data: In the case of PSM 2 MRP292363, the mixture was prepared, in the following sequence, weighing 402.09 g from pure carbon dioxide, 20.84 g from a 9 000 μmol/mol ethane in methane pre-mixture, 69.16 g from a 1 100 μmol/mol propane in nitrogen pre-mixture, 19.17 g from a 0.15 mol/mol oxygen in nitrogen pre-mixture, 19.63 g from pure nitrogen and 139.35 g from pure methane.

- Purity tables (composition) of the parent gases:

	Methane (5.5) - Air Liquide		**Carbon dioxide (4.8) - Air Liquide**	
COMPONENT	x_i (μmol/mol)	u_i (μmol/mol)	x_i (μmol/mol)	u_i (μmol/mol)
Carbon dioxide	0.05	0.029	**999 996.3**	**1.2**
Hydrogen			0.25	0.14
Oxygen	0.25	0.14	1	0.58
Nitrogen	1	0.58		
Water	1	0.58	1.5	0.87
Ethane	0.05	0.029		
Hydrocarbons	0.025	0.014	1	0.58
Methane	**999 997.58**	**83**		

	Nitrogen (BIP) - Air Products		**Oxygen (4.5) - Air Products**	
COMPONENT	x_i (μmol/mol)	u_i (μmol/mol)	x_i (μmol/mol)	u_i (μmol/mol)
Carbon monoxide	0.25	0.14	0.5	0.29
Carbon dioxide	0.25	0.14	0.5	0.29
Hydrogen	0.5	0.29	0.5	0.29
Oxygen	0.005	0.002 9	**999 991.5**	**3.1**
Nitrogen	**999 998.94**	**0.35**	5	2.9
Water	0.01	0.005 6	1.5	0.87
Hydrocarbons	0.05	0.029		
Methane			0.5	0.29

COMPONENT	Propane (3.5) - Air Liquide		Ethane (4.5) - Air Liquide	
	x_i (μmol/mol)	u_i (μmol/mol)	x_i (μmol/mol)	u_i (μmol/mol)
Carbon dioxide	2.5	1.4	0.5	0.29
Hydrogen	20	12	1.5	0.87
Oxygen	5.0	2.9	2.5	1.4
Nitrogen	20	12	10	5.8
Water	2.5	1.4	1.5	0.87
Propene	100	58		
Propane	**999 750**	**83**		
Ethene			2.5	1.4
Ethane			**999 974**	**7.6**
Hydrocarbons	100	58	7.5	4.3

– Verification measures: The PSMs gravimetric values were verified by the same analytical method than the method used for the comparison and their analytical uncertainties are considered for the PSMs assigned values.

Instrumentation

A 6890N Agilent GC for natural gas is used. The GC is equipped with a FID for methane, ethane and propane performance and a TCD for carbon dioxide and nitrogen performance, packed columns and helium gas is used as carrier. After rolling the cylinders, the sample and the PSMs are connected to pressure regulators and to a sample box and the sampling loop is flushed for three minutes before injection at the atmospheric pressure.

A paramagnetic SERVOMEX Xentra 4100 is used for oxygen performance. The sample and the PSMs are connected to pressure regulators and to a sample box and the gas is flushed for three minutes before measurement.

Calibration method and value assignment

Mixtures are analyzed under repeatability conditions during at least three days. Three results are selected for each component. The calibration method according ISO 6143 for a linear function is used in all cases. The assigned values for components concentration is the average of the three individual values obtained.

Uncertainty evaluation

The expression for combined standard uncertainty, as follows, includes the quadratic sum of individual standard uncertainties as obtained according ISO 6143 and the standard deviation of the mean of individual values for propane concentration:

$$u_c = \sqrt{\frac{1}{3}\cdot(u_1^2+u_2^2+u_3^2)+(\frac{s}{\sqrt{3}})^2}$$

The expanded uncertainty is obtained by multiplying the combined uncertainty with a k = 2 factor for a confidence level of 95 %.

Measurement report CMI

Cylinder number: 2031230

Measurement #1

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	27.8.2015	43,593	0,076	10
Carbon dioxide	27.8.2015	39,021	0,045	10
Nitrogen	27.8.2015	16,020	0,096	10
Hydrogen	27.8.2015	0,789	1,477	10
Oxygen	27.8.2015	0,501	0,190	10
Ethane	27.8.2015	0,061	0,664	10
Propane	27.8.2015	0,015	0,309	10

Measurement #2

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	12.10.2015	43,588	0,105	10
Carbon dioxide	12.10.2015	39,025	0,068	10
Nitrogen	12.10.2015	16,018	0,116	10
Hydrogen	12.10.2015	0,791	1,809	10
Oxygen	12.10.2015	0,502	0,158	10
Ethane	12.10.2015	0,062	0,770	10
Propane	12.10.2015	0,015	0,209	10

Measurement #3[1]

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	14.10.2015	43,595	0,046	10
Carbon dioxide	14.10.2015	39,020	0,027	10
Nitrogen	14.10.2015	16,022	0,050	10
Hydrogen	14.10.2015	0,788	2,614	10
Oxygen	14.10.2015	0,499	0,288	10
Ethane	14.10.2015	0,061	0,674	10

[1] If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

Propane	14.10.2015	0,015	0,269	10

Results

Component	Date (dd/mm/yy)	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
Methane	-	43,592	0,029	2
Carbon dioxide	-	39,022	0,025	2
Nitrogen	-	16,020	0,011	2
Hydrogen	-	0,789	0,063	2
Oxygen	-	0,501	0,012	2
Ethane	-	0,061	0,006	2
Propane	-	0,015	0,003	2

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.

CS 1		
Component:	(cmol/mol)	Expanded uncertainty (cmol/mol)
Methane	44.955	0.018
Carbon dioxide	39.515	0.016
Nitrogen	14.136	0.006
Hydrogen	0.878	0.038
Oxygen	0.473	0.007
Ethane	0.032	0.018
Propane	0.011	0.002

CS 2		
Component:	(cmol/mol)	Expanded uncertainty (cmol/mol)
Methane	43.658	0.017
Carbon dioxide	38.942	0.015
Nitrogen	16.124	0.007
Hydrogen	0.721	0.037
Oxygen	0.445	0.007
Ethane	0.087	0.017
Propane	0.023	0.002

CS 3		
Component:	(cmol/mol)	Expanded uncertainty (cmol/mol)
Methane	43.751	0.015
Carbon dioxide	37.122	0.013
Nitrogen	17.779	0.006
Hydrogen	0.792	0.033
Oxygen	0.481	0.006
Ethane	0.062	0.015
Propane	0.013	0.002

Instrumentation

Measured on Gas Chromatograph Agilent, with using columns (19095P – CO_2 carbonplot, 19095P-MS0, 19095P-S25), TCD and FID detectors, oven temperature 40 - 120 °C, carrier gas Helium. 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/TCD-FID	3 points, line

Uncertainty evaluation

Uncertainty estimation is given below:

$$U = k.u(x_i) \qquad [1]$$

u_c - combined uncertainty
k - coverage factor (k=2)

Standard deviation (2) is combination of standard deviation (type A) (3) and standard deviation (type B) (4).

$$u(\overline{x}_i) = \sqrt{u_a(\overline{x}_i)^2 + u_B(\overline{x}_i)^2} \qquad [2]$$

$$u_a(\overline{x}_i) = \sqrt{\frac{\sum_{j=1}^{n}(x_j - \overline{x}_i)^2}{n.(n-1)}} \qquad [3]$$

$$u_B(\overline{x}_i) = \sqrt{\frac{\sum_{j=1}^{n} u(x_j)^2}{n^2}} \qquad [4]$$

Measurement report INMETRO

Cylinder number: 2031225

Measurement #1

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	13/05/15	43.88577	0.23	6
Carbon dioxide	13/05/15	38.81713	0.10	6
Nitrogen	13/05/15	15.9499	0.22	6
Hydrogen				
Oxygen	13/05/15	0.5039	0.22	6
Ethane	13/05/15	0.062252	0.11	6
Propane	13/05/15	0.014944	0.28	6

Measurement #2

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	19/05/15	43.74296	0.08	6
Carbon dioxide	19/05/15	38.88702	0.31	6
Nitrogen	19/05/15	15.88262	0.12	6
Hydrogen	17/06/15	0.778178	0.22	6
Oxygen	19/05/15	0.50528	0.22	6
Ethane	19/05/15	0.062391	0.09	6
Propane	19/05/15	0.015016	0.51	6

Measurement #3

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	09/06/15	43.83876	0.24	6
Carbon dioxide	09/06/15	38.85532	0.30	6
Nitrogen	09/06/15	15.9377	0.21	6
Hydrogen	23/06/15	0.778775	0.33	6
Oxygen	09/06/15	0.505886	0.23	6
Ethane	09/06/15	0.062228	0.11	6
Propane	09/06/15	0.014982	0.37	6

Measurement #4

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	16/06/15	43.77658	0.13	6
Carbon dioxide	16/06/15	38.96547	0.97	6
Nitrogen	16/06/15	15.91526	0.14	6
Hydrogen	24/06/15	0.785393	0.16	6
Oxygen	16/06/15	0.504635	0.41	6
Ethane	16/06/15	0.062411	0.13	6
Propane	16/06/15	0.015099	0.20	6

Measurement #5

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	24/06/15	43.78849	0.17	6
Carbon dioxide	24/06/15	39.00193	0.08	6
Nitrogen	24/06/15	15.79706	0.10	6
Hydrogen	25/06/15	0.780848	0.47	6
Oxygen	24/06/15	0.503706	0.13	6
Ethane	24/06/15	0.062196	0.13	6
Propane	24/06/15	0.015022	0.16	6

Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
Methane	43.81	0.14	2
Carbon dioxide	38.88	0.21	2
Nitrogen	15.92	0.13	2
Hydrogen	0.7808	0.0089	2
Oxygen	0.5049	0.0028	2
Ethane	0.06232	0.00024	2
Propane	0.01501	0.00012	2

Calibration standards

Inmetro used maximum 6 own prepared mixtures (table 1.) and maximum 3 mixtures obtained from NPL (table 2.) were used for the calibration curve. All standards were prepared individually according to ISO 6142 “Gas analysis - Preparation of calibration gases - Gravimetric Method”.

Table 1. Calibration standards prepared by Inmetro

Cylinder number	PSM103819		PSM128541		PSM203638	
Component	**Assigned value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**	**Assigned value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**	**Assigned value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**
Methane	56.1401	0.0026	53.1129	0.0027	50.7743	0.0028
Carbon dioxide	32.7186	0.0020	34.8568	0.0021	35.8344	0.0021
Nitrogen	10.0055	0.0010	11.0648	0.0010	12.0600	0.0011
Hydrogen	0.81452	0.00024	0.70043	0.00020	0.91376	0.00025
Oxygen	0.3020	0.0012	0.2558	0.0022	0.3808	0.0013
Ethane	0.0200495	0.0000074	0.0150238	0.0000067	0.0350783	0.0000095
Propane	0.0051453	0.0000032	0.0038654	0.0000044	0.0089284	0.0000033
Cylinder number	**PSM203776**		**PSM203807**		**PSM203818**	
Component	**Assigned value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**	**Assigned value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**	**Assigned value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**
Methane	39.7733	0.0054	43.1831	0.0044	45.4586	0.0038
Carbon dioxide	42.2992	0.0040	40.0814	0.0033	38.8167	0.0028
Nitrogen	16.0232	0.0020	15.0335	0.0016	14.2183	0.0014
Hydrogen	1.20135	0.00037	1.10038	0.00033	0.99374	0.00029
Oxygen	0.6120	0.0022	0.5283	0.0019	0.4575	0.0017
Ethane	0.080265	0.000020	0.065743	0.000016	0.050856	0.000013
Propane	0.0203109	0.0000057	0.0166527	0.0000048	0.0129006	0.0000040

Table 2. Calibration standards

Cylinder number	NG537		NG543		NG544	
Component	**Assigned value (x) cmol/mol**	**Standard uncertainty (u(x)) cmol/mol**	**Assigned value (x) cmol/mol**	**Standard uncertainty (u(x)) cmol/mol**	**Assigned value (x) cmol/mol**	**Standard uncertainty (u(x)) cmol/mol**
Methane	59.96	0.1	30.42	0.055	44.99	0.075
Carbon dioxide	30	0.075	48.34	0.115	39.6	0.095
Nitrogen	9.945	0.016	20.23	0.035	14.909	0.0235
Oxygen	0.0997	0.0005	1.009	0.0045	0.5011	0.00225

Instrumentation

For the measurement of the Biogas mixture 2 equipment's where used:

1) Micro GC (Varian)

Model: 490

Channel 1: Biogas 2015-04-13.met-Channel 1. 10m MS5A Heated Injector, Backflush

Channel 2: 10m PPU Heated Injector, Backflush

Channel 3: 10m AL2O3-KCL Heated Injector, Backflush

Carrier: Helium or Nitrogen

2) GC CP-3800 (Varian)

The GC-NGA is equipped with a 12 ports Multi Position Valve (MPV). The system is divided in 2 channels: the Flame Ionization Detector (FID) channel and the Thermal Conductivity Detector (TCD) channel. Injections on both channels are done via a Gas Sampling Valve (GSV). The carrier is Helium
TCD Channel:
10 port switching valve, 6 Port switching valve, Hayesep T column. Mesh 80-100, l: 0.5m, id: 2 mm; Hayesep Q column. Mesh 80-100, l: 0.5m, id: 2mm; Molsieve 13x column, Mesh 80-1000l: 1.5m, id: 2mm;
FID Channel:
CP-1177 Split/split less injector, CP-Sil 5CB column, WCOT silica, l: 60 m, id: 0.25 mm.

Calibration method and value assignment

The sample and calibration standards were connected to a reducer and after flushing connected to the multi position valve. Every line was flushed separately and the flow for each mixture was set equally. For all the measurements the reducers were disconnected and connected to a different cylinder. Also a different position on the multiposition valve was used to connect the cylinder. The flushing and setting of the flow was done equal to the first measurement. Every mixture was injected 7 times were the first injection was dictated.

The calibration of the instrument was done according to ISO 6143. The calibration curve was made using the software XLgenline. The goodness of fit for all measurements was lower than 2.

Uncertainty evaluation

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

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

Uncertainty of the reproducibility (analysis – type A)

Measurement report MKEH
Cylinder number: 2031220

Measurement #1

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	number of replicates
Methane	29/07/2015	441.33	0.04	3
Carbon-dioxide		393.62	0.01	3
Nitrogen		151.79	0.04	3
Hydrogen		7.68	0.04	3
Oxygen		4.81	0.04	3
Ethane		0.621	0.40	3
Propane		0.150	0.81	3

Measurement #2

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	number of replicates
Methane	30/07/2015	441.24	0.06	3
Carbon-dioxide		393.58	0.05	3
Nitrogen		152.19	0.08	3
Hydrogen		7.65	0.08	3
Oxygen		4.56	0.08	3
Ethane		0.627	0.30	3
Propane		0.152	0.56	3

Measurement #3[1]

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	number of replicates
Methane	31/07/2015	441.19	0.03	3
Carbon-dioxide		393.72	0.03	3
Nitrogen		152.00	0.04	3
Hydrogen		7.63	0.04	3
Oxygen		4.68	0.04	3
Ethane		0.625	0.36	3
Propane		0.151	0.88	3

Results

Component	Date (dd/mm/yy)	Result (mmol/mol)	Expanded uncertainty (mmol/mol)	Coverage factor

Methane	31/07/2015	441.25	0.68	2
Carbon-dioxide		393.64	0.44	2
Nitrogen		151.99	0.29	2
Hydrogen		7.65	0.12	2
Oxygen		4.68	0.01	2
Ethane		0.624	0.008	2
Propane		0.151	0.004	2

Calibration standards

Nº OMH63

Component	Date (dd/mm/yy)	Result (mmol/mol)	Expanded uncertainty (mmol/mol)	Coverage factor
Methane	23/06/2015	440.43	0.28	2
Carbon-dioxide		380.30	0.07	2
Nitrogen		165.90	0.10	2
Hydrogen		4.849	0.028	2
Oxygen		7.736	0.026	2
Ethane		0.6217	0.0014	2
Propane		0.1560	0.0006	2

in 10 L aluminium cylinder (Luxfer) with stainless steel valve,

high purity Methane (Messer, Hungary, controlled by GC-FID-TCD for purity)
high purity Ethane (Air Liquide, controlled by GC-FID-TCD for purity)
high purity Propane (unknown source of the origin, controlled by GC-FID-TCD for purity)
high purity Carbon-dioxide (Siad, Hungary, controlled by GC-FID-TCD for purity)
high purity Hydrogen (Messer, Hungary, controlled by GC-FID-TCD for purity)
high purity Oxigen (Messer, Hungary, controlled by GC-FID-TCD for purity)
and Nitrogen (Messer, Hungary, controlled by GC-FID-TCD and electrochemical sensor and mirror dew point meter for purity) gases were used for the preparation of the primary standard gas.

The mass measurements of the gases were carried out by balances:

Mettler Toledo AE 240-S with repeatability of 0.25 mg and capacity of 200 g, and
Mettler Toledo XP 26003 L with repeatability of 0.0015 g and capacity of 15000 g.

Purity table of Parent Gases

Gas	Concentration %(mol/mol)	Uncertainty %(mol/mol)
Methane	99.995	± 0.006
Ethane	99.95	± 0.06
Propane	99.98	± 0.06
Nitrogen	99.995	± 0.006
Hydrogen	99.999	± 0.001
Oxygen	99.995	± 0.006
Carbon dioxide	99.998	± 0.003

Instrument Calibration:

MKEH primary standard No: OMH 63/2015.06.23.

The measurements were done with a MKEH primary standard.
The standard gas and the sample gas were changed in every 6 minutes.
The temperature and pressure correction were not done.

Sample Handling:

We used stainless steel valves for the cylinders and 25 mbar was set up on flow measurement, and the flow was stable.

Instrumentation

Gas chromatography (HP6890 GC-FID) was used to analyze biogas. The flow rate of the gases was controlled by EPC.

Column: Porapack PS 4.4m, 0.75mm ID, Sulfinert; oven temp.: 120˚C; Carrier gas: 4.5 bar He to FID.
Column: Hayesep A 8.8m, 0.075mm ID, Sulfinert; oven temp.: 120˚C; Carrier gas: 4.5 bar He to TCD.
Column: Hayesep Q 100/200, 1m, 1.00mm ID, Sulfinert and 5A Mole Sieve 80/100, 2m, 1.00mmmID, Sulfinert; oven temp.: 38˚C; Carrier gas: 4.5 bar Ar to TCD.

Calibration method and value assignment

Reference Method:
The measurement method was direct comparison with a standard which has almost the same nominal concentration as the sample. Gas chromatography (HP6890 GC-FID-TCD) was used to analyze Biogas at 38 and 120 ˚C. The bridge component was Methane during the calculations. After the calculation all the components were normalized to sum 1.000 mol/mol values.

Uncertainty evaluation

The potential sources of the uncertainty:
- Uncertainty of the primary reference material.
- Uncertainty of calibration measurement series.
- Standard deviation of measurement series.

Uncertainty table 1: Methane

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Standard reference material	440.43 (mmol/mol)	Normal	0.14 (mmol/mol)	1	0.03
Standard deviation of the calibration measurement series	10837 area	Normal	0.61 area	1	0.01
Standard deviation of the measurement series	10783 area	Normal	1.16 area	1	0.01
Variancia	438.227 (mmol/mol)		0.15 (mmol/mol)		0.034

Uncertainty table 2: Carbon dioxide

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Standard reference material	380.301 (mmol/mol)	Normal	0.036 (mmol/mol)	1	0.01
Standard deviation of the calibration measurement series	14036 area	Normal	2.71 area	1	0.02
Standard deviation of the measurement series	14433 area	Normal	3.26 area	1	0.02
Variancia	391.070 (mmol/mol)		0.122 (mmol/mol)		0.031

Uncertainty table 3: Nitrogen

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Standard reference material	165.90 (mmol/mol)	Normal	0.05 (mmol/mol)	1	0.03
Standard deviation of the calibration measurement series	5550 area	Normal	0.83 area	1	0.01
Standard deviation of the measurement series	5206 area	Normal	0.59 area	1	0.01
Variancia	155.63 (mmol/mol)		0.06 (mmol/mol)		0.036

Uncertainty table 4: Ethane

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Standard reference material	0.6217 (mmol/mol)	Normal	0.0014 (mmol/mol)	1	0.225
Standard deviation of the calibration measurement series	215.77 area	Normal	0.58 area	1	0.27
Standard deviation of the measurement series	215.13 area	Normal	0.14 area	1	0.06
Variancia	0.620 (mmol/mol)		0.002 (mmol/mol)		0.355

Uncertainty table 5: Propane

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Standard reference material	0.15604 (mmol/mol)	Normal	0.00058 (mmol/mol)	1	0.372
Standard deviation of the calibration measurement series	81.56 area	Normal	0.65 area	1	0.79
Standard deviation of the measurement series	78.54 area	Normal	0.06 area	1	0.08
Variancia	0.150 (mmol/mol)		0.001 (mmol/mol)		0.878

Uncertainty table 6: Hydrogen

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Standard reference material	4.849 (mmol/mol)	Normal	0.014 (mmol/mol)	1	0.29
Standard deviation of the calibration measurement series	105.31 area	Normal	0.21 area	1	0.20
Standard deviation of the measurement series	172.31 area	Normal	0.32 area	1	0.18
Variancia	7.93		0.03		0.39

	(mmol/mol)		(mmol/mol)		

Uncertainty table 7: Oxygen

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Standard reference material	7.736 (mmol/mol)	Normal	0.013 (mmol/mol)	1	0.17
Standard deviation of the calibration measurement series	19.91 area	Normal	0.07 area	1	0.34
Standard deviation of the measurement series	12.51 area	Normal	0.03 area	1	0.23
Variancia	4.860 (mmol/mol)		0.022 (mmol/mol)		0.44

References

1.1 Alink A., Deák É at all, **The first key comparison on Primary Standard gas Mixtures**, Metrologia **37** (2000), pp. 35-49

1.2 Adriaan M H van der Veen, Zsófia Nagyné Szilágyi *et al*, **Final Report on International comparison CCQM K23ac: Natural gas types I and III** 2007 *Metrologia* **44** 08001

1.3 Adriaan M H van der Veen, Zsófia Nagyné Szilágyi *et al*, **Final Report on International comparison CCQM K23b: Natural gas types II,** Metrologia 05/2010; **47**(1A) 08013

Measurement report NPL

Cylinder Number: 2031223

Measurement #1: GC FID[(a)] and TCD[(b)]

Component	Date (dd/mm/yy)	Result (cmol/mol)	standard uncertainty (cmol/mol)	No. of replicates
H_2[(b)]	22/07/2015	0.7981	0.0021	16
CH_4[(a)]	22/07/2015	43.74	0.08	17
C_2H_6[(a)]	22/07/2015	0.06173	0.00012	16
C_3H_8[(a)]	22/07/2015	-	-	-
CO_2[(b)]	22/07/2015	39.214	0.014	18
O_2[(b)]	22/07/2015	0.48077	0.00063	18
N_2[(b)]	22/07/2015	15.639	0.033	18

Measurement #2: GC FID[(a)] and TCD[(b)]

Component	Date (dd/mm/yy)	Result (cmol/mol)	standard uncertainty (cmol/mol)	No. of replicates
H_2[(b)]	23/07/2015	-	-	-
CH_4[(a)]	23/07/2015	43.80	0.08	18
C_2H_6[(a)]	23/07/2015	0.06174	0.00022	18
C_3H_8[(a)]	23/07/2015	-	-	18
CO_2[(b)]	23/07/2015	39.204748	0.000034	18
O_2[(b)]	23/07/2015	-	-	-
N_2[(b)]	23/07/2015	15.681	0.0037	18

Measurement #3: GC FID[(a)] and TCD[(b)]

Component	Date (dd/mm/yy)	Result (cmol/mol)	standard uncertainty (cmol/mol)	No. of replicates
H_2[(b)]	03/08/2015	0.7910	0.0015	14
CH_4[(a)]	03/08/2015	43.8449	0.006	18
C_2H_6[(a)]	03/08/2015	0.062022	0.000034	16
C_3H_8[(a)]	03/08/2015	0.014825	0.000041	14
CO_2[(b)]	03/08/2015	39.2122	0.014	16
O_2[(b)]	03/08/2015	0.48109	0.00058	17
N_2[(b)]	03/08/2015	15.656	0.026	18

Measurement #4: GC FID[(a)] and TCD[(b)]

Component	Date (dd/mm/yy)	Result (cmol/mol)	standard uncertainty (cmol/mol)	No. of replicates
H_2[(b)]	04/08/2015	-	-	-
CH_4[(a)]	04/08/2015	43.8147	0.021	17
C_2H_6[(a)]	04/08/2015	0.061802	0.000049	18
C_3H_8[(a)]	04/08/2015	0.014876	0.000020	18
CO_2[(b)]	04/08/2015	39.222	0.021	18

O_2[(b)]	04/08/2015	-	-	-
N_2[(b)]	04/08/2015	15.680	0.010	18

Measurement #5: GC FID[(a)] and TCD[(b)]

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard uncertainty (cmol/mol)	No. of replicates
H_2[(b)]	05/08/2015	-	-	-
CH_4[(a)]	05/08/2015	43.8456	0.0047	17
C_2H_6[(a)]	05/08/2015	0.061807	0.000027	17
C_3H_8[(a)]	05/08/2015	0.014861	0.000020	18
CO_2[(b)]	05/08/2015	39.200	0.005	18
O_2[(b)]	05/08/2015	-	-	-
N_2[(b)]	05/08/2015	15.683	0.0038	17

Final Result:

Component	Date (dd/mm/yy)	Result (cmol/mol)	expanded uncertainty (cmol/mol)	coverage factor
H_2	20/10/2015	0.7946	0.0032	2
CH_4	20/10/2015	43.815	0.044	2
C_2H_6	20/10/2015	0.06182	0.00025	2
C_3H_8	20/10/2015	0.014854	0.000059	2
CO_2	20/10/2015	39.210	0.039	2
O_2	20/10/2015	0.4809	0.0014	2
N_2	20/10/2015	15.667	0.047	2

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

Details of the measurement method used

Reference method

The amount fraction of the seven components in the comparison mixture was measured using two gas chromatographs:

- Analytical Controls "Hi-speed RGA" gas chromatograph (AC Analytical Controls, Netherlands) with six columns (3 m x 0.32 mm x 4 µm SPB-1, 25 m x 0.32 mm x 8 µm Al_2O_3 Plot 'S', 25 m x 0.32 mm x 8 µm Al_2O_3 Plot 'S', 0.25 m x $^1/_{16}$″ (ID 1 mm) Silcosteel HayeSep Q (80/100), 1 m x $^1/_{16}$″ (ID 1 mm) Silcosteel HayeSep N (80/100), 1 m x $^1/_{16}$″ (ID 1 mm) Silcosteel HayeSep Q (80/100) + 2 m x $^1/_{16}$″ (ID 1 mm) Silcosteel molecular sieve 5A (80/100) and 2 m x $^1/_{16}$″ (ID 1 mm) Silcosteel molecular sieve 13X (80/100)), six valves and three detectors - one flame ionisation detector (FID) and two thermal conductivity detectors (TCDs). The instrument was modified at NPL to implement splitless injection to improve the repeatability of the analysis.

- Agilent 7890A gas chromatograph with an FID and a TCD. The instrument has two columns (8.8m Porapak-R 100/120 mesh 1/16'' OD, 0.75mm ID connected to TCD and a 4.4 m Porasil-P

followed by 4.4 m Porapak-PS connected to FID).

Calibration standards

A Primary Reference Gas Mixture (PRGM) of nominally 0.75 cmol/mol hydrogen, 0.05 cmol/mol ethane, 0.015 cmol/mol propane, 39 cmol/mol carbon dioxide 0.45 cmol/mol oxygen and 16.5 cmol/mol nitrogen in methane was prepared in accordance with ISO 6142 and in a BOC 10 litre cylinder with Spectraseal passivation. The mixture was validated against NPL's suite of Primary Standard Mixtures (PSMs).

The mixture was prepared by first adding ethane from a pure source to an evacuated cylinder via a transfer vessel. Methane and carbon dioxide were then added sequentially from pure sources in the gas phase directly to the cylinder via 1/16" tubing. Propane, oxygen, nitrogen and hydrogen were also added from three pre-mixtures (a nominal 1000 µmol/mol propane in nitrogen, a nominal 25 cmol/mol hydrogen in nitrogen and a nominal 3 cmol/mol oxygen in carbon dioxide). After the mixture had been prepared it was homogenised by heating the cylinder in an inverted position at 60°C for 2 hours, immediately followed by horizontally rolling about the vertical axis.

The mixture was used in determining the amount fraction of the comparison mixture. The amount fraction of the PRGM (NPL A499) was 0.7663 ± 0.0014 cmol/mol hydrogen, 0.06156 ± 0.00005 cmol/mol ethane, 0.014053 ± 0.000005 cmol/mol propane, 38.7872 ± 0.0044 cmol/mol carbon dioxide, 0.45970 ± 0.00061 cmol/mol oxygen, 16.5192 ± 0.0040 cmol/mol nitrogen and 43.3920 ± 0.0054 cmol/mol methane. (Uncertainties are stated as expanded (k = 2) uncertainties.) The purity of all source gases was analysed and found to be >99.999 % in each case.

Instrument calibration, data analysis and quantification

As the PRGM described above was prepared with a composition that differed by 5 % (relative) or less from the composition of the comparison mixture for all components, this ensured that the uncertainty contribution from any deviation from the linearity of the analyser response was negligible.

The comparison mixture and the NPL PRGM were connected to the GC (via an automated switching valve) using purpose-built minimised dead volume connectors and Silcosteel-passivated $^{1}/_{16}$″ internal diameter stainless steel tubing.

via a minimised dead-volume connector (using the internal screw thread of the cylinder valve) and a 1/16″ Silcosteel sample line, which were purged thoroughly before use. NPL-designed flow restrictors were used to allow a stable sample flow of 15 ml min^{-1} to be maintained throughout the analysis. At least six repeat measurements were performed by alternating between the two mixtures. The responses were recorded as peak area and the average peak area of the repeated measurement was calculated.

Uncertainty evaluation

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

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

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

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

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

Where n is the number of ratios. The amount fraction of each component in the comparison mixture, x_u, is then calculated by:

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

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

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

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

quantity	unit	example value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_s	cmol/mol	43.3920	0.0026	1.0105	0.0026	A	normal
$\bar{r}$	-	1.0105	0.00009	43.39200	0.00394	A	normal
x_u	**cmol/mol**	**43.8456**					
$u(x_u)$	**cmol/mol**	**0.0047**					
$U(x_u)$	**cmol/mol**	**0.0095**					

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

quantity	unit	value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_1	cmol/mol	43.7445	0.0774	0.20	0.0155	A	normal
x_2	cmol/mol	43.8449	0.0766	0.20	0.0153	A	normal
x_3	cmol/mol	43.7985	0.0055	0.20	0.0011	A	normal
x_4	cmol/mol	43.8416	0.0211	0.20	0.0042	A	normal
x_5	cmol/mol	43.8456	0.0047	0.20	0.0009	A	normal
x_f	**cmol/mol**	**43.8150**					
$u(x_f)$	**cmol/mol**	**0.0222**					
$U(x_f)$	**cmol/mol**	**0.0444**					

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

Measurement report SP
Cylinder number: 103000332854

Measurement #1

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	number of replicates
Methane	05/03/15	437.5	0.1	2
Carbon dioxide	05/03/15	389.1	0.2	2
Nitrogen	05/03/15	159.8	0.4	2
Hydrogen	05/03/15	8.1	2.0	2
Oxygen	05/03/15	4.9	2.1	2
Ethane	05/03/15	0.675	1.3	2
Propane	05/03/15	0.156	1.7	2

Measurement #2

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	number of replicates
Methane	11/03/15	439.1	0.1	2
Carbon dioxide	11/03/15	389.3	0.2	2
Nitrogen	11/03/15	158.4	0.4	2
Hydrogen	11/03/15	8.1	2.1	2
Oxygen	11/03/15	5.3	1.8	2
Ethane	11/03/15	0.675	1.5	2
Propane	11/03/15	0.153	1.9	2

Measurement #3[1]

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	number of replicates
Methane	12/03/15	437.9	0.1	2
Carbon dioxide	12/03/15	390.4	0.2	2
Nitrogen	12/03/15	158.5	0.4	2
Hydrogen	12/03/15	8.1	2.2	2
Oxygen	12/03/15	5.1	1.8	2
Ethane	12/03/15	0.662	1.7	2
Propane	12/03/15	0.157	1.7	2

[1] If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

Results

Component	Date (dd/mm/yy)	Result (mmol/mol)	Expanded uncertainty (mmol/mol)	Coverage factor
Methane	19/03/15	438.2	2.9	2
Carbon dioxide	19/03/15	389.6	2.6	2
Nitrogen	19/03/15	158.9	1.7	2
Hydrogen	19/03/15	8.1	0.18	2
Oxygen	19/03/15	5.1	0.12	2
Ethane	19/03/15	0.670	0.035	2
Propane	19/03/15	0.1555	0.022	2

Obs: all the results are expressed in mmol/mol.

Calibration standards

Two Calibration standards containing all the compounds except O_2 delivered by NPL, Cylinder NG479 and NG480.

- Method of preparation: gravimetry. Purity analysis with gas chromatography (FID, TCD, MS)
- The standards were prepared by NPL. Our results are traceable to the values given by NPL on these standards.

Instrumentation

The analyses were performed on a Varian 450-GC GC/TCD/FID (gas chromatograph/thermal conductivity detector/flame ionisation detector) equipped with three columns:

A molecular Sieve 5A, 60-80 Mesh, 1 m x 1/8´´ x 2.0 mm connected to the TCD

A Hayesep Q, 80-100 Mesh, 1.8 m x 1/8´´ x 2.0 mm connected to the TCD

A PoraBOND Q, 25 m x 0.53 mm x 10 µm connected to the FID

Calibration method and value assignment

A two-points calibration was carried out for each compound by using calibration standards (cylinders) with a specified known concentration. The response versus concentration function was then used to estimate concentration of analyte in a separately analysed sample

Uncertainty evaluation

See appendix 1 where the uncertainty evaluation is detailed. The expanded uncertainties have been calculated using the software GUM workbench. A mean value (n=2) for each measurement was reported.

Measurement report SMU

Cylinder number: **2031195**

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Methane	4.3.2015	0.43738	0.06	6
Carbon dioxide	4.3.2015	0.39192	0.07	6
Nitrogen	4.3.2015	0.15709	0.08	6
Hydrogen	2.4.2015	0.00806	0.89	4
Oxygen	4.3.2015	0.0045106	0.11	6
Ethane	23.3.2015	0.0006207	0.56	6
Propane	23.3.2015	0.00015011	0.49	6

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Methane	11.3.2015	0.43780	0.05	6
Carbon dioxide	11.3.2015	0.39267	0.14	6
Nitrogen	11.3.2015	0.15712	0.04	6
Hydrogen	9.4.2015	0.00799	0.64	5
Oxygen	11.3.2015	0.004527	0.10	6
Ethane	24.3.2015	0.0006200	0.31	6
Propane	24.3.2015	0.00014998	0.22	6

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Methane	18.3.2015	0.43776	0.06	6
Carbon dioxide	18.3.2015	0.39269	0.15	6
Nitrogen	18.3.2015	0.15718	0.07	6
Hydrogen	10.4.2015	0.008022	0.52	5
Oxygen	18.3.2015	0.0045440	0.13	6
Ethane	25.3.2015	0.00062020	0.29	6
Propane	25.3.2015	0.00015066	0.28	6

Results

Component	Result (mol/mol)	Expanded uncertainty (mol/mol)	Coverage factor
Methane	**0.43765**	**0.00066**	**2**
Carbon dioxide	**0.3924**	**0.0013**	**2**
Nitrogen	**0.15713**	**0.00026**	**2**
Hydrogen	**0.00802**	**0.00013**	**2**
Oxygen	**0.004527**	**0.000040**	**2**
Ethane	**0.0006203**	**0.0000051**	**2**
Propane	**0.0001503**	**0.0000012**	**2**

Calibration standards

All calibration standards were made gravimetrically according ISO 6142 and verified against SMU Primary standard gas mixtures in accordance to ISO 614. Impurities in parent gases - Hydrogen, Nitrogen, Methane, CO_2, C_2H_6, C_3H_8 and Oxygen were analysed on GC and FTIR.

Weighing: SMU used automatic weighting on automatic balance, the filled cylinder mass was not determined absolutely, but as a difference between filled cylinder mass and reference cylinder mass. The result was an arithmetic mean of determined differences. Its standard uncertainty consists of standard deviation of arithmetic mean and of uncertainties of those loaded weights, which are loaded only for one of the cylinder - either filled cylinder or reference cylinder and of uncertainty of display resolution of automatic comparator balance. Minimum number of determined single differences was 6.

SMU gravimetric preparation of gas mixture consists of following basic steps:

1. Calculation of purity tables of parent gases. If the parent gas was produced by the SMU as a premixture, it has a purity table yet. In the case of pure gas, additional measurements of impurities were accomplished. In the case that measurements of some components were not accomplished, data were taken from manufacturers. The value of mole fraction of the main component was calculated (as a difference from 1).
2. The schedule of the consecutive filling of parent gases + calculations of needed masses and their corresponding pressures.
3. Set up of the cylinder.
4. Evacuation of the cylinder.
5. Weighting of the evacuated cylinder on automatic balance.
6. Filling of the cylinder by the counted amount of the first parent gas.
7. Weighting of the cylinder with the first added gas.
8. Completing of gas mixture preparation - consecutive fillings and weightings of the cylinder (steps 6 and 7).
9. Homogenisation of the gas mixture.
10. Calculation of the mole fractions of components in the prepared gas mixture.
11. Analytical validation of mole fractions.
12. Assigning of the certified values.

Various types of calibration standards were used in this comparison, please find them in following table.

SMU calibration standards for Biogas analysis

Cylinder number	Methane (mol/mol)	CO_2 (mol/mol)	N_2 (mol/mol)	H_2 (mol/mol)	O_2 (mol/mol)	Ethane (mol/mol)	Propane (mol/mol)
0077F_6*	0.1023	-	0.7950	0.00741	-	0.0006919	0.0001577
0030F_3*	0.07386	-	0.8133	0.00818	-	0.0004480	0.0001021
0095F_5*	0.06268	-	0.7896	0.01071	-	0.0002946	0.0002512
MY9727_3*	0.1394	-	0.01632	0.06156	-	-	-
MY9728_3*	0.1272	-	0.02655	0.07148	-	-	-
9304E_4	0.9744	0.01340	0.01014	-	0.00204	-	-
9328E_3	0.9623	0.01975	0.01492	-	0.00301	-	-
0041F_4	0.4102	0.4118	0.1718	-	0.00615	-	-
0048F_3	0.6933	0.1546	0.1505	-	-	0.000783	0.0004664
0049F_3	0.6553	0.1681	0.1749	-	-	0.001244	0.0003225

*this standard contains Helium as not certified component

Instrumentation

GC method (Varian Chromatograph)

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:

Equipment	Specifications
GC Varian	
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 (of PSM)	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

Component	Detector	Analytical curve
Methane	TCD	quadratic
Carbon dioxide	TCD	quadratic
Nitrogen	TCD	quadratic
Hydrogen	TCD	quadratic
Oxygen	TCD	linear
Ethane	FID	quadratic
Propane	FID	quadratic

Calibration method and value assignment

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 with sample signals. Data were subjected to the b_least program (weighted least square regression). The result of the measurement sequence was the average of molar fractions.
At b_least linear and quadratic models of analytical curves were used.
No corrections were used.
Uncertainty of instrument response consisted from figure characterized roughly immediate repeatability and from signal drift estimated. From each run was made one calibration curve with sample signals. These figures together with molar fraction data were subjected to b_least program (weighted least square regression). Each run produced sample molar fraction with its standard uncertainty. From all runs results = average of molar fractions in one sequence were standard deviation found (uncertainty of type A) and from runs results uncertainties the mean (through squares) was found (uncertainty of type B). These 2 figures were combined to give result uncertainty.

For each i^{-th} day the average x_i was calculated *(1).* Standard uncertainty assigned *to* each i^{-th} day result *(4)* is from standard deviation of the average *(2)* and average from all b_least uncertainties that day *(3).*

$$\bar{x}_i = \frac{\sum_{j=1}^{n} x_j}{n} \qquad (1)$$

$$u_1(\bar{x}_i) = \sqrt{\frac{\sum_{j=1}^{n} (x_j - \bar{x}_i)^2}{n*(n-1)}} \qquad (2)$$

$$u_2(\bar{x}_i) = \sqrt{\frac{\sum_{j=1}^{n} u(x_j)^2}{n^2}} \qquad (3)$$

$$u(\bar{x}_i) = \sqrt{u_1(\bar{x}_i)^2 + u_2(\bar{x}_i)^2} \qquad (4)$$

To estimate result uncertainty from 3 days results we have kept “Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method” (Annual Book of ASTM Standards E 691-87) with some approximations.

Uncertainty evaluation

To estimate result uncertainty from 3 days results we have kept "Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method" (Annual Book of ASTM Standards E 691-87) with some approximations.

$$s_R = \sqrt{s_{\bar{x}}^2 + s_r \frac{n-1}{n}} \qquad (5)$$

$$s_r = \sqrt{\sum_{i=1}^{p} u(\bar{x}_i)^2 \Big/ p} \qquad (6)$$

$$s_{\bar{x}} = \frac{\max(\Delta x)}{\sqrt{3}} \qquad (7)$$

$$\Delta x = \bar{x}_1 - \bar{x}_2 \qquad (8)$$

p – number of days (3)
n – number of measurements in 1 day
index i represents particular day
index j represents particular result (evaluated) from one calibration curve

$$\bar{x} = \frac{\sum_{i=1}^{p} \bar{x}_i}{p} \qquad (9)$$

Final result is average from 3 day results

As final **standard uncertainty** we assigned to the result *(9)* max(s_R or s_r)

$$u(\bar{x}) = \max(s_r; s_R) \qquad (10)$$

Expanded uncertainty (k=2) of final result

$$U(\bar{x}) = 2 \cdot u(\bar{x})$$

References

ISO 6142:2001	Gas analysis – Preparation of calibration gas mixtures – Gravimetric method.
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 TÜBİTAK UME

Cylinder number: VSL2031194

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Methane	27/05/2015	437255	0.20	10
Carbon dioxide		390575	0.04	10
Nitrogen		158455	0.05	10
Hydrogen		7977.6	0.07	10
Oxygen		4480.7	0.06	10
Ethane		622.5	0.67	10
Propane		148.3	0.38	10

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Methane	02/06/2015	438012	0.17	10
Carbon dioxide		390290	0.10	10
Nitrogen		158322	0.10	10
Hydrogen		7943.4	0.12	10
Oxygen		4465.3	0.12	10
Ethane		622.0	0.72	10
Propane		147.7	0.76	10

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Methane	03/06/2015	438685	0.26	10
Carbon dioxide		389588	0.07	10
Nitrogen		158017	0.09	10
Hydrogen		7941.4	0.09	10
Oxygen		4457.1	0.07	10
Ethane		620.8	0.42	10
Propane		149.3	0.52	10

Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates

Methane	20/07/2015	438300	0.34	10
Carbon dioxide		390307	0.15	10
Nitrogen		158494	0.12	10
Hydrogen		7937.4	0.09	10
Oxygen		4457.7	0.12	10
Ethane		623.1	0.57	10
Propane		148.3	0.78	10

Measurement #5

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Methane	21/07/2015	438544	0.21	10
Carbon dioxide		390409	0.08	10
Nitrogen		158410	0.07	10
Hydrogen		7940.4	0.19	10
Oxygen		4464.5	0.08	10
Ethane		623.6	0.77	10
Propane		149.0	0.56	10

Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Methane	31/07/2015	438159	1271	2
Carbon dioxide		390234	610	2
Nitrogen		158340	248	2
Hydrogen		7948.1	13.3	2
Oxygen		4465.1	6.8	2
Ethane		622.4	3.4	2
Propane		148.5	0.8	2

Calibration standards

Primary reference gas mixtures used in calibration are given in the Table 1. All the primary standards are mixtures of biogas. They were prepared individually according to ISO 6142 "Gas analysis - Preparation of calibration gases - Gravimetric Method" at TÜBİTAK UME. Several pre-mixtures were individually prepared, and then, these pre-mixtures were diluted to prepare three reference gas standards. Pure methane (5.5 grade), hydrogen (5.0 grade) and oxygen (5.0 grade) were from Linde Gas Germany. Carbon dioxide (5.0 grade) and nitrogen (6.0 grade) were from Linde Gas Turkey and the rest (ethane and propane, all 3.5 grade) were from Air Liquide Germany. The content of the impurities in the pure gases were determined based on the gas producers' specifications. The uncertainties of the mixtures given in Table 1 were determined by combining the standard uncertainties of weighing, purity and molar masses.

Table 1. List of primary reference gas mixtures

Item	**Prepared By**	**Cylinder Number**	**Component**	**Mole Fraction** (µmol/mol)	**Uncertainty (k=1)** (µmol/mol)
1	UME	298308	Methane	427067	214
			Carbon dioxide	344424	172
			Nitrogen	208518	104
			Hydrogen	9748.9	4.9
			Oxygen	9871.8	4.9
			Ethane	295.79	0.15
			Propane	73.24	0.04
2	UME	298312	Methane	447966	224
			Carbon dioxide	374571	187
			Nitrogen	164076	82
			Hydrogen	7738.6	3.9
			Oxygen	4914.6	2.5
			Ethane	586.96	0.29
			Propane	145.34	0.07
3	UME	298328	Methane	434994	217
			Carbon dioxide	427447	214
			Nitrogen	127609	64
			Hydrogen	4853.0	2.4
			Oxygen	4001.1	2.0
			Ethane	876.38	0.44
			Propane	217.01	0.11

Instrumentation

The propane in nitrogen was 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. The conditions for the analyses are given below:

Conditions:

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 324.89 mL/min
Septum Purge Flow :On 3 mL/min
Split Ratio :80 :1
Split Flow :317.91 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
Flame	:On
Electrometer	:On

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
Filament	:On

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
Filament	:On

Calibration method and value assignment

After the arrival of the cylinder from VSL, it was stored in the laboratory where the analyses were carried out. Three primary standard gas mixtures were also stored in the same laboratory during all the measurements. The cylinder and the calibration standards were equipped with pressure reducers and connected to computer programmed multiposition valve gas sampling box. They were flushed before the first measurement. The flow rates of sample and standard gases were controlled by a mass flow controller at 40 ml/min.

The data was collected using ChemStation software. Each sample in the sequence was injected 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 “B_Least” 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 for linear function.

The assigned value was calculated by averaging the results of five independent measurements.

Uncertainty evaluation

The measurement uncertainty of sample was determined according to ISO 6143 “Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures” standard, using the B_Least software.

The combined standard uncertainty was determined by the following equation:

$$u_c = \sqrt{u_m^2 + u_g^2}$$

where

u_m, standard uncertainty from measurements

u_g, standard uncertainty from gravimetric preparation

u_m % rel. (determined by selecting the largest uncertainty value among the obtained uncertainties for each measurement)

u_g % rel. (determined by selecting the largest uncertainty value among the uncertainties of primary reference gas mixtures)

u_c was determined as % rel and stated in relevant table.

The expanded uncertainty was determined by multiplying the combined standard uncertainty by a coverage factor of 2 with a confidence interval of 95%.

Measurement report VNIIM

Laboratory: D.I. Mendeleyev Institute for Metrology (VNIIM), Research Department for the State Measurement Standards in the field of Physico-Chemical Measurements.

Cylinder number: 2031221

Measurement 1

Component	Date	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
Hydrogen	01.07.2015	0.7875	0.134	2×5 sub-measurements
Oxygen		0.4147	0.138	
Nitrogen		15.633	0.063	
Methane		43.665	0.070	
Carbon dioxide		39.460	0.100	
Ethane		0.06180	0.100	
Propane		0.01484	0.120	

Measurement 2

Component	Date	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
Hydrogen	02.07.2015	0.7901	0.218	2×5 sub-measurements
Oxygen		0.4138	0.192	
Nitrogen		15.609	0.084	
Methane		43.613	0.071	
Carbon dioxide		39.453	0.080	
Ethane		0.06185	0.104	
Propane		0.01484	0.101	

Measurement 3

Component	Date	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
Hydrogen	03.07.2015	0.7896	0.238	2×5 sub-measurements
Oxygen		0.4138	0.192	
Nitrogen		15.589	0.181	
Methane		43.613	0.156	
Carbon dioxide		39.377	0.257	
Ethane		0.06176	0.140	

Propane		0.01484	0.042	

Measurements №№ 1-3 were carried out with different calibration standards each.

Results

Component	Date	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Relative expanded uncertainty, %	Coverage factor
Hydrogen	10.07.2015	0.7891	0.0031	0.39	k=2
Oxygen		0.4141	0.0012	0.29	
Nitrogen		15.61	0.03	0.20	
Methane		43.63	0.046	0.10	
Carbon dioxide		39.43	0.06	0.15	
Ethane		0.06180	0.00018	0.30	
Propane		0.01484	0.00006	0.38	

1 Calibration standards

1.1 Preparation of calibration gas mixtures was carried out by gravimety in 2 stages.

Preparation of the pre-mixtures included preparation of

3 binary mixtures - O_2/N_2 (at ⊐ 10 cmol/mol) and

3 four-component mixtures - [H_2(⊐ 23 cmol/mol) + C_2H_6(⊐ 1.8 cmol/mol) + C_3H_8(⊐ 0.4 cmol/mol)]/N_2.

Preparation of target calibration gas mixtures

3 target calibration gas mixtures were prepared in Luxfer Al cylinders, V=5 dm^3. Composition of calibration standards is shown in the tables 1-3.

Table 1

Cylinder M365602		
Component	Amount of substance fraction, cmol/mol	u_{grav}, cmol/mol (k=1)
Hydrogen	0.8030	0.0003
Oxygen	0.42361	0.00005
Nitrogen	15.7758	0.0006
Methane	43.4839	0.0010
Carbon dioxide	39.4358	0.0008
Ethane	0.062669	0.000015
Propane	0.015147	0.000006

Table 2

Cylinder M365606		
Component	Amount of substance fraction, cmol/mol	u_{grav}, cmol/mol (k=1)
Hydrogen	0.79860	0.00023
Oxygen	0.41960	0.00004
Nitrogen	15.6492	0.0005
Methane	43.5154	0.0007
Carbon dioxide	39.5393	0.0006

Ethane	0.062853	0.000015
Propane	0.015048	0.000007

Table 3

Cylinder M365663		
Component	Amount of substance fraction, cmol/mol	u_{grav}, cmol/mol (k=1)
Hydrogen	0.7986	0.0003
Oxygen	0.42051	0.00004
Nitrogen	15.7315	0.0006
Methane	43.2820	0.0008
Carbon dioxide	39.6894	0.0006
Ethane	0.062852	0.000015
Propane	0.015048	0.000007

1.2 Verification measurements were carried out on the same instrument as for the comparison cylinder (description of instrumentation is shown below). Uncertainty from verification is included in the uncertainty budget.

1.3 Purity analysis of the parent gases was carried out by GC- FID, TCD
Results of purity analysis are shown in the tables 4-10

Table 4. Methane (cylinder № 324184)

Component	Amount of substance fraction	u, µmol/mol (k=1)
CH_4	99.998629 cmol/mol	-
N_2	6.88 µmol/mol	0.12
O_2	2.83 µmol/mol	0.04
CO_2	0.8 µmol/mol	0.4
C_2H_6	1.0 µmol/mol	0.6
C_3H_8	0.50 µmol/mol	0.29
C_4H_{10} (n-butane)	0.50 µmol/mol	0.29
H_2	0.50 µmol/mol	0.29

Table 5. Carbon dioxide (cylinder № 74318)

Component	Amount of substance fraction, µmol/mol	u, µmol/mol (k=1)
CO_2	99.999345 cmol/mol	-
H_2	5.43 µmol/mol	0.09
He	0.5 µmol/mol	0.29
N_2	0.25 µmol/mol	0.14
O_2	0.25 µmol/mol	0.14
CH_4	0.100 µmol/mol	0.003
CO	0.020 µmol/mol	0.012

Table 6. Propane (cylinder № 15049)

Component	Amount of substance fraction	u, µmol/mol (k=1)
C_3H_8	99.993235 cmol/mol	-
N_2	21.3 µmol/mol	1.6

C_3H_6	18.9 µmol/mol	1.1
C_4H_{10} (n-butane)	15.4 µmol/mol	0.8
C_2H_6	5.66 µmol/mol	0.28
O_2	3.44 µmol/mol	0.26
i-C_4H_{10}	1.77 µmol/mol	0.11
CH_4	1 µmol/mol	0.6
Ar	0.181 µmol/mol	0.014

Table 7. Oxygen (cylinder № 910287)

Component	Amount of substance fraction	u, µmol/mol (k=1)
O_2	99.9999881cmol/mol	—
CO_2	0.0768 µmol/mol	0.0037
CH_4	0.0338 µmol/mol	0.0011
CO	0.0075 µmol/mol	0.0043

Table 8. Ethane (cylinder № 4877)

Component	Amount of substance fraction	u, µmol/mol (k=1)
C_2H_6	99.998429 cmol/mol	—
N_2	7.26 µmol/mol	0.08
H_2	2.92 µmol/mol	0.05
O_2	1.25 µmol/mol	0.03
CO_2	0.343 µmol/mol	0.008
He	0.5 µmol/mol	0.29
CO	0.031 µmol/mol	0.03
CH_4	0.024 µmol/mol	0.03
C_4H_{10} (n-butane)	2.13 µmol/mol	0.06
C_5H_{12} (n-pentane)	0.5 µmol/mol	0.29
C_6H_{14} (n-hexane)	0.5 µmol/mol	0.29
i-C_5H_{12}	0.5 µmol/mol	0.29

Table 9 Nitrogen (monoblock)

Component	Amount of substance fraction	u, µmol/mol (k=1)
N_2	99.9998484 cmol/mol	—
H_2O	0.500 µmol/mol	0.017
Ar	0.313 µmol/mol	0.006
CO_2	0.030 µmol/mol	0.017
O_2	0.030 µmol/mol	0.003
CH_4	0.015 µmol/mol	0.009
H_2	0.0025 µmol/mol	0.0014
CO	0.0010 µmol/mol	0.0006

Table 10 Hydrogen (cylinder № 94353)

Component	Amount of substance fraction	u, µmol/mol (k=1)
H_2	99.9994404 cmol/mol	—
N_2	5.4 µmol/mol	0.3
O_2	0.15 µmol/mol	0.09
CO_2	0.030 µmol/mol	0.017
CH_4	0.015 µmol/mol	0.009

CO	0.001 µmol/mol	0.0006

2 Instrumentation

The measurements were performed using Gas Chromatograph “Chromos GC -1000” (Chromos, Dzerzhinsk, Russia), equipped with 4 detectors (channels)

Data collection: Software “Chromos Setup 2.16.44”

Channel 1 (H_2; N_2; CH_4):
Detector: TCD 1
Column: NaX, 4 m × 3 mm
Carrier gas: Ar
Gas flow:10 ml/min
Injected dose: 1cm^3
Detector temperature: 150°C
Temperature program of the column thermostat: 60°C – 3 min, 20°C/min, 160°C – 0 min, 10°C/min, 200°C.

Channel 2 (O_2; N_2; CH_4):
Detector: TCD 2
Column: NaX, 2 m × 3 mm
Carrier gas: He
Gas flow:15 ml/min
Injected dose: 1cm^3
Detector temperature: 150°C
Temperature program of the column thermostat: 60°C – 3 min, 20°C/min, 160°C – 0 min, 10°C/min, 200°C.

Channel 3 (CO_2; C_2H_6; C_3H_8):
Detector: TCD 3
Column: Haysep Q, 2 m × 3 mm
Carrier gas: He
Gas flow:15 ml/min
Injected dose: 1cm^3
Detector temperature: 150°C
Temperature program of the column thermostat: 60°C – 3 min, 20°C/min, 160°C – 0 min, 10°C/min, 200°C.

Channel 4 (C_2H_6; C_3H_8):
Detector: FID
Column: Haysep R, 2 m × 3 mm
Carrier gas: He
Gas flow:15 ml/min
Injected dose: 1cm^3
Detector temperature: 150°C
Temperature program of the column thermostat: 60°C – 3 min, 20°C/min, 160°C – 0 min, 10°C/min, 200°C.

3 Measurement procedure

Single point calibration method was used to determine components mole fraction in the comparison mixture (X mixture).

Measurement sequence was in the order:
Calibr. mixture 1 - X mixture – Calibr.mixture 1- X mixture – Calibr.mixture 1;
Calibr. mixture 2 - X mixture – Calibr.mixture 2 - X mixture – Calibr.mixture 2;

Calibr. mixture 3 - X mixture – Calibr.mixture 3 - X mixture – Calibr.mixture 3.

4 Uncertainty evaluation

Component	Measurement result, cmol/mol	u_{grav} (purity+ weighing), cmol/mol	u_{ver} cmol/mol	u_{meas} cmol/mol	u (combined standard uncertainty), cmol/mol	U (expanded uncertainty, k=2), cmol/mol	U_0 (relative expanded uncertainty, %
Hydrogen	0.7891	0.0003	0,0014	0.00062	0.0016	0.0031	0.39
Oxygen	0.4141	0.00005	0.00051	0.00024	0.00058	0.0012	0.28
Nitrogen	15.61	0.0006	0.0126	0.0090	0.0155	0.0311	0.20
Methane	43.63	0.0010	0.0151	0.0171	0.0228	0.0456	0.10
Carbon dioxide	39.43	0.0008	0.0212	0.0217	0.0304	0.0607	0.15
Ethane	0.06180	0.000015	0.000077	0.000047	0.000092	0.000184	0.30
Propane	0.01484	0.000006	0.000027	0.000005	0.000028	0.000056	0.38

Date: 17/07/2015

Measurement report VSL

Cylinder number: 1224

Measurement #1

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	2015-08-31	43.70	0.02	6
Carbon dioxide	2015-08-31	39.31	0.03	6
Nitrogen	2015-08-31	15.70	0.01	6
Hydrogen	2015-08-31	0.79	0.04	6
Oxygen	2015-08-31	0.40	0.04	6
Ethane	2015-08-24	0.062	0.03	6
Propane	2015-08-24	0.015	0.02	6

Measurement #2

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	2015-09-04	43.71	0.01	6
Carbon dioxide	2015-09-04	39.28	0.03	6
Nitrogen	2015-09-04	15.69	0.03	6
Hydrogen	2015-09-04	0.79	0.03	6
Oxygen	2015-09-04	0.40	0.03	6
Ethane	2015-08-25	0.062	0.08	6
Propane	2015-08-25	0.015	0.04	6

Measurement #3

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Methane	2015-09-08	43.69	0.02	6
Carbon dioxide	2015-09-08	39.31	0.01	6
Nitrogen	2015-09-08	15.70	0.01	6
Hydrogen	2015-09-08	0.79	0.01	6
Oxygen	2015-09-08	0.40	0.13	6
Ethane	2015-08-27	0.062	0.03	6
Propane	2015-08-27	0.015	0.03	6

Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
Methane	43.70	0.026	2
Carbon dioxide	39.30	0.032	2
Nitrogen	15.70	0.013	2
Hydrogen	0.79	0.0014	2
Oxygen	0.40	0.0019	2
Ethane	0.062	0.00013	2
Propane	0.015	0.000021	2

Calibration standards

All Primary Standard gas Mixtures (PSMs) for the measurements of biogas are multi compound mixtures. Preparation and validation of the PSM's were performed according ISO 6142-1 [1]. The standard uncertainty is based on the uncertainty of the gravimetric preparation process and the purity analysis of the parent gases.

For the PSM's two different carbon dioxide parent gases were used.

Table 2: Purity table methane APCH4

Compound	Mol fraction x (mol/mol)	Uncertainity u(x) (mol/mol)
Methane	0.99999860	0.00000060
Carbon dioxide	0.000000050	0.000000030
Ethane	0.000000050	0.000000030
Propane	0.0000000050	0.0000000030
Hydrogen	0.000000050	0.000000030
Nitrogen	0.00000100	0.00000060
Oxygen	0.00000025	0.00000014

Table 3: Purity table Carbon dioxide AP9367

Compound	Mol fraction x (mol/mol)	Uncertainity u(x) (mol/mol)
Carbon monoxide	0.0000000120	0.0000000025
Carbon dioxide	0.99999774	0.00000035
Water	0.00000050	0.00000025
Nitrogen	0.00000150	0.00000023
Oxygen	0.000000246	0.000000065

Table 4: Purity table Carbon dioxide AP6453

Compound	Mol fraction x (mol/mol)	Uncertainity u(x) (mol/mol)
Argon	0.00000730	0.00000040
Carbon dioxide	0.9999710	0.0000020
Ethane	0.0000003080	0.0000000040

Nitrogen	0.0000141	0.0000012
Oxygen	0.00000730	0.00000030

Table 5: Purity table Nitrogen APN26b

Compound	Mol fraction x (mol/mol)	Uncertainity u(x) (mol/mol)
Argon	0.0000050	0.0000030
Methane	0.0000000080	0.0000000050
Carbon monoxide	0.0000000150	0.0000000090
Carbon dioxide	0.0000000100	0.0000000060
Hydrogen	0.000000025	0.000000015
Water	0.0000000100	0.0000000060
Nitrogen	0.9999949	0.0000060
Oxygen	0.0000000050	0.0000000030

Table 6: Purity table Hydrogen AP8449

Compound	Mol fraction x (mol/mol)	Uncertainity u(x) (mol/mol)
Methane	0.000000025	0.000000014
Carbon monoxide	0.00000000100	0.00000000060
Carbon dioxide	0.000000025	0.000000014
Hydrogen	0.99999955	0.00000020
Water	0.00000025	0.00000014
Nitrogen	0.000000100	0.000000058
Oxygen	0.000000050	0.000000029

Table 7: Purity table Oxygen LI0656

Compound	Mol fraction x (mol/mol)	Uncertainity u(x) (mol/mol)
Argon	0.0000020	0.0000010
Methane	0.0000000330	0.0000000030
Carbon monoxide	0.0000000100	0.0000000020
Carbon dioxide	0.0000000100	0.0000000060
Water	0.000000040	0.000000010
Nitrogen	0.0000030	0.0000017
Oxygen	0.9999949	0.0000022

Table 8: Purity table Ethane SC0084

Compound	Mol fraction x (mol/mol)	Uncertainity u(x) (mol/mol)
Ethane	0.9999756	0.0000030
Nitrogen	0.0000112	0.0000018
Oxygen	0.0000132	0.0000011

Table 9: Purity table Propane AP4621

Compound	Mol fraction x (mol/mol)	Uncertainity u(x) (mol/mol)
Argon	0.0000040	0.0000020

Ethane	0.0000603	0.0000014
Propene	0.00004700	0.00000060
Propane	0.999829	0.000010
1,3-butadiene	0.000000146	0.000000010
iso-butene	0.0000001450	0.0000000050
n-butane	0.000000590	0.000000030
iso-butane	0.0000448	0.0000015
Nitrogen	0.0000101	0.0000012
Oxygen	0.0000040	0.0000020

Verification measures

The calibration curves for one of the measurements (first) are given in tables 9 through 15, which are obtained with CurveFit software.

Table 10: Calibration curve of Methane.

Mixture	x cmol/mol	$u(x)$ cmol/mol	y a.u.	u(y) a.u.	$\Delta x/u(x)$	$\Delta y/u(y)$
VSL338377	38.78	0.0029	990.41	0.13	-0.17	0.31
VSL400230	39.065	0.0037	997.50	0.18	0.22	-0.42
VSL143505	58.94	0.0023	1482.28	0.24	0.05	-0.23
VSL143724	63.65	0.0021	1595.14	0.10	-0.08	0.16
VSL247675	69.33	0.0019	1730.88	0.11	0.03	-0.07

Table 11: Calibration curve of Carbon dioxide.

Mixture	x cmol/mol	$u(x)$ cmol/mol	y a.u.	u(y) a.u.	$\Delta x/u(x)$	$\Delta y/u(y)$
VSL247675	9.87	0.00073	228.34	0.04	-0.16	0.37
VSL143505	14.99	0.00094	346.089	0.03	0.29	-0.40
VSL248507	38.68	0.0022	884.64	0.07	-0.61	0.85
VSL338377	39.83	0.0021	910.57	0.17	-0.05	0.19
VSL400230	43.852	0.0029	1001.23	0.13	0.61	-1.21

Table 12: Calibration curve of Nitrogen.

Mixture	x cmol/mol	$u(x)$ cmol/mol	y a.u.	u(y) a.u.	$\Delta x/u(x)$	$\Delta y/u(y)$
VSL143724	9.98	0.0011	667.012	0.13	0.02	-0.04
VSL400230	14.99	0.0015	998.98	0.08	-0.40	0.31
VSL248507	15.78	0.0013	1051.15	0.13	0.32	-0.49
VSL338377	19.75	0.0012	1313.73	0.27	-0.01	0.03
VSL143505	24.98	0.0015	1658.63	0.13	-0.01	0.01

Table 13: Calibration curve of Hydrogen.

Mixture	x cmol/mol	$u(x)$ cmol/mol	y a.u.	u(y) a.u.	$\Delta x/u(x)$	$\Delta y/u(y)$
VSL247675	0.10	0.000044	50.27	0.03	-0.03	0.04
VSL143505	0.49	0.00018	249.64	0.06	0.47	-0.32
VSL248507	0.81	0.00050	403.90	0.08	-1.45	0.46
VSL338377	1.51	0.00060	755.53	0.27	0.71	-0.64
VSL400230	2.03	0.00080	1012.82	0.16	-0.29	0.12

Table 14: Calibration curve of Oxygen.

Mixture	x cmol/mol	$u(x)$ cmol/mol	y a.u.	u(y) a.u.	$\Delta x/u(x)$	$\Delta y/u(y)$
VSL400230	0.050	0.000016	968.96	0.49	0.10	-0.15
VSL338377	0.10	0.000020	1956.48	3.07	-0.21	1.63
VSL143724	0.30	0.000052	5974.92	2.72	0.45	-1.16
VSL143505	0.50	0.000076	9934.06	4.72	-0.40	1.21
VSL247675	0.80	0.00016	16184.89	41.17	0.15	-1.90

Table 15: Calibration curve of Ethane.

Mixture	x cmol/mol	$u(x)$ cmol/mol	y a.u.	u(y) a.u.	$\Delta x/u(x)$	$\Delta y/u(y)$
VSL400230	0.0099	0.0000030	997.89	1.02	0.10	-0.35
VSL338377	0.020	0.0000040	1991.83	1.70	-0.22	0.83
VSL143724	0.040	0.000014	3995.67	3.45	0.08	-0.21
VSL143505	0.070	0.000017	6984.42	1.67	0.27	-0.26
VSL247675	0.10	0.000022	10014.64	2.09	-0.15	0.15

Table 16: Calibration curve of Propane.

Mixture	x cmol/mol	$u(x)$ cmol/mol	y a.u.	u(y) a.u.	$\Delta x/u(x)$	$\Delta y/u(y)$
VSL400230	0.0020	0.0000010	997.30	0.30	0.09	-0.07
VSL338377	0.0040	0.0000010	2007.14	1.53	-0.27	0.65
VSL143724	0.0080	0.0000030	4050.72	4.48	0.43	-1.16
VSL143505	0.014	0.0000050	7091.60	2.74	-0.17	0.20
VSL247675	0.020	0.0000060	10194.86	2.16	0.03	-0.02

Instrumentation

The compounds are determined on two different GC's

GC-1 (Biogas analyzer):
Methane, Carbon dioxide, Nitrogen, Hydrogen and Oxygen.

GC: Agilent 7980A

Channels: Back channel: pre-column HayeSep Q and HayeSep T+ Thermal conductivity detector (TCD). Helium as carrier, carbon dioxide and methane are determined.
Aux Channel: Hayesep/Molsieve column + TCD. Argon as carrier gas: Hydrogen, oxygen and nitrogen are determined.

Sample Method: 35°C for 6 minutes, with 10°C/min to 100°C hold for 0.5 minutes.

Sample introduction:	Multi position gas sampling valves, injection at ambient pressure.
Data collection:	HP Chemstation Software

GC-14:
Ethane and Propane

GC:	Agilent 7980A
Channels:	Back channel: 10' x 1/8" Sulfinert, Molsieve 5A + flame ionization detector (FID).
Sample Method:	100 °C for 20 minutes.
Sample introduction:	Multi position gas sampling valves, injection at ambient pressure.
Data collection:	HP Chemstation Software

Calibration method and value assignment

The set of standards used for a measurement and the mixtures to be analysed are connected to the gas chromatograph. A measurement of a cylinder consist of 6 injections that are averaged and corrected for area using the following equation [2].

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

Where Y_i is the corrected response, A_i is the average of the areas of the sample (6 injections) and $A_{ref,i}$ is the standard pressure.

After the area correction the calibration curve was obtained in accordance with ISO6143 [3]. A parabolia was used for all the components as calibration function.

Uncertainty evaluation

The calibration curves where obtained in accordance with ISO 6143 [3]. As indicated, a straight line was used. The value for amount of fraction (results) is obtained by reverse use of the calibration curve [3]. The associated uncertainty is obtained using the law of propagation of uncertainty. To arrive at the final result, the results of the three measurements were averaged. The standard error of the mean was combined with the pooled uncertainty from evaluating the data. The expanded uncertainty was obtained by multiplying the standard uncertainty with a coverage factor of $k = 2$.

References

[1] International Organization for Standardization, "ISO 6142-1:2015(E) – Gas analysis -- Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures", ISO Geneva, 2015

[2] van der Veen A.M.H., Ziel P.R., Oudwater R., Quist Y.M., Alberti D., Zalewska E.T. (2012) Natural gas analysis - Development of a method for retaining the calibration status of a gas chromatograph, Delft VSL, report number: S-CH.09.34

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