

International Comparison

Adriaan M.H. van der Veen¹, Hans-Joachim Heine², Freek N.C. Brinkmann¹, Paul R. Ziel¹, Ed W.B. de Leer¹, Wang Lin Zhen³, Kenji Kato⁴, Leonid A. Konopelko⁵, Tatjana A. Popova⁵, Yuri I. Alexandrov⁵, Elena N. Kortchagina⁵, Yuri A. Kustikov⁵, Stanislav Musil⁶, Martin J.T. Milton⁷, Franklin Guenther⁸, George Rhoderick⁸

¹NMi Van Swinden Laboratorium B.V. (NMi VSL), Schoemakerstraat 97, 2628 VK Delft, the Netherlands

²Bundesanstalt für Materialforschung und -prüfung (BAM), Abteilung I, Unter den Eichen 87, D-12205 Berlin, Germany

³National Research Center for Certified Reference Materials (NRCCRM), No.7, District 11, Heping Street, 100013 Beijing, P.R. China

⁴National Metrology Institute of Japan (NMIJ), 305-8565 Umezono 1-1-1, Tsukuba Ibaraki, Japan

⁵D .I. Mendeleev Institute for Metrology (VNIIM), Laboratory of State Standards in the Field of Analytical Measurements, 19, Moskovsky Prospekt, 198005 St-Petersburg, Russia

⁶Slovak Institute of Metrology (SMU), Karloveská 63, 742 55 Bratislava, Slovak Republic

⁷National Physical Laboratory (NPL), Teddington, Middlesex, TW11 0LW, UK

⁸National Institute of Standards and Technology (NIST), Chemical Science and Technology Laboratory, 100 Bureau Drive, Gaithersburg MD, USA

Final Report CCQM K16 - Natural gas types IV and V

Field

Amount of substance

Subject

Comparison in the field of natural gas analysis

Participants

NRCCRM (CR), BAM (DE), NMIJ (JP), NMi VSL (NL), VNIIM (RU), SMU (SK), NPL (UK), NIST (US)

Organising body

CCQM

Rationale

The measurement of composition of natural gas mixtures is commonly used for the calculation of its calorific value. Natural gas is a fossil fuel and its economic value is mainly determined by its calorific value. Other aspects that might impact the economic value of natural gas, such as its sulphur content, have not been addressed in this key comparison. The calorific value has been requested from the participating national metrology institutes (NMIs) as well, to study the impact of the uncertainty from measuring the composition on the calorific value.

At the highest metrological level, natural gas standards are commonly prepared gravimetrically as PSMs (Primary Standard Mixtures). At this level, two series of mixtures have been prepared (one with a low and one with a high calorific value), with hydrocarbons up to C₆ (hexane) to complement and extend the earlier key comparisons in this area (CCQM-K1e-g)

[1]. The mixtures in CCQM-K1 contained only components up to C₄ (butane). The compositions of the mixtures used in this key comparison have been chosen to be typical for respectively low and high calorific value mixtures.

Participants

Table 1 lists the participants in this key comparison.

Table 1: List of participants

Acronym	Country	Institute
BAM	DE	Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany
NRCCRM	CR	National Research Center for Certified Reference Materials, Beijing, PR China
NMIJ	JP	National Metrology Institute of Japan, Tsukuba, Japan
NMi VSL	NL	NMi Van Swinden Laboratorium B.V., Delft, the Netherlands
VNIIM	RU	D.I. Mendeleev Institute for Metrology, St. Petersburg, Russia
SMU	SK	Slovak Institute of Metrology, Bratislava, Slovak Republic
NPL	UK	National Physical Laboratory, Teddington, Middlesex, United Kingdom
NIST	US	National Institute of Standards and Technology, Gaithersburg MD, United States of America

Two NMIs, CSIRO-NML (Australia) and BNM-LNE (France), participated in a related study (CCQM-P49). Both comparisons were run using the same batch of mixtures and essentially the same protocol; the only differences are that CCQM-K16 is a *key comparison*, whereas CCQM-P49 is a *study*, and that for participating in CCQM-K16 it was mandatory to measure all components in the two natural gas mixtures [2].

Measurement standards

Two mixtures have been submitted, one with a low calorific value, and one with a high calorific value. Table 2 shows the nominal composition of the mixtures used (expressed as amount of substance fractions).

Table 2: Nominal composition of the mixtures

Component	Low calorific mixture x (% mol/mol)	High calorific mixture x (% mol/mol)
Nitrogen	12.0	1.20
Carbon dioxide	4.0	0.80
Helium	0.50	
Ethane	0.75	11.00
Propane	0.30	4.50
<i>iso</i> -Butane	0.20	0.10
<i>n</i> -Butane	0.20	0.10
<i>iso</i> -Pentane	0.050	0.035
<i>n</i> -Pentane	0.050	0.035
<i>neo</i> -Pentane	0.050	0.050
<i>n</i> -Hexane	0.050	0.020
Methane	81.85 (balance)	82.16 (balance)

The mixtures have been prepared gravimetrically and subsequently verified. The preparation required the use of pre-mixtures. The preparation method has been designed in such a way, that losses of higher hydrocarbons due to e.g. adsorption effects are effectively eliminated. The verification of the mixtures is a quality measure, that is, it should give proof of the validity of the property values obtained from gravimetry and purity verification. In principle, the uncertainty of verification adds to the uncertainty of the reference values, as the uncertainty from verification is not negligible in comparison to the combined uncertainty from gravimetry and purity verification of the parent gases/liquids.

For the low calorific mixture, five cylinders were prepared individually according to ISO 6142 [7]. The content of the impurities in all pure gases were determined before use by GC-DID, GC-FID and / or GC-TCD. Depending on the concentration of the components, gas mixtures were prepared individually from pure gases or from pre-mixtures, which were individually prepared from pure gases. The following pre-mixtures were made

1. 50% helium in methane
2. 25% carbon dioxide in nitrogen
3. 2.0% n-butane and 2.0% iso-butane in methane
4. 7.5% ethane, 3.0% propane, and 0.5% neo-pentane in pre-mixture 1

After preparation, the gas mixtures were verified by analytical comparisons with existing gravimetrically prepared standards. Only when no significant difference between the analysed and the calculated gravimetric composition is found, the gas mixtures are accepted as a sample candidate. Each of the five gas mixtures was divided by pressure equalization in three cylinders. After dividing all cylinders were verified once more by analytical comparisons with existing gravimetrically prepared standards.

The preparation of the high calorific mixtures at NMi VSL has been carried out using the normal procedure for the preparation of gas mixtures [6]. The mixtures were prepared from three types of pre-mixtures:

- Type A: 0.2% n-hexane in methane (40 bar)
- Type B: 0.35% n-pentane, 0.35% iso-pentane, and 0.5% neo-pentane in methane (100 bar)
- Type C: 1% n-butane, 1% iso-butane, 8% carbon dioxide and 12% nitrogen in methane (100 bar)

All pre-mixtures have been made in the same matrix (methane) as that of the final mixtures. The target composition of all mixtures was identical (see table 2). After preparation, the mixtures have been verified by comparing the key comparison mixtures with PSMs from the standards maintenance programme. The mixtures have been verified using GC/TCD (nitrogen, carbon dioxide, methane, ethane, propane, and iso-butane) and GC/FID (n-butane, pentanes, n-hexane). Table 3 gives the standard uncertainty of the comparison of the mixtures (u_{ver}) and the repeatability standard deviation (s_r) for the high calorific mixture.

Table 3: Verification uncertainty high calorific mixture

Component	s_r (% relative)	u_{ver} (% relative)
nitrogen	0.20	0.16
carbon dioxide	0.30	0.10
methane	0.10	0.04

Component	s_r (% relative)	u_{ver} (% relative)
ethane	0.15	0.04
propane	0.15	0.10
iso-butane	0.15	0.16
n-butane	0.10	0.17
iso-pentane	0.20	0.16
n-pentane	0.20	0.15
neo-pentane	0.20	0.15
n-hexane	0.30	0.15

Measurement protocol

The laboratories were requested to use their normal procedure for the measurement of the composition of the gas mixtures. For participation in this key comparison, it had been requested that participants determine all components in the mixture, and not just a subset. The participants were asked to perform at least three measurements, on different days with independent calibrations. It was allowed to use the same set of measurement standards for these calibrations.

The participants were requested to describe their methods of measurement, and the models used for evaluating the measurement uncertainty. A typical numerical example of the evaluation of measurement uncertainty had to be included as well (for each component). It was not required to reproduce all numerical data underlying the results reported and the uncertainties thereof, but the report of the evaluation of measurement uncertainty should at least allow the address which components have been included in the evaluation, and what their quantitative impact on the uncertainty of the results reported is.

Laboratories were allowed to submit an estimate for the calorific value. These results are not formal part of this key comparison. An exception has been made for one laboratory, which has provided an experimental value. This result is described in detail in annex C of this report.

Schedule

The schedule of this key comparison was as follows:

Until July 2001	Preparation of the gas mixtures
August 1, 2001	Shipment of distribution cylinders to participating laboratories
August 1, 2001	Start of comparison
November 15, 2001	Close of comparison
November 22, 2001	Cylinders and reports due to pilot laboratory

Only three laboratories reported within three weeks after the deadline (22 November 2001). It was allowed to submit reports until 28 February 2002. In one case the NMI was excused, as the shipment of the cylinder from NMI VSL failed, due to problems with the shipping company. Upon advice of the receiving NMI, the cylinder was shipped again and reached in November 2002 the participant.

The cylinder for NIST was lost somewhere between the destination airport and the NMI. Consequently, this laboratory did not submit any data. Apart from these two incidents, no major problems regarding the shipment were encountered.

Some laboratories did not use the forms as supplied with the protocol. The description of methods (annex A) and uncertainty evaluation procedures (annex B) differed widely, de-

spite the efforts made in developing the protocol to get the information in a more or less harmonised way. Furthermore, in some reports the units as indicated were changed, which meant that quite some results had to be converted into the appropriate units prior to evaluating the key comparison data. These corrections have been made in accordance to the protocol.

In particular, the description of the evaluation method for measurement uncertainty widely differed, both in length as well as in content. The idea of the protocol was to provide information on the model used for evaluating measurement uncertainty, as well as getting an idea of what sources of uncertainty are the most important ones. In many cases, the statements regarding uncertainty are nicely supported by information about the evaluation method, and the values of the major uncertainty components. Some participants have used one model for all components, and shortened the description accordingly.

Measurement equation

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

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

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

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

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} + \Delta x_{i,stab} + \Delta x_{i,nr} \quad (1)$$

The value obtained from equation (1) is sometimes referred to as "gravimetric value". Assuming independence of the terms in equation (1), the expression for the combined standard uncertainty becomes

$$u^2(x_{i,prep}) = u^2(x_{i,grav}) + u^2(\Delta x_{i,purity}) + u^2(\Delta x_{i,stab}) + u^2(\Delta x_{i,nr}). \quad (2)$$

For the mixtures used in this key comparison, the following statements hold (for all components involved). First of all, the preparation method has been designed in such a way that

$$\Delta x_{i,nr} = 0, \quad (3)$$

and its standard uncertainty as well. Furthermore, long-term stability study data has shown that

$$\Delta x_{i,stab} = 0, \quad (4)$$

and its standard uncertainty as well. In practice, this means that the scattering of the results over time in the long-term stability study can be explained solely from the analytical uncertainty (e.g. calibration, repeatability of measurement). On this basis, using the the-

ory of analysis of variance [8,9] the conclusion can be drawn that the uncertainty due to long-term stability can be set to zero.

Summarising, the model reduces to

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} \quad (5)$$

and for the associated standard uncertainty, the following expression is obtained

$$u^2(x_{i,prep}) = u^2(x_{i,grav}) + u^2(\Delta x_{i,purity}) \quad (6)$$

The validity of the mixtures has been demonstrated by verifying the composition as calculated from the preparation data with that obtained from (analytical chemical) measurement. In order to have a positive demonstration of the preparation data (including uncertainty, the following condition should be met [7]

$$|x_{i,prep} - x_{i,ver}| \leq 2\sqrt{u^2(x_{i,prep}) + u^2(x_{i,ver})} \quad (7)$$

The factor 2 is a coverage factor (normal distribution, 95% level of confidence). The assumption must be made that both preparation and verification are unbiased. Such bias has never been observed. The uncertainty associated with the verification highly depends on the experimental design followed. In this particular key comparison, an approach has been chosen which is consistent with CCQM-K3 [10] and takes advantage of the work done in the gravimetry study CCQM-P23 [11].

The reference value of mixture i in a key comparison¹ can be defined as

$$x_{i,ref} = \langle x_{i,ref} \rangle + \delta x_{i,ref} \quad (8)$$

where

$$x_{i,ref} = x_{i,prep} + \Delta x_{i,ver} \quad (9)$$

Since the amount of substance fraction from preparation is used as the basis, the expectation of the correction $\langle \Delta x_{i,ver} \rangle$ due to verification can be taken as zero, which is consistent with the assumption made earlier that both preparation and verification are unbiased. Thus, (9) can be expressed as

$$x_{i,ref} = \langle x_{i,prep} \rangle + \delta x_{i,prep} + \delta \Delta x_{i,ver} \quad (10)$$

This expression forms the basis for the evaluation of degrees of equivalence in this key comparison. For all mixtures, it has been required that

$$\Delta x_{i,ver} = 0, \quad (11)$$

that is, there is no correction from the verification. The verification experiments have demonstrated that within the uncertainty of the verification experiment (table 3), the gravimetric values of the key comparison mixtures agreed with older measurement standards.

The expression for the standard uncertainty of a reference value becomes thus

$$u^2(x_{i,ref}) = u^2(x_{i,prep}) + u^2(\Delta x_{i,ver}) \quad (12)$$

¹ This definition of a reference value is consistent with the definition of a key comparison reference value, as stated in the mutual recognition arrangement (MRA) [4].

The values for $u(\Delta x_{i,ver})$ are given in the tables containing the results of this key comparison.

Measurement methods

The measurement methods used by the participants are described in annex A of this report. The methods used for the processing of data, including the evaluation of measurement uncertainty are given in annex B of this report.

Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as [4]

$$\Delta x_i = D_i = x_i - x_{\text{KCRV}}, \quad (13)$$

and the uncertainty of the difference D_i at 95% level of confidence. Here x_{KCRV} denotes the key comparison reference value, and x_i the result of laboratory i .² Appreciating the special conditions in gas analysis, it can be expressed as

$$\Delta x_i = D_i = x_i - x_{i,\text{ref}}. \quad (14)$$

The standard uncertainty of D_i can be expressed as

$$u^2(\Delta x_i) = u^2(x_i) + u^2(x_{i,\text{prep}}) + u^2(\Delta x_{i,\text{ver}}), \quad (15)$$

assuming that the aggregated error terms are uncorrelated. As discussed, the combined standard uncertainty of the reference value comprises that from preparation and that from verification for the mixture involved. A bilateral degree of equivalence is defined as [4]

$$D_{ij} = D_i - D_j, \quad (16)$$

and the uncertainty of this difference at 95% level of confidence. Under the assumption of independence of D_i and D_j , the standard uncertainty of D_{ij} can be expressed as

$$u^2(D_{ij}) = u^2(x_i) + u^2(x_{i,\text{prep}}) + u^2(x_{i,\text{ver}}) + u^2(x_j) + u^2(x_{j,\text{prep}}) + u^2(x_{j,\text{ver}}). \quad (17)$$

The assumption of independence is not satisfied by the preparation and verification procedures. It is well known that the use of pre-mixtures leads to correlations in the final mixtures. The standard uncertainty from verification is based on the residuals of a straight line through the data points (response versus composition), and these residuals are correlated too. However, the uncertainty of a degree of equivalence is still dominated by the uncertainty of the laboratory, so that these correlations, which certainly influence D_{ij} and its uncertainty, will have little practical impact.

In the figures 1-23, the degrees of equivalence for all participating laboratories are given relative to the gravimetric value. The uncertainties are, as required by the MRA [4], given as 95% confidence intervals. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor $k = 2$ was used. For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty (stated at a confidence level of 95%) from the laboratory was divided by the reported coverage factor. All laboratories stated $k = 2$.

NMIJ received the cylinder supposed to contain low calorific mixture empty, whereas NIST did not receive the high calorific mixture at all. For that reason, there are no results for these laboratories for the respective mixtures.

² Each laboratory receives one cylinder, so that the same index can be used for both a laboratory and a cylinder.

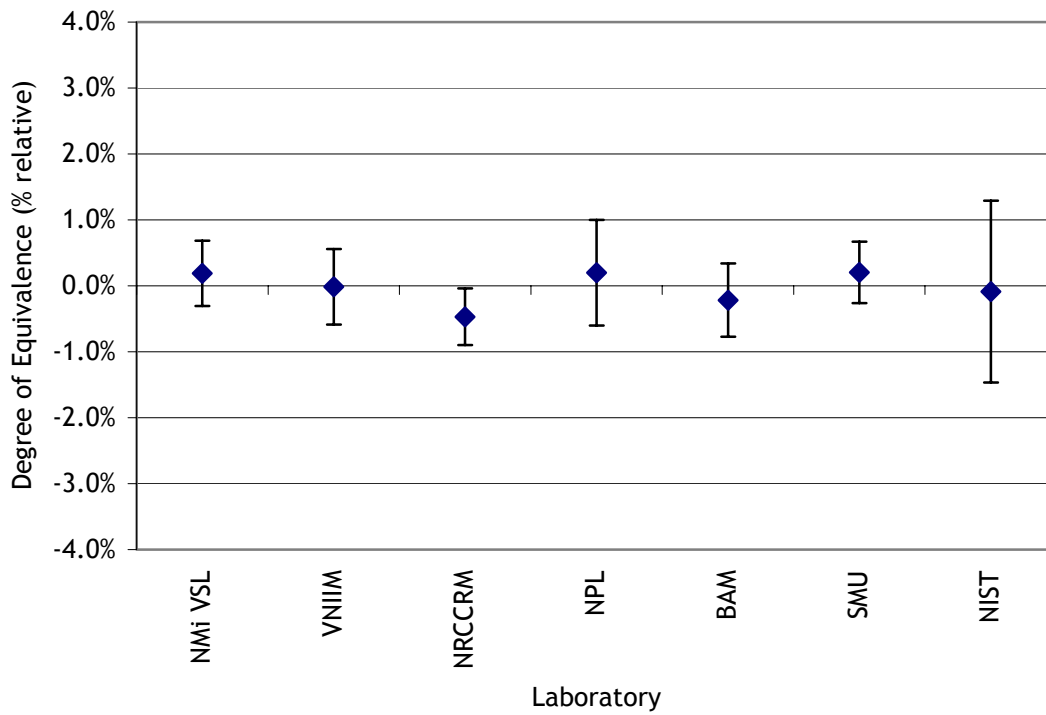


Figure 1: Degrees of equivalence for nitrogen (low calorific mixture)

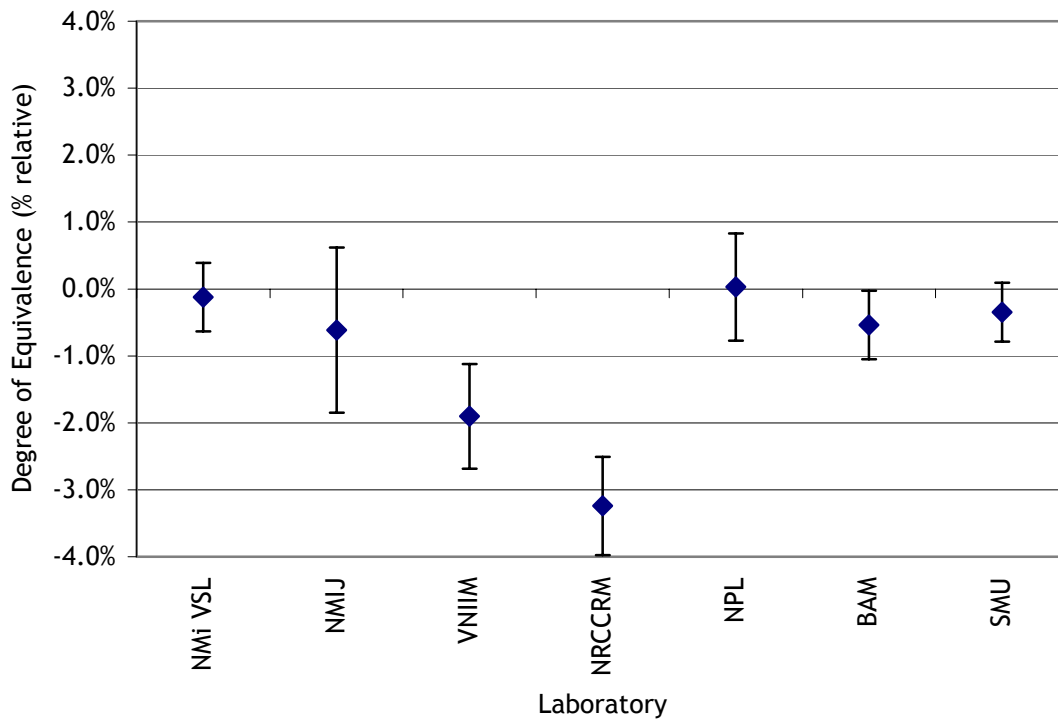


Figure 2: Degrees of equivalence for nitrogen (high calorific mixture)

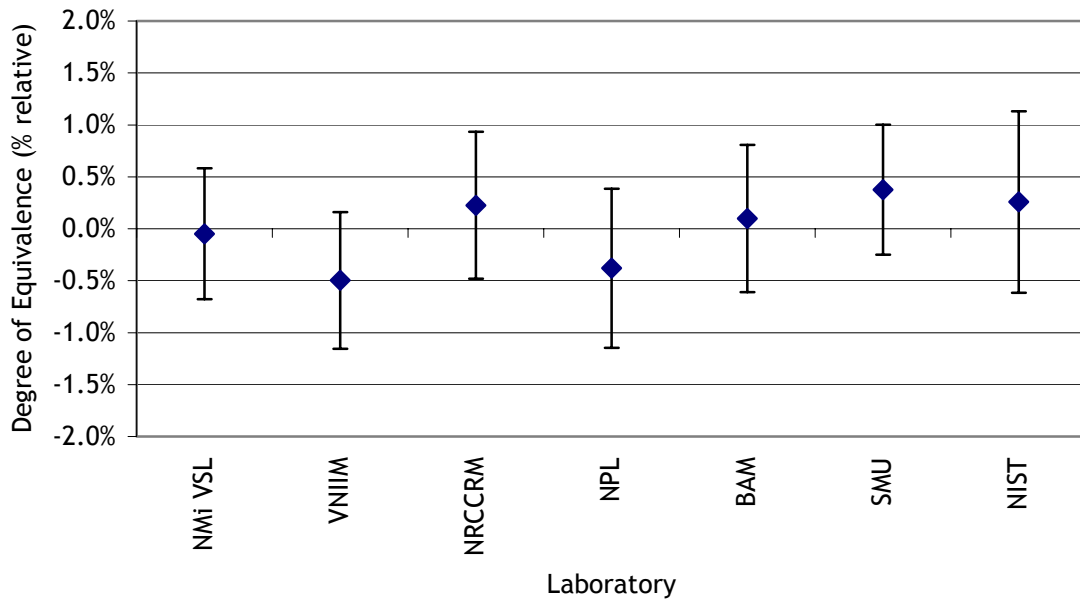


Figure 3: Degrees of equivalence for carbon dioxide (low calorific mixture)

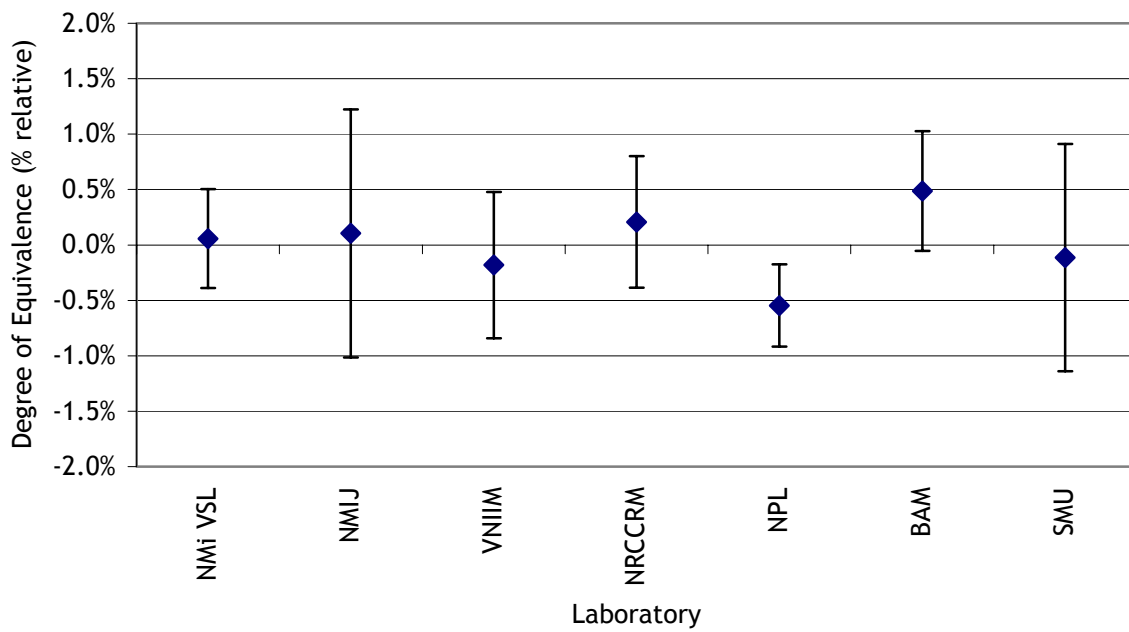


Figure 4: Degrees of equivalence for carbon dioxide (high calorific mixture)

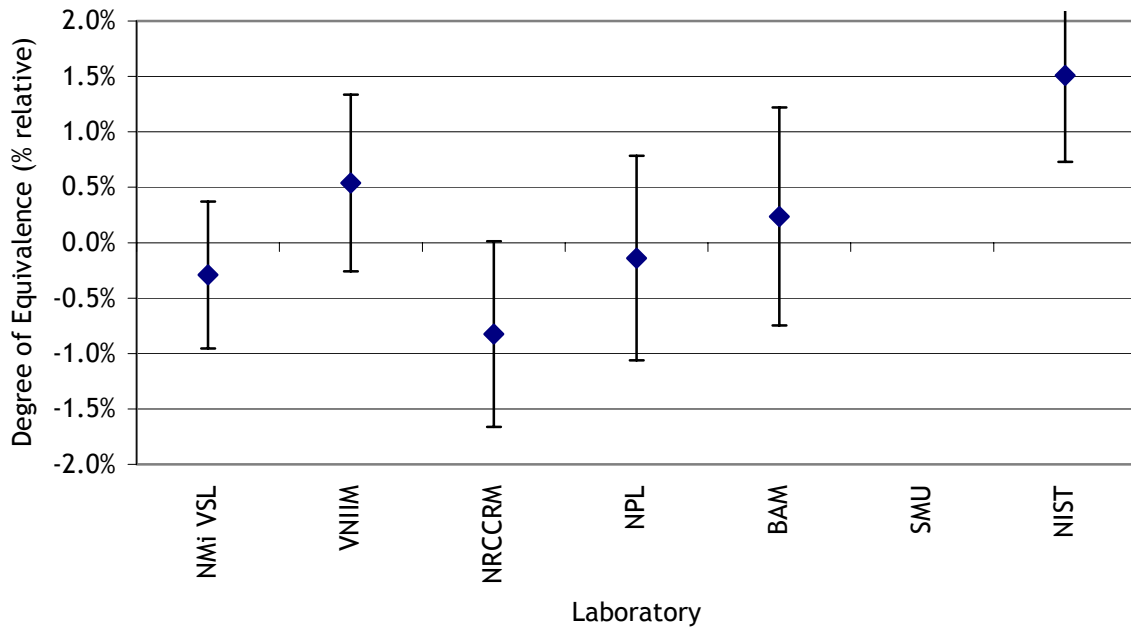


Figure 5: Degrees of equivalence for helium (low calorific mixture)

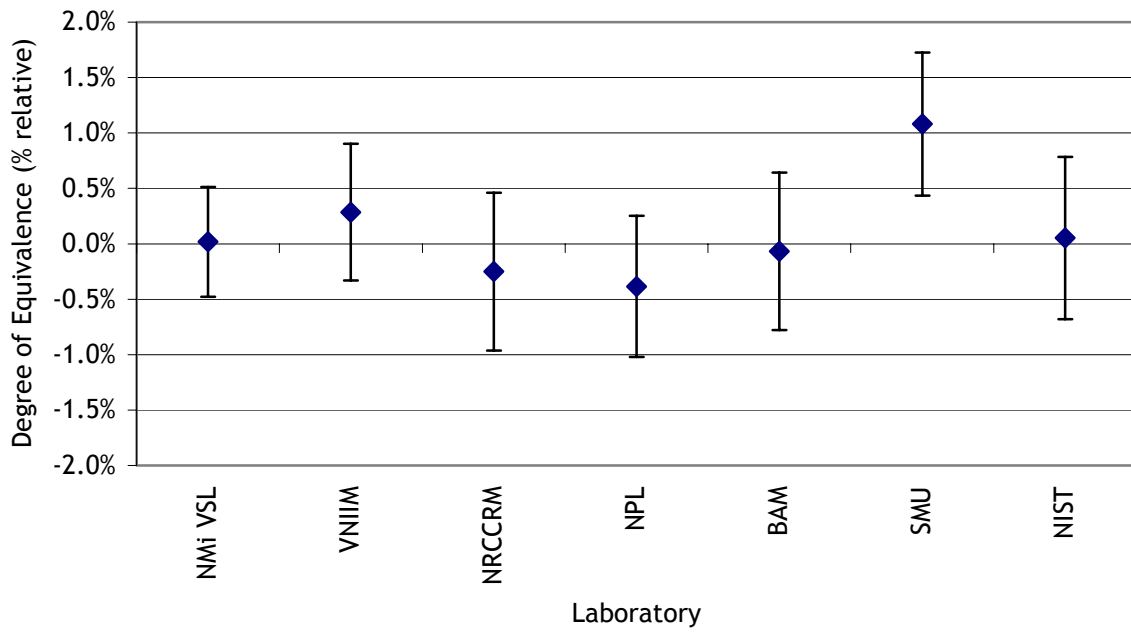


Figure 6: Degrees of equivalence for ethane (low calorific mixture)

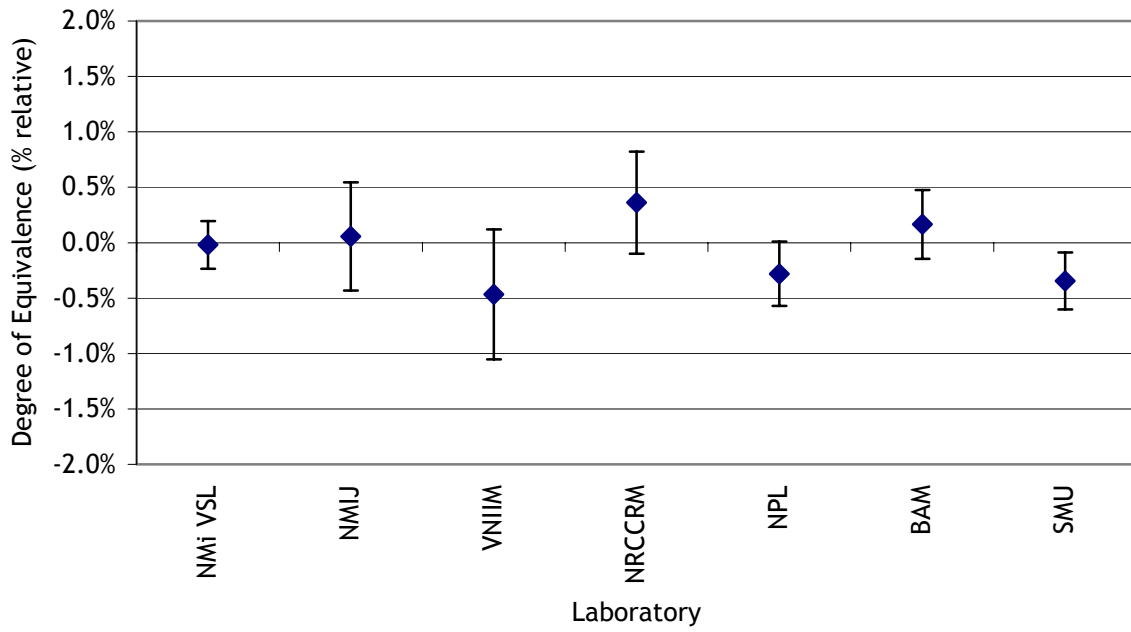


Figure 7: Degrees of equivalence for ethane (high calorific mixture)

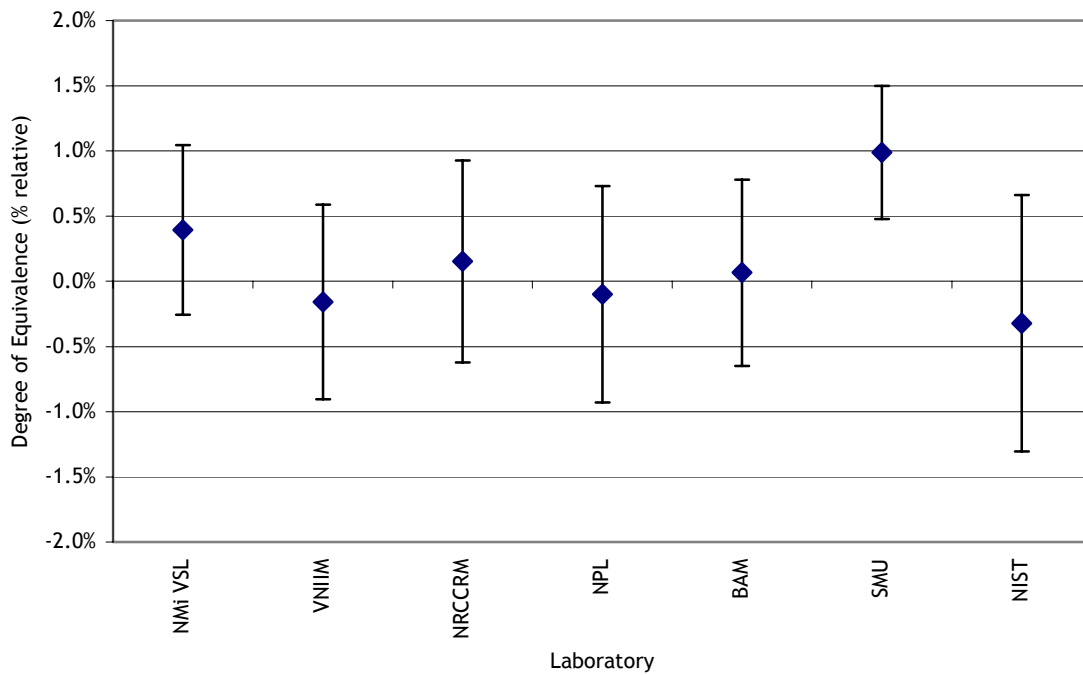


Figure 8: Degrees of equivalence for propane (low calorific mixture)

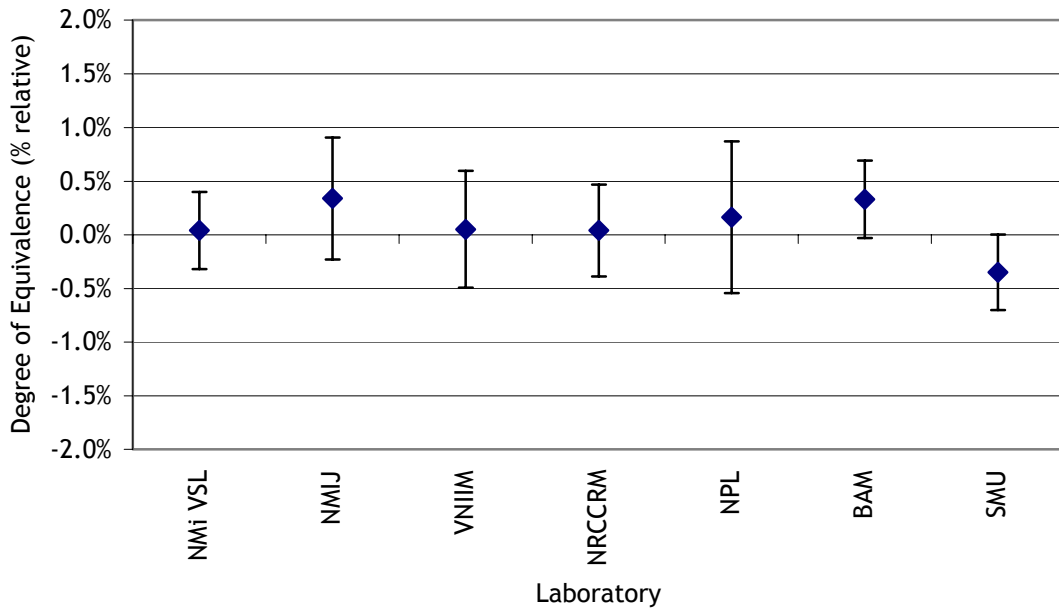


Figure 9: Degrees of equivalence for propane (high calorific mixture)

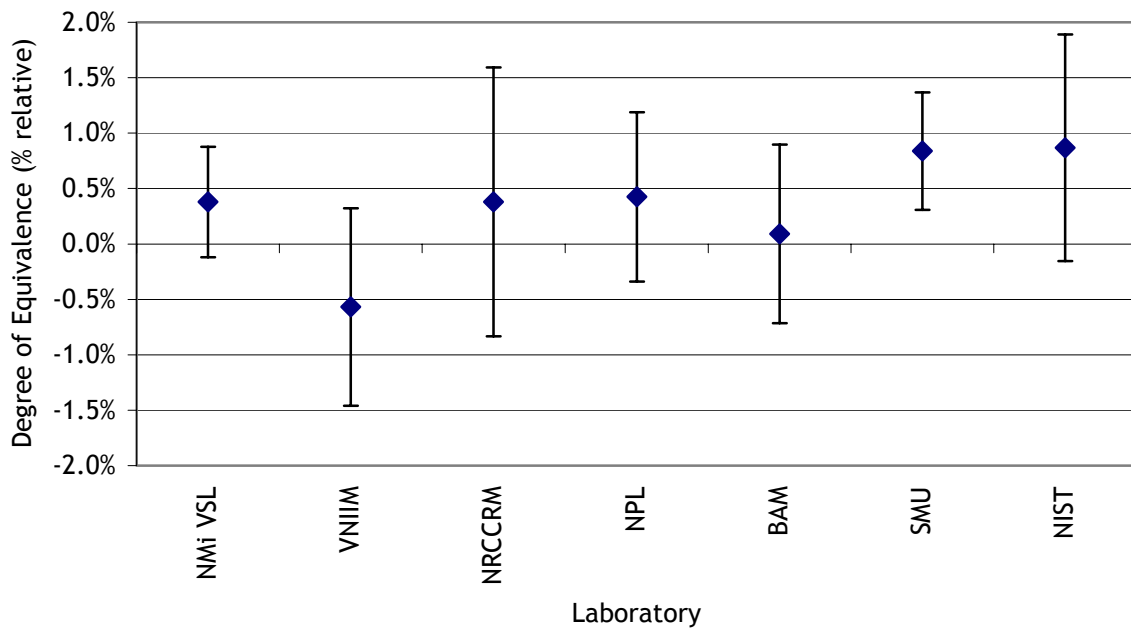


Figure 10: Degrees of equivalence for *iso*-butane (low calorific mixture)

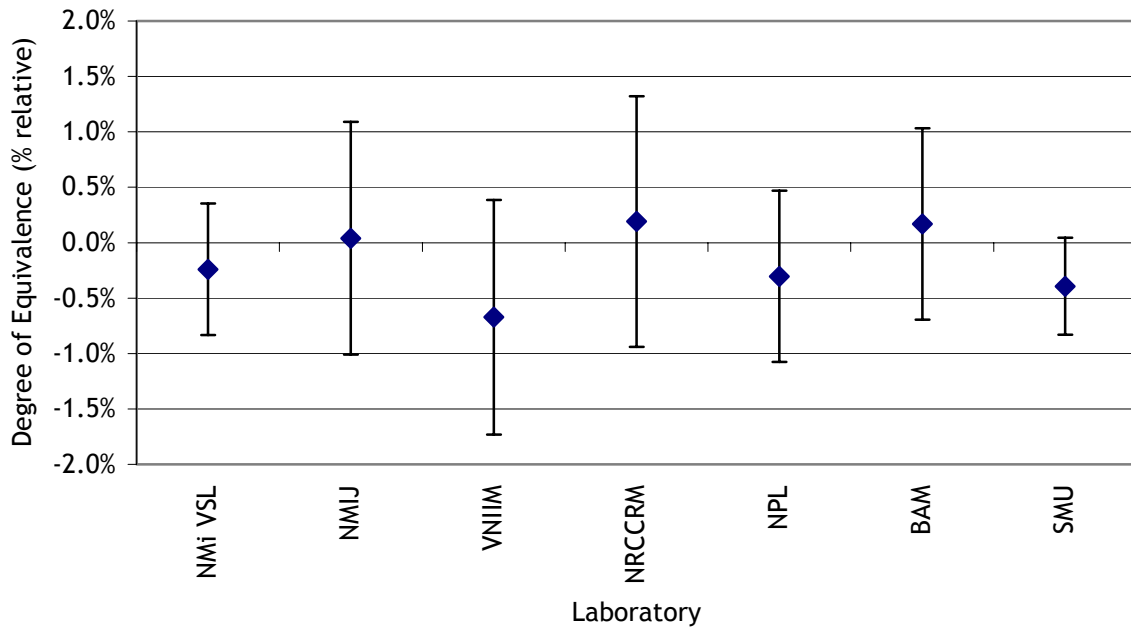


Figure 11: Degrees of equivalence for *iso*-butane (high calorific mixture)

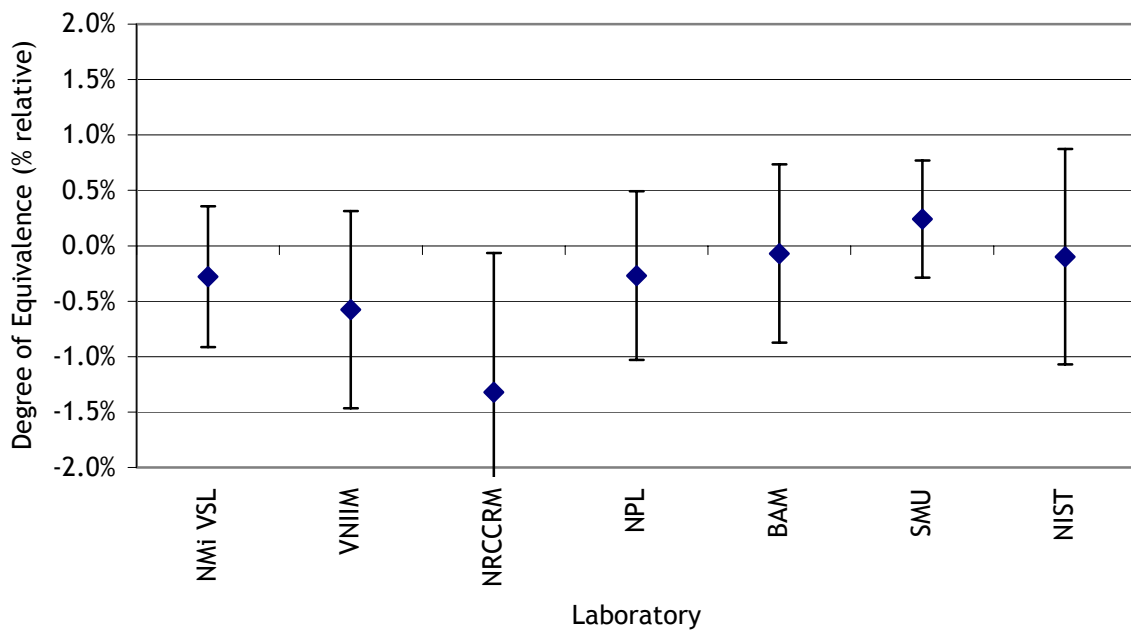


Figure 12: Degrees of equivalence for *n*-butane (low calorific mixture)

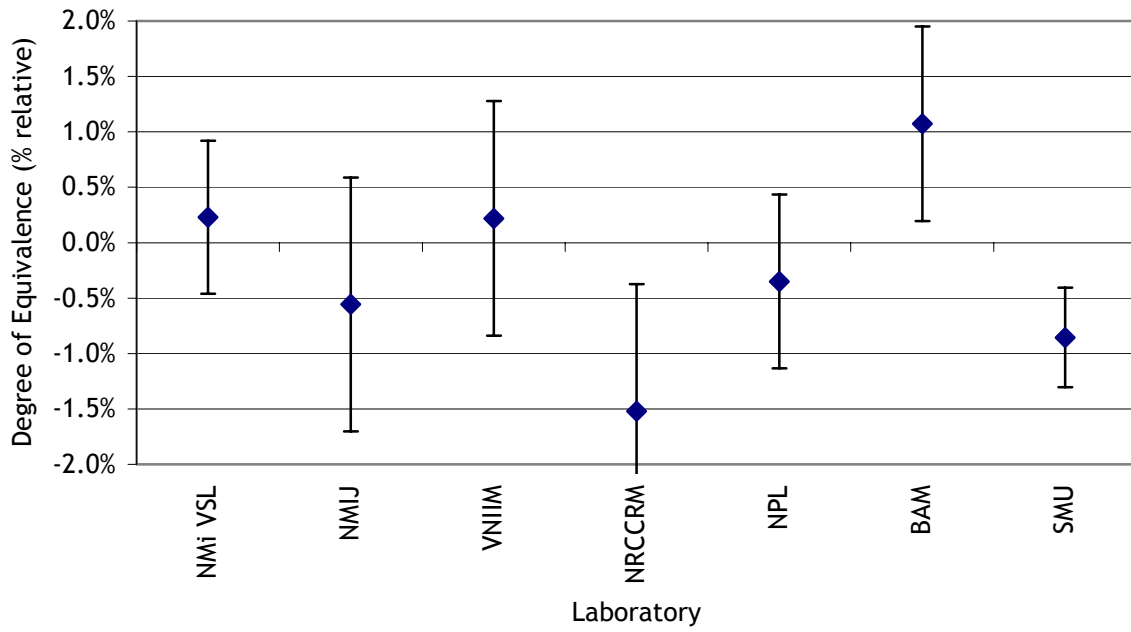


Figure 13: Degrees of equivalence for *n*-butane (high calorific mixture)

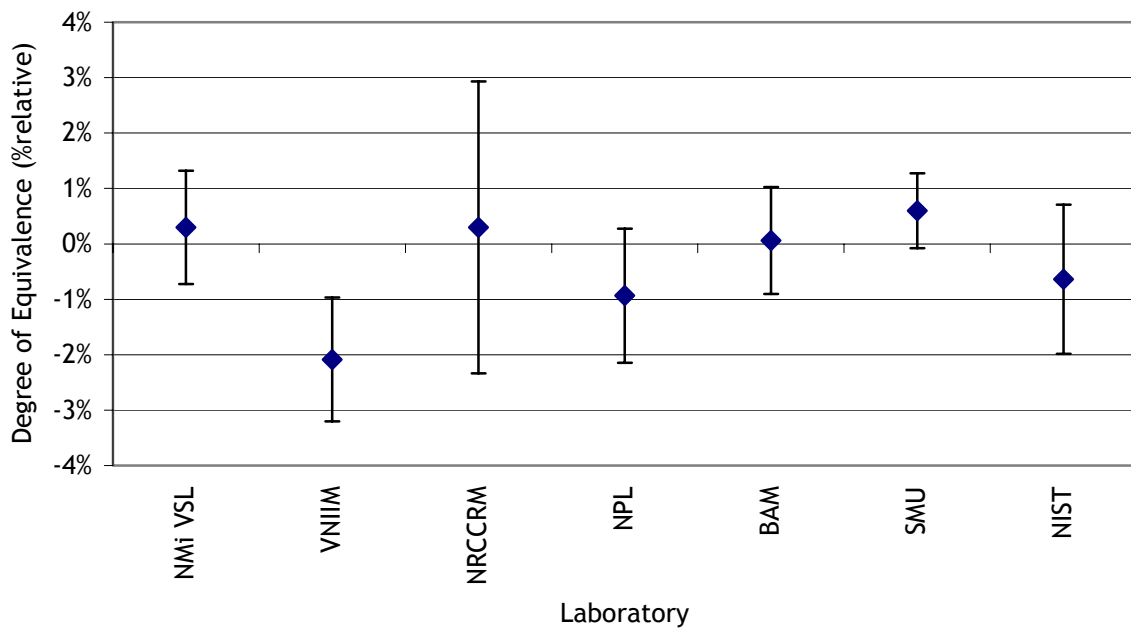


Figure 14: Degrees of equivalence for *iso*-pentane (low calorific mixture)

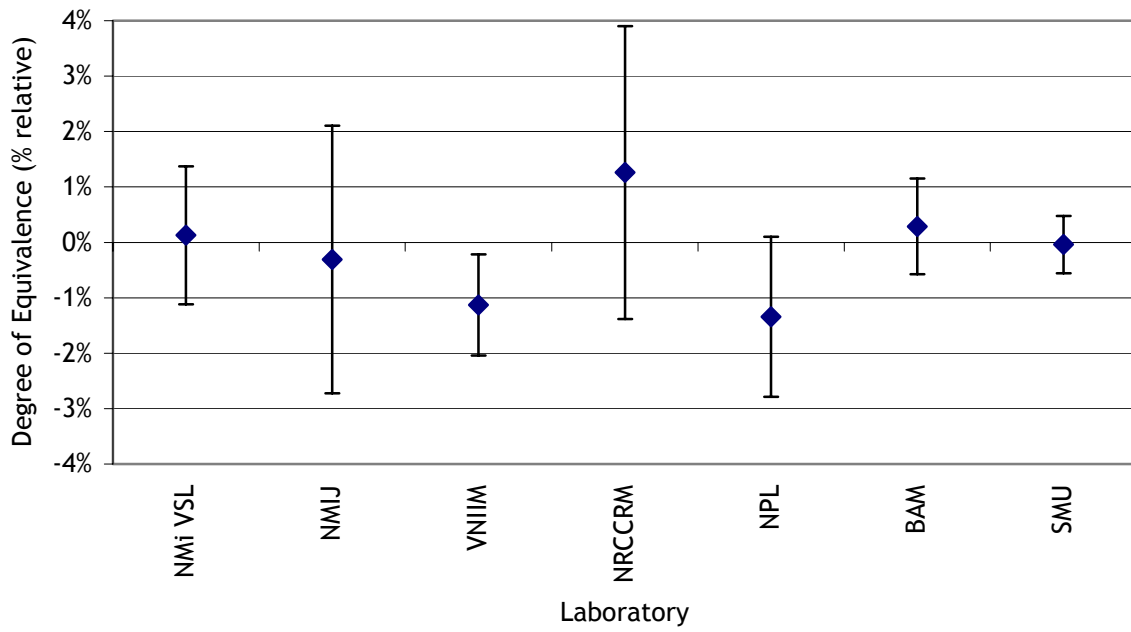


Figure 15: Degrees of equivalence for *iso*-pentane (high calorific mixture)

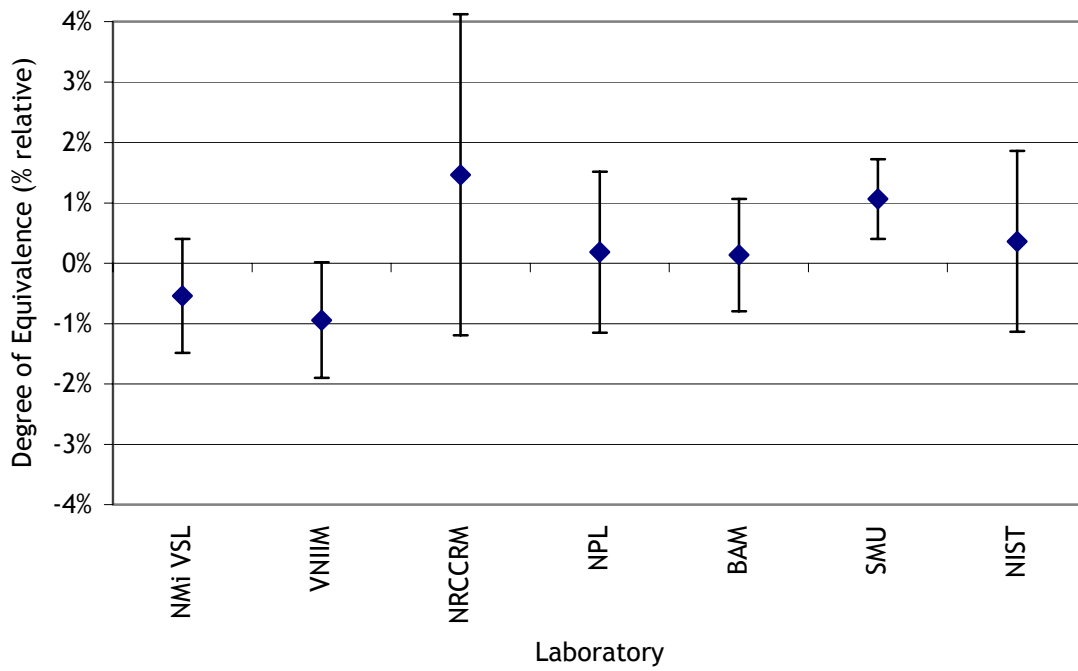


Figure 16: Degrees of equivalence for *n*-pentane (low calorific mixture)

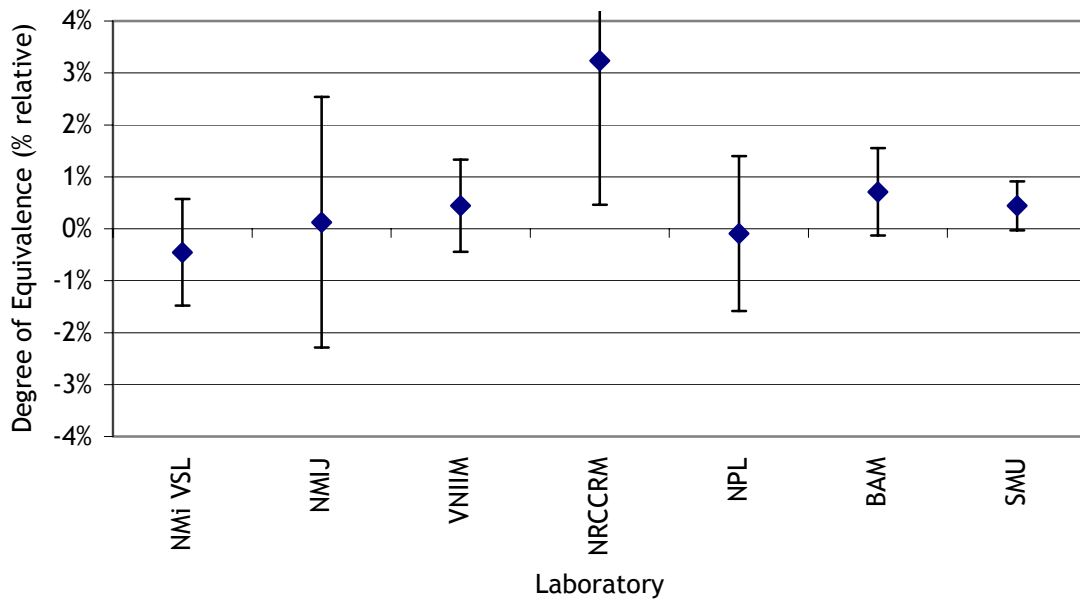


Figure 17: Degrees of equivalence for *n*-pentane (high calorific mixture)

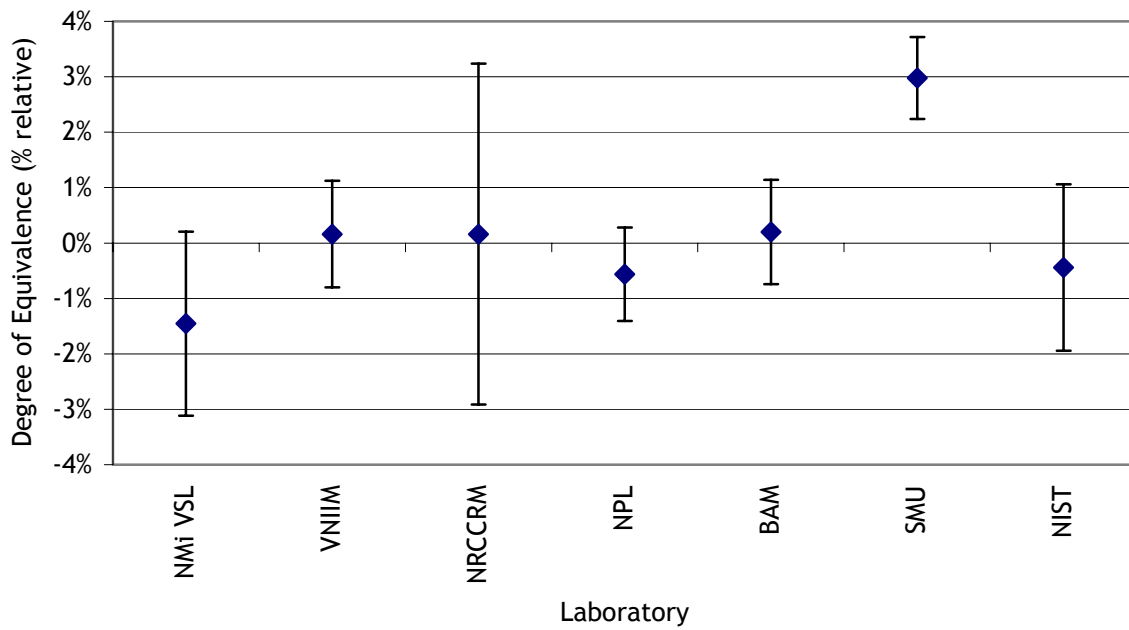


Figure 18: Degrees of equivalence for *neo*-pentane (low calorific mixture)

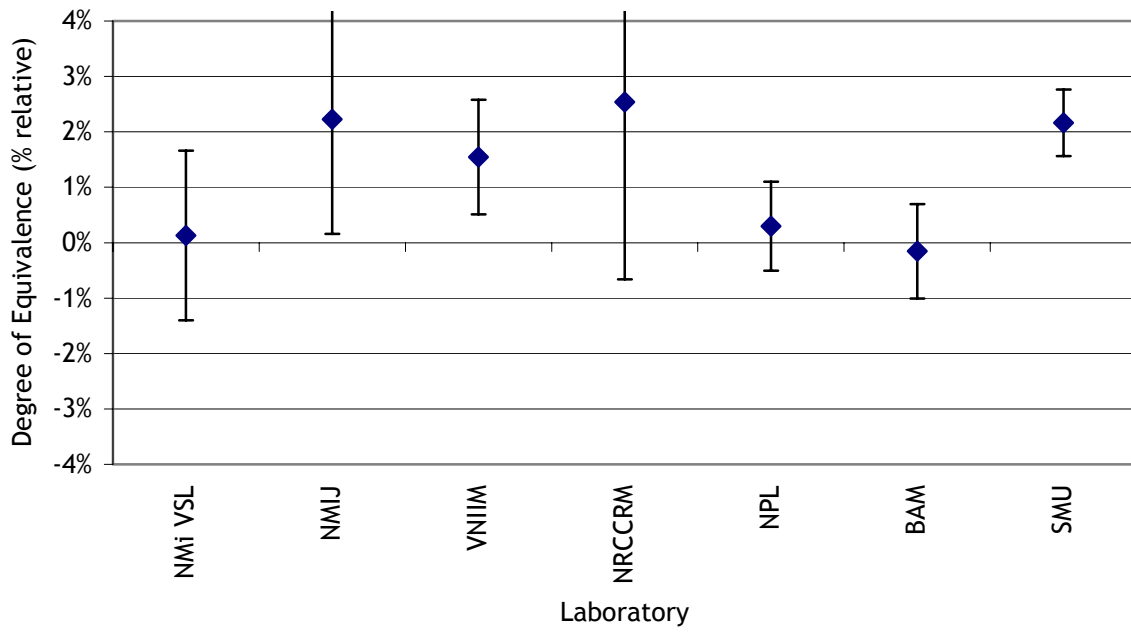


Figure 19: Degrees of equivalence for *neo*-pentane (high calorific mixture)

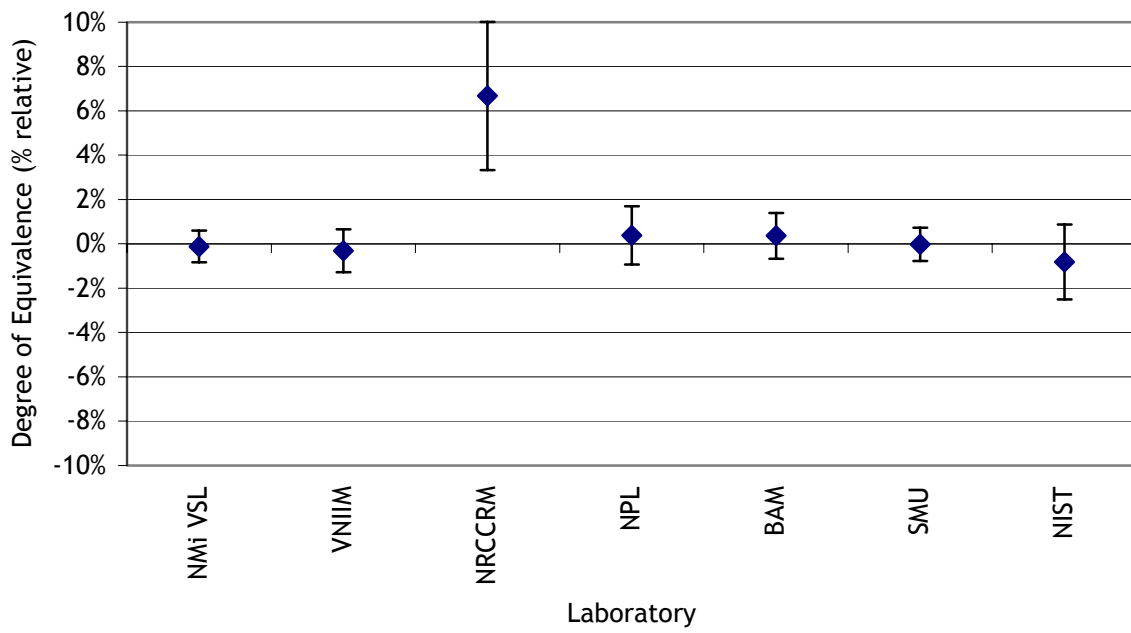


Figure 20: Degrees of equivalence for *n*-hexane (low calorific mixture)

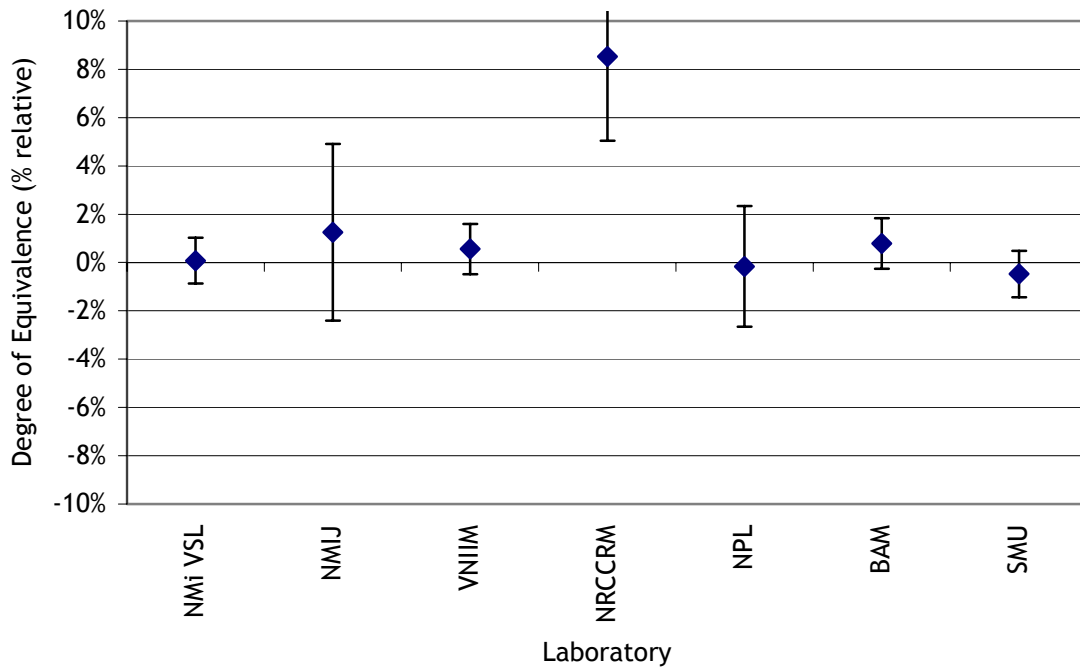


Figure 21: Degrees of equivalence for *n*-hexane (high calorific mixture)

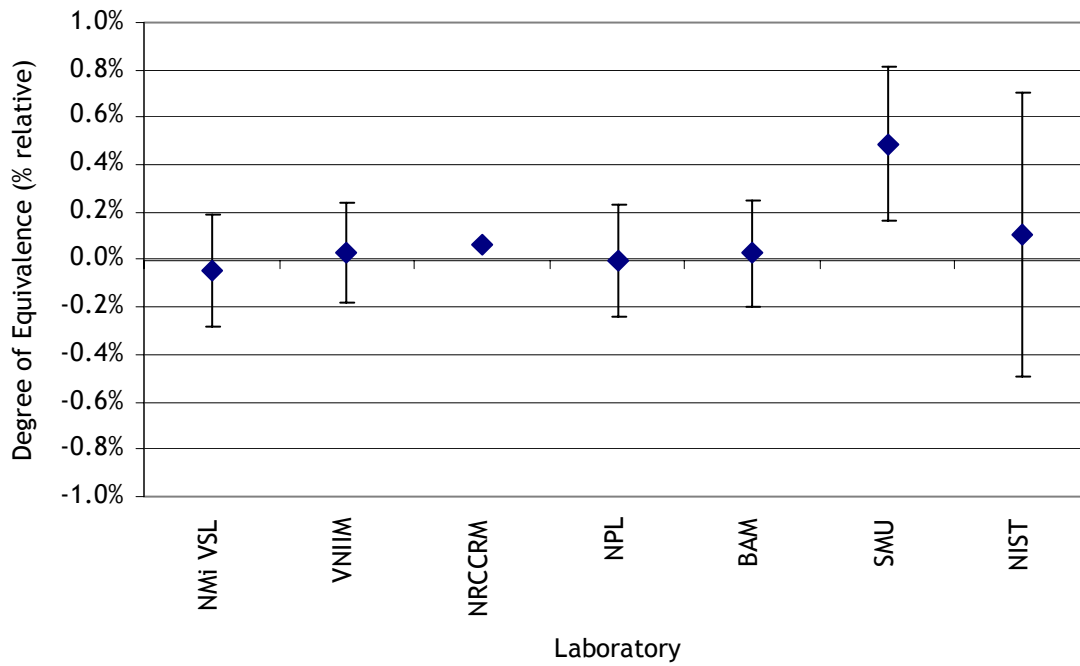


Figure 22: Degrees of equivalence for methane (low calorific mixture)

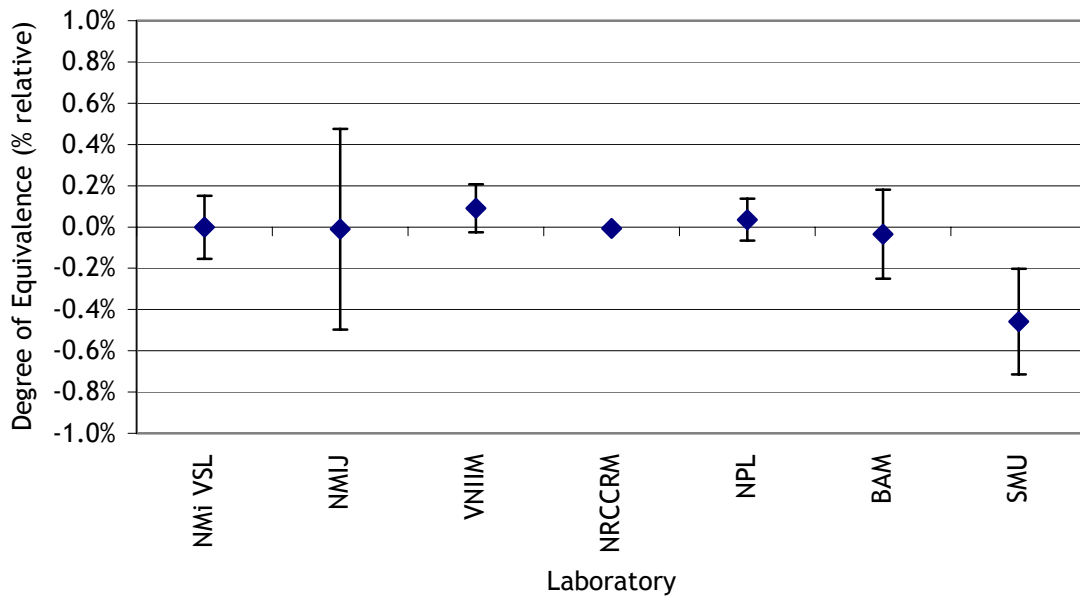


Figure 23: Degrees of equivalence for methane (high calorific mixture)

Results

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

- x_{prep} amount of substance fraction, from preparation (10^{-2} mol/mol)
- u_{prep} uncertainty of x_{prep} (10^{-2} mol/mol)
- u_{ver} uncertainty from verification (10^{-2} mol/mol)
- u_{ref} uncertainty of reference value (10^{-2} mol/mol)
- x_{lab} result of laboratory (10^{-2} mol/mol)
- U_{lab} stated uncertainty of laboratory, at 95% level of confidence (10^{-2} mol/mol)
- k_{lab} stated coverage factor
- Δx difference between laboratory result and reference value (10^{-2} mol/mol)
- $\Delta x/x$ relative difference between laboratory result and reference value (% , relative)
- k assigned coverage factor for degree of equivalence
- $U(\Delta x)$ Expanded uncertainty of difference Δx , at 95% level of confidence³ (10^{-2} mol/mol)

Table 4: Results for nitrogen, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	12.1069	0.0007	0.0240	0.0240	12.13	0.036	2	0.023	0.19%	2	0.060	0.50%
VNIIM	BAM-062	12.1050	0.0007	0.0240	0.0240	12.103	0.050	2	-0.002	-0.02%	2	0.069	0.57%
NRCCRM	BAM-054	12.1070	0.0007	0.0240	0.0240	12.05	0.02	2	-0.057	-0.47%	2	0.052	0.43%
NPL	96054981	12.0841	0.0007	0.0240	0.0240	12.108	0.084	2	0.024	0.20%	2	0.097	0.80%
BAM	96054974	12.2176	0.0007	0.0240	0.0240	12.191	0.048	2	-0.027	-0.22%	2	0.068	0.56%
SMU	BAM-075	12.1205	0.0007	0.0240	0.0240	12.145	0.030	2	0.025	0.20%	2	0.057	0.47%
NIST	96054912	12.1205	0.0007	0.0240	0.0240	12.11	0.16	2	-0.010	-0.09%	2	0.167	1.38%

³ As defined in the MRA [4], a degree of equivalence is given by Δx and $U(\Delta x)$.

Table 5: Results for nitrogen, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	1.2035	0.0001	0.0019	0.0019	1.202	0.005	2	-0.0015	-0.12%	2	0.0062	0.51%
NMIJ	VSL128591	1.1954	0.0001	0.0019	0.0019	1.188	0.014	2	-0.0074	-0.62%	2	0.0148	1.23%
VNIIM	VSL129386	1.1922	0.0002	0.0019	0.0019	1.170	0.009	2	-0.0227	-1.90%	2	0.0093	0.78%
NRCCRM	VSL129368	1.2102	0.0000	0.0019	0.0019	1.171	0.008	2	-0.0392	-3.24%	2	0.0089	0.73%
NPL	VSL129395	1.2084	0.0001	0.0019	0.0019	1.209	0.009	2	0.0004	0.03%	2	0.0097	0.80%
BAM	VSL129373	1.2010	0.0001	0.0019	0.0019	1.195	0.005	2	-0.0065	-0.54%	2	0.0061	0.51%
SMU	VSL129367	1.1950	0.0001	0.0019	0.0019	1.191	0.004	2	-0.0041	-0.35%	2	0.0053	0.44%

Table 6: Results for carbon dioxide, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	4.00893	0.0005	0.012	0.01201	4.007	0.008	2	-0.0019	-0.05%	2	0.0253	0.63%
VNIIM	BAM-062	4.00893	0.0005	0.012	0.01201	3.989	0.011	2	-0.0199	-0.50%	2	0.0264	0.66%
NRCCRM	BAM-054	4.00893	0.0005	0.012	0.01201	4.018	0.015	2	0.0091	0.23%	2	0.0283	0.71%
NPL	96054981	4.00135	0.0005	0.012	0.01201	3.986	0.019	2	-0.0152	-0.38%	2	0.0306	0.77%
BAM	96054974	4.07698	0.0005	0.012	0.01201	4.081	0.016	2	0.0040	0.10%	2	0.0288	0.71%
SMU	BAM-075	4.04459	0.0005	0.012	0.01201	4.060	0.008	2	0.0152	0.38%	2	0.0253	0.63%
NIST	96054912	4.04459	0.0005	0.012	0.01201	4.055	0.026	2	0.0104	0.26%	2	0.0354	0.87%

Table 7: Results for carbon dioxide, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	0.80184	0.00007	0.00080	0.00080	0.802	0.003	2	0.0005	0.06%	2	0.0036	0.45%
NMIJ	VSL128591	0.79837	0.00006	0.00080	0.00080	0.799	0.009	2	0.0008	0.10%	2	0.0089	1.12%
VNIIM	VSL129386	0.79625	0.00016	0.00080	0.00081	0.795	0.005	2	-0.0014	-0.18%	2	0.0052	0.66%
NRCCRM	VSL129368	0.80632	0.00017	0.00081	0.00082	0.808	0.005	2	0.0017	0.21%	2	0.0048	0.59%
NPL	VSL129395	0.80509	0.00006	0.00081	0.00081	0.8007	0.0025	2	-0.0044	-0.55%	2	0.0030	0.37%
BAM	VSL129373	0.80016	0.00007	0.00080	0.00080	0.804	0.004	2	0.0039	0.49%	2	0.0043	0.54%
SMU	VSL129367	0.79620	0.00006	0.00080	0.00080	0.795	0.008	2	-0.0009	-0.11%	2	0.0082	1.02%

Table 8: Results for helium, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	0.50607	0.00020	0.0015	0.0015	0.5046	0.0015	2	-0.0015	-0.29%	2	0.0034	0.67%
VNIIM	BAM-062	0.50607	0.00020	0.0015	0.0015	0.5088	0.0027	2	0.0027	0.54%	2	0.0041	0.80%
NRCCRM	BAM-054	0.50607	0.00020	0.0015	0.0015	0.5019	0.003	2	-0.0042	-0.82%	2	0.0043	0.84%
NPL	96054981	0.50791	0.00018	0.0015	0.0015	0.5072	0.0036	2	-0.0007	-0.14%	2	0.0047	0.93%
BAM	96054974	0.50860	0.00018	0.0015	0.0015	0.5098	0.0040	2	0.0012	0.24%	2	0.0050	0.99%
NIST	96054912	0.50813	0.00016	0.0015	0.0015	0.5158	0.0026	2	0.0077	1.51%	2	0.0040	0.78%

Table 9: Results for ethane, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	0.7459	0.0002	0.0015	0.0015	0.7460	0.0022	2	0.0001	0.02%	2	0.0037	0.50%
VNIIM	BAM-062	0.7459	0.0002	0.0015	0.0015	0.7480	0.0035	2	0.0021	0.29%	2	0.0046	0.62%
NRCCRM	BAM-054	0.7459	0.0002	0.0015	0.0015	0.7440	0.0044	2	-0.0019	-0.25%	2	0.0053	0.71%
NPL	96054981	0.7486	0.0002	0.0015	0.0015	0.7457	0.0037	2	-0.0029	-0.38%	2	0.0048	0.64%
BAM	96054974	0.7496	0.0002	0.0015	0.0015	0.7491	0.0044	2	-0.0005	-0.07%	2	0.0053	0.71%
SMU	BAM-075	0.7489	0.0002	0.0015	0.0015	0.7570	0.0038	2	0.0081	1.08%	2	0.0048	0.65%
NIST	96054912	0.7489	0.0002	0.0015	0.0015	0.7493	0.0046	2	0.0004	0.05%	2	0.0055	0.73%

Table 10: Results for ethane, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	11.1332	0.0008	0.0045	0.0045	11.131	0.022	2	-0.002	-0.02%	2	0.024	0.22%
NMIJ	VSL128591	10.9239	0.0008	0.0044	0.0044	10.93	0.05	2	0.006	0.06%	2	0.053	0.49%
VNIIM	VSL129386	11.0184	0.0016	0.0044	0.0047	10.97	0.06	2	-0.051	-0.47%	2	0.065	0.59%
NRCCRM	VSL129368	11.0201	0.0015	0.0044	0.0047	11.06	0.05	2	0.040	0.36%	2	0.051	0.46%
NPL	VSL129395	11.0430	0.0007	0.0044	0.0045	11.01	0.03	2	-0.031	-0.28%	2	0.032	0.29%
BAM	VSL129373	10.9924	0.0008	0.0044	0.0045	11.01	0.03	2	0.018	0.16%	2	0.034	0.31%
SMU	VSL129367	11.0100	0.0008	0.0044	0.0045	10.972	0.027	2	-0.038	-0.34%	2	0.028	0.26%

Table 11: Results for propane, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	0.29026	0.00010	0.0006	0.00061	0.2914	0.0015	2	0.0011	0.39%	2	0.0019	0.65%
VNIIM	BAM-062	0.29026	0.00010	0.0006	0.00061	0.2898	0.0018	2	-0.0005	-0.16%	2	0.0022	0.75%
NRCCRM	BAM-054	0.29026	0.00010	0.0006	0.00061	0.2907	0.0019	2	0.0004	0.15%	2	0.0023	0.77%
NPL	96054981	0.29131	0.00010	0.0006	0.00061	0.2910	0.0021	2	-0.0003	-0.10%	2	0.0024	0.83%
BAM	96054974	0.29171	0.00010	0.0006	0.00061	0.2919	0.0017	2	0.0002	0.07%	2	0.0021	0.72%
SMU	BAM-075	0.29144	0.00010	0.0006	0.00061	0.29432	0.00088	2	0.0029	0.99%	2	0.0015	0.52%
NIST	96054912	0.29144	0.00010	0.0006	0.00061	0.2905	0.0026	2	-0.0009	-0.32%	2	0.0029	0.98%

Table 12: Results for propane, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	4.4882	0.0005	0.0045	0.0045	4.4900	0.0135	2	0.002	0.04%	2	0.016	0.36%
NMIJ	VSL128591	4.4928	0.0003	0.0045	0.0045	4.5080	0.0239	2	0.015	0.34%	2	0.026	0.57%
VNIIM	VSL129386	4.5447	0.0009	0.0045	0.0046	4.5470	0.0230	2	0.002	0.05%	2	0.025	0.55%
NRCCRM	VSL129368	4.4952	0.0009	0.0045	0.0046	4.4970	0.0170	2	0.002	0.04%	2	0.019	0.43%
NPL	VSL129395	4.5056	0.0003	0.0045	0.0045	4.5130	0.0306	2	0.007	0.16%	2	0.032	0.71%
BAM	VSL129373	4.5021	0.0004	0.0045	0.0045	4.5170	0.0136	2	0.015	0.33%	2	0.016	0.36%
SMU	VSL129367	4.4937	0.0004	0.0045	0.0045	4.4780	0.0130	2	-0.016	-0.35%	2	0.016	0.35%

Table 13: Results for *iso*-butane, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	0.20074	0.00020	0.0004	0.00045	0.2015	0.0006	2	0.0008	0.38%	2	0.0011	0.54%
VNIIM	BAM-062	0.20074	0.00020	0.0004	0.00045	0.1996	0.0016	2	-0.0011	-0.57%	2	0.0018	0.91%
NRCCRM	BAM-054	0.20074	0.00020	0.0004	0.00045	0.2015	0.0023	2	0.0008	0.38%	2	0.0025	1.23%
NPL	96054981	0.20013	0.00019	0.0004	0.00044	0.2010	0.0013	2	0.0008	0.42%	2	0.0016	0.79%
BAM	96054974	0.20002	0.00019	0.0004	0.00044	0.2002	0.0014	2	0.0002	0.09%	2	0.0017	0.83%
SMU	BAM-075	0.20165	0.00019	0.0004	0.00044	0.20334	0.00071	2	0.0017	0.84%	2	0.0011	0.56%
NIST	96054912	0.20165	0.00019	0.0004	0.00044	0.2034	0.0019	2	0.0018	0.87%	2	0.0021	1.04%

Table 14: Results for *iso*-butane, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	0.10084	0.00001	0.00016	0.00016	0.1006	0.0005	2	-0.0002	-0.24%	2	0.0006	0.59%
NMIJ	VSL128591	0.09933	0.00001	0.00016	0.00016	0.0994	0.0010	2	0.0000	0.04%	2	0.0010	1.05%
VNIIM	VSL129386	0.09907	0.00002	0.00016	0.00016	0.0984	0.0010	2	-0.0007	-0.67%	2	0.0010	1.06%
NRCCRM	VSL129368	0.10141	0.00002	0.00016	0.00016	0.1016	0.0011	2	0.0002	0.19%	2	0.0011	1.13%
NPL	VSL129395	0.10125	0.00001	0.00016	0.00016	0.1009	0.0007	2	-0.0003	-0.30%	2	0.0008	0.77%
BAM	VSL129373	0.10063	0.00001	0.00016	0.00016	0.1008	0.0008	2	0.0002	0.17%	2	0.0009	0.86%
SMU	VSL129367	0.10013	0.00001	0.00016	0.00016	0.0997	0.0003	2	-0.0004	-0.39%	2	0.0004	0.44%

Table 15: Results for *n*-butane, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	0.20126	0.00007	0.0004	0.00041	0.2007	0.0010	2	-0.0006	-0.28%	2	0.0013	0.64%
VNIIM	BAM-062	0.20126	0.00007	0.0004	0.00041	0.2001	0.0016	2	-0.0012	-0.58%	2	0.0018	0.89%
NRCCRM	BAM-054	0.20126	0.00007	0.0004	0.00041	0.1986	0.0024	2	-0.0027	-1.32%	2	0.0025	1.26%
NPL	96054981	0.20064	0.00005	0.0004	0.00040	0.2001	0.0013	2	-0.0005	-0.27%	2	0.0015	0.76%
BAM	96054974	0.20054	0.00005	0.0004	0.00040	0.2004	0.0014	2	-0.0001	-0.07%	2	0.0016	0.80%
SMU	BAM-075	0.20260	0.00005	0.0004	0.00040	0.2031	0.0007	2	0.0005	0.24%	2	0.0011	0.53%
NIST	96054912	0.20260	0.00007	0.0004	0.00041	0.2024	0.0018	2	-0.0002	-0.10%	2	0.0020	0.97%

Table 16: Results for *n*-butane, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	0.09987	0.00005	0.00017	0.00018	0.1001	0.0006	2	0.0002	0.23%	2	0.0007	0.70%
NMIJ	VSL128591	0.10005	0.00005	0.00017	0.00018	0.0995	0.0011	2	-0.0006	-0.56%	2	0.0012	1.15%
VNIIM	VSL129386	0.09978	0.00006	0.00017	0.00018	0.1000	0.0010	2	0.0002	0.22%	2	0.0011	1.06%
NRCCRM	VSL129368	0.10043	0.00006	0.00017	0.00018	0.0989	0.0011	2	-0.0015	-1.52%	2	0.0012	1.15%
NPL	VSL129395	0.10028	0.00005	0.00017	0.00018	0.0999	0.0007	2	-0.0004	-0.35%	2	0.0008	0.79%
BAM	VSL129373	0.09966	0.00005	0.00017	0.00018	0.1007	0.0008	2	0.0011	1.07%	2	0.0009	0.88%
SMU	VSL129367	0.09917	0.00005	0.00017	0.00018	0.09832	0.00029	2	-0.0008	-0.86%	2	0.0005	0.46%

Table 17: Results for *iso*-pentane, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	0.05035	0.00011	0.00013	0.00017	0.0505	0.0005	2	0.0002	0.30%	2	0.0006	1.12%
VNIIM	BAM-062	0.05035	0.00011	0.00013	0.00017	0.0493	0.0005	2	-0.0011	-2.09%	2	0.0006	1.20%
NRCCRM	BAM-054	0.05035	0.00011	0.00013	0.00017	0.0505	0.0013	2	0.0002	0.30%	2	0.0013	2.67%
NPL	96054981	0.05024	0.00011	0.00013	0.00017	0.04977	0.00055	2	-0.0005	-0.94%	2	0.0006	1.29%
BAM	96054974	0.04946	0.00011	0.00013	0.00017	0.0495	0.0004	2	0.0000	0.06%	2	0.0005	1.06%
SMU	BAM-075	0.04861	0.00011	0.00013	0.00017	0.0489	0.0002	2	0.0003	0.60%	2	0.0004	0.81%
NIST	96054912	0.04861	0.00011	0.00013	0.00017	0.0483	0.0006	2	-0.0003	-0.64%	2	0.0007	1.42%

Table 18: Results for *iso*-pentane, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	0.03506	0.00001	0.00006	0.00006	0.0351	0.0004	2	0.0000	0.13%	2	0.0004	1.24%
NMIJ	VSL128591	0.03513	0.00001	0.00006	0.00006	0.0350	0.0008	2	-0.0001	-0.31%	2	0.0008	2.41%
VNIIM	VSL129386	0.03510	0.00001	0.00006	0.00006	0.0347	0.0003	2	-0.0004	-1.13%	2	0.0003	0.92%
NRCCRM	VSL129368	0.03470	0.00001	0.00006	0.00006	0.0351	0.0009	2	0.0004	1.26%	2	0.0009	2.64%
NPL	VSL129395	0.03519	0.00001	0.00006	0.00006	0.0347	0.0005	2	-0.0005	-1.34%	2	0.0005	1.44%
BAM	VSL129373	0.03495	0.00001	0.00006	0.00006	0.03505	0.00028	2	0.0001	0.29%	2	0.0003	0.87%
SMU	VSL129367	0.03453	0.00001	0.00006	0.00006	0.03452	0.00014	2	0.0000	-0.04%	2	0.0002	0.52%

Table 19: Results for *n*-pentane, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	0.04987	0.00011	0.00013	0.00017	0.0496	0.0004	2	-0.0003	-0.54%	2	0.0005	1.05%
VNIIM	BAM-062	0.04987	0.00011	0.00013	0.00017	0.0494	0.0004	2	-0.0005	-0.94%	2	0.0005	1.05%
NRCCRM	BAM-054	0.04987	0.00011	0.00013	0.00017	0.0506	0.0013	2	0.0008	1.46%	2	0.0013	2.69%
NPL	96054981	0.04897	0.00011	0.00013	0.00017	0.0491	0.0006	2	0.0001	0.18%	2	0.0007	1.41%
BAM	96054974	0.05129	0.00011	0.00013	0.00017	0.05136	0.00040	2	0.0001	0.14%	2	0.0005	1.02%
SMU	BAM-075	0.04982	0.00011	0.00013	0.00017	0.0504	0.0002	2	0.0005	1.06%	2	0.0004	0.79%
NIST	96054912	0.04982	0.00011	0.00013	0.00017	0.0500	0.0007	2	0.0002	0.36%	2	0.0008	1.56%

Table 20: Results for *n*-pentane, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	0.03506	0.00001	0.00004	0.00004	0.0349	0.0003	2	-0.0002	-0.45%	2	0.0004	1.03%
NMIJ	VSL128591	0.03518	0.00001	0.00004	0.00004	0.0352	0.0008	2	0.0000	0.13%	2	0.0008	2.42%
VNIIM	VSL129386	0.03514	0.00001	0.00004	0.00004	0.0353	0.0003	2	0.0002	0.44%	2	0.0003	0.89%
NRCCRM	VSL129368	0.03471	0.00001	0.00004	0.00004	0.0358	0.0010	2	0.0011	3.24%	2	0.0010	2.78%
NPL	VSL129395	0.03519	0.00001	0.00004	0.00004	0.0352	0.0005	2	0.0000	-0.09%	2	0.0005	1.49%
BAM	VSL129373	0.03495	0.00001	0.00004	0.00004	0.03520	0.00028	2	0.0002	0.71%	2	0.0003	0.84%
SMU	VSL129367	0.03454	0.00001	0.00004	0.00004	0.03469	0.00014	2	0.0002	0.44%	2	0.0002	0.47%

Table 21: Results for *neo*-pentane, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	0.04952	0.00006	0.00013	0.00014	0.0488	0.0008	2	-0.0007	-1.45%	2	0.0008	1.68%
VNIIM	BAM-062	0.04952	0.00006	0.00013	0.00014	0.0496	0.0004	2	0.0001	0.16%	2	0.0005	0.99%
NRCCRM	BAM-054	0.04952	0.00006	0.00013	0.00014	0.0496	0.0015	2	0.0001	0.16%	2	0.0015	3.08%
NPL	96054981	0.04970	0.00006	0.00013	0.00014	0.04942	0.00033	2	-0.0003	-0.56%	2	0.0004	0.88%
BAM	96054974	0.04976	0.00006	0.00013	0.00014	0.04986	0.00039	2	0.0001	0.20%	2	0.0005	0.97%
SMU	BAM-075	0.04972	0.00006	0.00013	0.00014	0.0512	0.00026	2	0.0015	2.98%	2	0.0004	0.78%
NIST	96054912	0.04972	0.00006	0.00013	0.00014	0.0495	0.0007	2	-0.0002	-0.44%	2	0.0008	1.52%

Table 22: Results for *neo*-pentane, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	0.05073	0.00004	0.00008	0.00009	0.0508	0.0008	2	0.0001	0.13%	2	0.0008	1.54%
NMIJ	VSL128591	0.05056	0.00004	0.00008	0.00009	0.0517	0.0010	2	0.0011	2.23%	2	0.0010	2.07%
VNIIM	VSL129386	0.05052	0.00004	0.00008	0.00009	0.0513	0.0005	2	0.0008	1.55%	2	0.0005	1.05%
NRCCRM	VSL129368	0.05022	0.00000	0.00008	0.00008	0.0515	0.0016	2	0.0013	2.54%	2	0.0016	3.20%
NPL	VSL129395	0.05093	0.00004	0.00008	0.00009	0.0511	0.0004	2	0.0002	0.30%	2	0.0004	0.82%
BAM	VSL129373	0.05058	0.00004	0.00008	0.00009	0.0505	0.0004	2	-0.0001	-0.16%	2	0.0004	0.82%
SMU	VSL129367	0.04998	0.00004	0.00007	0.00009	0.0511	0.0003	2	0.0011	2.16%	2	0.0003	0.62%

Table 23: Results for *n*-hexane, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	0.05156	0.00012	0.00015	0.00020	0.05150	0.00021	2	-0.0001	-0.12%	2	0.0004	0.72%
VNIIM	BAM-062	0.05156	0.00012	0.00015	0.00019	0.0514	0.0004	2	-0.0002	-0.31%	2	0.0005	0.97%
NRCCRM	BAM-054	0.05156	0.00012	0.00015	0.00019	0.0550	0.0017	2	0.0034	6.67%	2	0.0017	3.35%
NPL	96054981	0.05034	0.00011	0.00015	0.00019	0.05053	0.00059	2	0.0002	0.38%	2	0.0007	1.31%
BAM	96054974	0.04931	0.00011	0.00015	0.00019	0.04949	0.00041	2	0.0002	0.37%	2	0.0005	1.03%
SMU	BAM-075	0.05061	0.00011	0.00015	0.00019	0.05060	0.00023	2	0.0000	-0.02%	2	0.0004	0.75%
NIST	96054912	0.05061	0.00011	0.00015	0.00019	0.0502	0.0008	2	-0.0004	-0.81%	2	0.0009	1.69%

Table 24: Results for *n*-hexane, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	0.019985	0.000003	0.000030	0.000030	0.02000	0.00018	2	0.00002	0.08%	2	0.00019	0.95%
NMIJ	VSL128591	0.020108	0.000003	0.000030	0.000030	0.02036	0.00073	2	0.00025	1.25%	2	0.00074	3.66%
VNIIM	VSL129386	0.019988	0.000005	0.000030	0.000030	0.02010	0.00020	2	0.00011	0.56%	2	0.00021	1.04%
NRCCRM	VSL129368	0.019846	0.000000	0.000030	0.000030	0.02154	0.00069	2	0.00169	8.54%	2	0.00069	3.49%
NPL	VSL129395	0.019851	0.000003	0.000030	0.000030	0.01982	0.00049	2	-0.00003	-0.16%	2	0.00050	2.50%
BAM	VSL129373	0.019913	0.000003	0.000030	0.000030	0.02007	0.00020	2	0.00016	0.79%	2	0.00021	1.05%
SMU	VSL129367	0.019724	0.000003	0.000030	0.000030	0.01963	0.00018	2	-0.00009	-0.48%	2	0.00019	0.96%

Table 25: Results for methane, low calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	96054927	81.7384	0.0027	0.082	0.0820	81.700	0.098	2	-0.038	-0.05%	2	0.19	0.23%
VNIIM	BAM-062	81.7384	0.0027	0.082	0.0820	81.762	0.051	2	0.024	0.03%	2	0.17	0.21%
NRCCRM	BAM-054	81.7384	0.0027	0.082	0.0820	81.79		2	0.052	0.06%	2		
NPL	96054981	81.7659	0.0027	0.082	0.0820	81.76	0.10	2	-0.004	0.00%	2	0.19	0.23%
BAM	96054974	81.5543	0.0027	0.082	0.0820	81.58	0.08	2	0.022	0.03%	2	0.18	0.22%
SMU	BAM-075	81.6826	0.0027	0.082	0.0820	82.08	0.21	2	0.397	0.49%	2	0.27	0.33%
NIST	96054912	81.6826	0.0027	0.082	0.0820	81.77	0.46	2	0.087	0.11%	2	0.49	0.60%

Table 26: Results for methane, high calorific mixture

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
NMi VSL	VSL128434	82.0312	0.0010	0.0328	0.0328	82.03	0.11	2	-0.001	0.00%	2	0.13	0.15%
NMIJ	VSL128591	82.2487	0.0009	0.0329	0.0329	82.24	0.39	2	-0.009	-0.01%	2	0.40	0.49%
VNIIM	VSL129386	82.1084	0.0021	0.0328	0.0329	82.18	0.07	2	0.075	0.09%	2	0.10	0.12%
NRCCRM	VSL129368	82.1262	0.0020	0.0329	0.0329	82.12		2	-0.006	-0.01%	2		
NPL	VSL129395	82.0947	0.0009	0.0328	0.0329	82.12	0.05	2	0.029	0.04%	2	0.08	0.10%
BAM	VSL129373	82.1631	0.0010	0.0329	0.0329	82.13	0.16	2	-0.029	-0.04%	2	0.18	0.22%
SMU	VSL129367	82.1665	0.0010	0.0329	0.0329	81.79	0.20	2	-0.376	-0.46%	2	0.21	0.26%

Discussion of results

For nitrogen, NRCCRM reports results that deviate from the reference value more than the expanded uncertainty⁴ (figure 1). VNIIM reports for the high calorific mixture a result that deviates from the reference value more than the expanded uncertainty. All results for the low calorific mixture agree within 0.5% relative with the reference value. For the high calorific mixture, the results of VNIIM and NRCCRM deviate more than 1% relative from the reference value.

NPL reports for carbon dioxide for the high calorific mixture a result that deviates more than the expanded uncertainty from the reference value (figure 3). For the low calorific mixture, all results agree within 0.5% relative with the reference value. For the high calorific mixture, the same holds, except for NPL, for which the relative deviation is 0.55%.

Helium was only included in the low calorific mixture (figure 5). NIST reported a result that deviates more from the reference value than the expanded uncertainty. All results, except that from NIST, agree within 1% relative with the reference value. SMU did not report a result at all, thus violating the protocol for this key comparison.

For ethane, SMU reported for both mixtures results that deviate more than the expanded uncertainty (figure 6). Apart from SMU (relative deviation 1.08%), all results for the low calorific mixture agreed within 1% relative with the reference value. For the high calorific mixture, all results agreed within 0.5% relative.

For propane, SMU reports for the low calorific mixture a result that deviates more than the expanded uncertainty (figure 8). For the high calorific mixture, this laboratory reports a result for which the deviation is about equal to the expanded uncertainty. All laboratories report results that agree within 0.5% relative for the low calorific mixture (except SMU: 0.99%), and within 0.5% relative for the high calorific mixture.

SMU reports for iso-butane in the low calorific mixture a result that deviates more than the expanded uncertainty (figure 10). All results agree within 1% relative for both mixtures.

For n-butane, NRCCRM reports results that deviate more than 1% relative from the reference values, and which deviate more than the expanded uncertainty (figure 12). With one exception (BAM, high calorific mixture) all laboratories report results within 1% relative of the reference value.

VNIIM reports for iso-pentane results that deviate more than the expanded uncertainty (figure 14). The relative deviations are -2.09% (low calorific mixture) and -1.13% (high calorific mixture). NPL reports for the high calorific mixture a result that deviates -1.34% (for the low calorific mixture: -0.99%). The deviations computed for some other laboratories have for both mixtures the same sign (NMI VSL, NRCCRM, and BAM). With the exceptions as mentioned, all results agree within 1% relative with the reference value for both mixtures.

NRCCRM and SMU report results that deviate more than the expanded uncertainty for n-pentane for the low calorific mixture; for the high calorific mixture, the result of NRCCRM deviates more than the expanded uncertainty, the deviation of the result of SMU is about equal to the expanded uncertainty (figure 16). Apart from the exceptions mentioned, all results agree within 1% relative for both mixtures.

For neo-pentane, NRCCRM reports a result for the high calorific mixture that deviates more than the expanded uncertainty (figure 18). NMI VSL reports for the low calorific

⁴ Throughout this section, the term "expanded uncertainty" implies a level of confidence of 95%.

mixture a result that deviates -1.45% relative, which is smaller than the expanded uncertainty. SMU reports a result for the low calorific mixture that deviates 2.98% relative, which is more than the expanded uncertainty; the same holds for the high calorific mixture (relative deviation: 2.16%). NMIJ and VNIIM report for the high calorific mixture results for neo-pentane that deviate more than the respective expanded uncertainty. With the exceptions as mentioned, all results agree within 1% relative. Including the result of NMi VSL for the low calorific mixture, the agreement is within 1.5% relative.

NRCCRM reports for n-hexane results that deviate considerably from the reference value; for the low calorific mixture, the deviation is 6.67% relative, for the high calorific mixture, it is 8.54% relative (figure 20). Both deviations are greater than their expanded uncertainty. With one exception (NMIJ, high calorific mixture, 1.25% relative), all other results agree within 1% relative.

NRCCRM did not state the uncertainty of their results for methane. The results of SMU differ more from the reference value than the expanded uncertainty, for both mixtures (figure 22). Apart from SMU and the result of NIST for the low calorific mixture (0.11% relative deviation), all results agreed within 0.1% relative.

“How far does the light shine?”

Results from key comparisons can be used to review CMCs (calibration and measurement capabilities). This section of the report is intended for this purpose only and provides some guidance to reviewers of CMC-claims. Unlike the rest of this report, the contents of this section are an “expert opinion” and are based on the best available knowledge in the field at present. Table 27 gives the ranges and components for which the results of this key comparison give direct support on the basis of

- interpolation
- some mild extrapolation

From broad experience in the field of natural gas analysis, it is known that when the detector response is known for the ranges as indicated in table 27, measuring two mixtures in these ranges allows predicting the measurement uncertainty for other amount-of-substance fraction levels. An essential requirement is that all components in a gas mixture are in the gas phase down to a temperature of 0 °C (no condensation should take place in the mixture at 0 °C).

Table 27: Components and ranges

Component	Range x (% , mol/mol)
Nitrogen	0.5 -- 20
Carbon dioxide	0.5 -- 10
Helium	0.1 -- 2.0
Ethane	0.5 -- 20
Propane	0.10 -- 10
<i>iso</i> -Butane	0.05 -- 1
<i>n</i> -Butane	0.05 -- 1
<i>iso</i> -Pentane	0.02 -- 0.2
<i>n</i> -Pentane	0.02 -- 0.2
<i>neo</i> -Pentane	0.02 -- 0.2
<i>n</i> -Hexane	0.01 -- 0.2
Methane	60 -- 98

CMCs for unsaturated components up to C₅ in this matrix (methane) may be supported by the results of this key comparison, provided that the analytical technique and measurement procedure can be related directly to the measurement methods used in this key comparison.

Finally, it should be kept in mind that there is no automatism that a result obtained in one key comparison validates a whole measurement range or a range of measurement standards. On the other hand, when relations can be established between measurements, or measurement standards, the participation in a key comparison can be considered to be part of the proof of the validity of the claimed CMC. The more direct the relation between the CMC in question and a result from this key comparison, the more convincing such proof will be.

Conclusions

The key comparison CCQM-K16 has demonstrated that the results of the laboratories agreed within 1% relative with the reference value for most components. Exceptions are: nitrogen for the low calorific mixture (0.5%), carbon dioxide (0.5%), ethane and propane (0.5%), and methane (0.1%).

In some cases, larger differences were observed, which frequently exceeded the expanded uncertainty of the difference at 95% level of confidence. This problem was most frequently observed with NRCCRM and SMU (in this order), and to a lesser extent with laboratories VNIIM and NMIJ.

The underpinning of the uncertainty statements was generally good, but some harmonisation and possibly better specification of what is required may be helpful to make the reports dealing with the evaluation of measurement uncertainty better readable.

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Coordinators

BAM
Hans-Joachim Heine
Abteilung I
Unter den Eichen 87
D-12 200 Berlin
Germany
Phone +49 30 8104 3434
Fax +49 30 8104 1227
E-mail Hans-Joachim.Heine@bam.de

NMI Van Swinden Laboratorium B.V.
Department of Chemistry
Adriaan M.H. van der Veen
Schoemakerstraat 97
2628 VK Delft
the Netherlands
Phone +31 15 2691 733
Fax +31 15 261 29 71
E-mail avdveen@nmi.nl

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Annex A: Methods of measurement

NMi VSL

Three different GC's were used in the analyses, one specifically set up for natural gas analysis (used for He, N₂, CO, CH₄, C₂H₆, C₃H₈ and i-C₄H₁₀), one for analysis of pentanes (used for n-C₄H₁₀, neo-C₅H₁₂, i-C₅H₁₂ and n-C₅H₁₂) and one for analysis of hexane:

1. Natural Gas Analyser (NGA):

GC:	HP5890 Series II
Columns:	UCW 982 (12%), 2 ft, 1/8 in od, 80/100 mesh. DC-200 (25%), 15 ft, 1/8 in od, 80/100 mesh. Porapak Q, 6ft, 1/8 in od, 80/100 mesh. Molsieve 13X, 4 ft, 1/8 in od, 45/60 mesh. Molsieve 13X, 10 ft, 1/8 in od, 45/60 mesh.
Detectors:	2 Thermal Conductivity Detectors (μ -TCD)
Valves:	2 sampling valves, and 2 switching valves for column isolation
Sample introduction:	Multi position gas sampling valves, injection at ambient pressure. Sample is introduced by both sampling valves
Oven Temperature:	67 °C, isothermal
Carrier:	He and N ₂
Data Collection:	HP integrator 3396, peak data from the integrator are automatically collected.

The NGA has a separate column, carrier, sampling valve and detector for analysis of He. The sample is separated by the 4 ft Molsieve and is back flushed after the detection of He. N₂ is used as carrier. The other components are separated in one system using He as carrier. After injection heavier components (pentanes and hexanes) are retained by the UCW column, while the rest of the sample is separated over the DC-200 column. After a certain time the UCW column is switched from its place before the DC-200 column to being placed directly behind the DC-200 column, while the flow through the UCW column is reversed. This allows the heavier components to be flushed back from the UCW column and to leave the system through the detector. Just before elution of the lighter components (N₂, CH₄, C₂H₆ and CO₂) from the UCW column, the Porapak and 10 ft. Molsieve columns are switched on-stream. After a certain time both columns are switched off-stream again. Then the C₂H₆ and CO₂ are loaded onto the Porapak column and the N₂ and CH₄ are loaded onto the Molsieve column. After this the propane and the butanes elute from the UCW column and are sent directly through the detector. After elution of n-butane, the Porapak column is switched on-stream again allowing the C₂H₆ and CO₂ to elute. After elution of C₂H₆, the Molsieve column is switched on-stream again allowing the N₂ and CH₄ to elute.

2. Pentane analysis:

GC:	HP5890
Columns:	Porapak PS, 12ft, 1/8 in od, special packing.
Detectors:	Flame Ionisation Detector (FID)
Valves:	2 sampling valves
Sample introduction:	Multi position gas sampling valves, injection at ambient pressure.
Oven Temperature:	140 °C, isothermal
Carrier:	He
Data Collection:	HP integrator 3396

Samples are injected on-column by 1 of the 2 sampling valves.

3. Hexane analysis:

GC: HP5890
 Columns: DC-200 (25%), 15 ft, 1/8 in od, 80/100 mesh.
 Detectors: Flame Ionisation Detector (FID) with Ni-catalyst
 Valves: 1 sampling valve, 1 valve for column choice and 1 valve for detector choice.
 Sample introduction: Multi position gas sampling valves, injection at ambient pressure.
 Oven Temperature: 90 °C, isothermal
 Carrier: N₂
 Data Collection: HP integrator 3396, peak data from the integrator are automatically collected.
 For the analysis of hexane the GC is only used in the configuration described, but the instrument also has a Molsieve column and a TCD installed.

The response for *n*-hexane has been corrected for atmospheric pressure influence.

The gross calorific (Superior) value has been calculated using ISO 6976: 1996 (E). Reported are the Ideal gas calorific value of the mixture and the Real gas calorific value. Input parameters were the reported results for each component and their respective combined uncertainties.

NMIJ

The table below shows the summary of the instruments used for each component. The concentrations of each component were determined by conventional gas chromatography using packed columns made of stainless steel. These column-packing materials were a Unibeads-C and a Porapak Q and were coupled with a thermal conductivity detector (TCD) or a flame ionization detector (FID). Two gas chromatographs GC-14A and GC-17A (manufactured by Shimadzu corp.) were used for these analyses. All data were collected with CHROMATOPAC C-R6A manufactured by same corp.

Component	Detector	column	make and type
Nitrogen	TCD	Unibeads C (i.d.3 mm, length 5 m)	GC-14A (Shimadzu)
Carbon di-			
Methane	FID	Unibeads C (i.d.3 mm, length 2 m)	
Ethane			
Propane			
<i>iso</i> -Butane			
<i>n</i> -Butane	FID	Porapak Q (i.d.3 mm, length 8 m)	GC-17A (Shimadzu)
<i>iso</i> -Pentane			
<i>n</i> -Pentane			
<i>neo</i> -Pentane			
<i>n</i> -Hexane			

VNIIM

Within the framework of CCQM-K16 comparison determination of natural gas composition was made agency complexes of apparatus in the rank of State Primary Standard of units of mole fraction and mass concentration of components in gas mediums (GET 154). These complexes are following:

A1 - Standard chromatographic complex for certification of parent pure gases and substances. This complex was used for determination of impurities in pure gases and organic substances on purpose to determining the main component content.

A2 - Standard gas mixing gravimetric complex for reproduction of units of mole fraction of components. This complex was used for preparation of primary standard gas mixtures (calibration standards) in cylinders.

A9 - Standard chromatographic complex for certification of natural gas. This complex was used for determination of mole fraction of components of the natural gas samples presented for the comparison.

The gas chromatograph was calibrated according to ISO 6974. It was made four independent measurements under repeatability conditions with four independent calibrations: calibration → measurement → calibration → measurement (etc.). One single measurement result was obtained from 6 readings without recalibrations.

Calculation of gross calorific value was made on results of determining components content of the natural gas samples according to ISO 6976.

Determination of heat of combustion a natural gas sample by means of the calorimeter method was performed with the calorimeter that is a part of the state primary standard for the unit of combustion energy (GET 16-96).

The standard comprises an isoperibol water calorimeter, a temperature-measuring set-up and an assembly for preparing and dosing gases. The procedure of combustion and the calorimeter itself are based on the principles introduced by Rossini⁵ and Pilcher⁶ [1,2]. Calibration of the calorimeter is realized by burning a high purity methane (99,95 %), the superior heat of combustion of which (HCH₄) according to ISO 6976:95 is equal to 37.10 MJ/m³ (95% confidence limit of approximately ±0,05 MJ/m³) under the standard conditions for combustion, p=101.325 kPa, T=298.16 K, and standard conditions for volume measurements, p=101.325 kPa, T=293.16 K.

NRCCRM

The methods of analysis and the instruments are listed in the table below.

Component	Instrument used	Detector	Calibration method
N ₂ , He	GC-8A(Shimadzu)	TCD	Single point and linearity calibration
CO ₂	GC-8A(Shimadzu)	TCD,FID	
C ₁ -C ₆	HP6890(Agilent) GC-9A(Shimadzu)	FID	

The calibration gas mixtures were prepared by gravimetric method. The purity of raw gases and impurities interested were determined with a standard normalized method by

⁵ Rossini F.D., "The Heats of Combustion of Methane and Carbon Monoxide", Journal of Research National Bureau of Standards, V.6, 1931, pp. 37-49

⁶ Pittam D.A. and Pilcher G.J. J.Chem. Soc. Faraday Trans. 1. 68 (1972), pp. 2224 - 2229

GC. The measure uncertainty of purities is less than 0.1%. The balance we used is H2-30K made in Japan (capacity: 30kg, readability: 1mg).

Having taken a series measurements, we can eliminate or decrease most parts of uncertainties (including those related to the balance and the poises, gas cylinder component gases) to the level that can be ignored. Hereby, for gravimetric method, we mainly take two parts of uncertainty into account. They are resolution of balance (1mg) and uncertainties in the poises used (1mg).

NPL

Analysis was undertaken using a Varian CP-2003 'Micro' Gas Chromatograph with four modules, each comprising an injector, column and detector. This method is used for routine analysis of Natural Gas mixtures at NPL. The sample was passed through a single inlet point before being divided for injection onto the GC columns. Details of the experimental conditions for each species measured are given below:

Species	CH ₄ & N ₂	He	CO ₂ , C ₂ H ₆ & C ₃ H ₈	C ₄ H ₁₀ to C ₆ H ₁₄
Column	HaySep A	CP-MolSieve 5 μ	CP-Sil	HaySep A
Detector	TCD	TCD	TCD	TCD
Carrier Gas	Helium	Argon	Helium	Helium
Column Temp	40 °C	45 °C	100 °C	30 °C
Column Press	200 kPa	130 kPa	200 kPa	50 kPa
Injection Time	5 ms	5 ms	30 ms	50 ms

BAM

For the analysis of the mixtures, two GCs were used, with specifically applications.

1. For the determination of:

Nitrogen (N₂), Carbon Dioxide (CO₂), Ethane (C₂H₆), Propane (C₃H₈), n-Butane (n-C₄H₁₀), 2-Methyl-Propane (I-C₄H₁₀), n-Pentane (n-C₅H₁₂), 2-Methyl-Butane (i-C₅H₁₂), 2,2-di-Methyl-Propane (neo-C₅H₁₂), n-Hexane (n-C₆H₁₄) and Methane (CH₄).

GC: Perkin Elmer AutoSystem XL (two channel system) with a stream selection valve for 4 streams and 2 gas sampling valves.

Channel A: for the determination of N₂, CO₂, C₂H₆, C₃H₈, n-C₄H₁₀, I-C₄H₁₀, neo-C₅H₁₂ and CH₄*.

Carrier Gas: Helium

Columns: Column system with two packed columns
(6 ft x 1/8" Porapak R, 80/100 mesh and
6 ft x 1/8" Mol-Sieve 13X, 80/100 mesh.)

Oven Temperature: 50 °C to 150 °C

Detector: μ -TCD

Data Collection: Total Chrom Workstation

Channel B: for the determination of C₃H₈, n-C₄H₁₀, I-C₄H₁₀, n-C₅H₁₂, i-C₅H₁₂, neo-C₅H₁₂ and n-C₆H₁₄.

Carrier Gas: Helium

Columns: Capillary column, 50 m x 0,32 μ m LP-SIL-8-CB

Oven Temperature: 50 °C to 150 °C

Detector: FID

Data Collection: Total Chrom Workstation

2. For the determination of: Helium (He)
GC: HP 5890 Series II with a stream selection valve for 4 streams and 1 gas sampling valve.
Carrier Gas: Nitrogen
Columns: packed column, 2m*1/8" Carbo-Sieve 60/80 mesh.
Oven Temperature: 50 °C, isothermal
Detector: μ -TCD
Data Collection: Total Chrom Workstation

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.

The content of the impurities in all pure gases were determined before use by GC-DID, GC-FID and/or GC-TCD.

After preparation the standards were verified by analytical comparisons against existing gravimetrically prepared standards. Only when no significant difference between the analysed and the calculated gravimetric composition is found, the "new prepared candidate" is accepted as a new standards

For the analysis of all components multi component standards with methane as balance gas were used.

All stated calorific values are superior and of real gas and were calculated according to ISO 6976 (1995). Firstly calorific value of ideal gas was calculated using data for superior and 25 °C from table 3 at ISO standard. Then it was divided by compression factor Z of mixture at 25 °C. At calculation of Z some extrapolations of component Z_i from data at table 2 (15 °C and 20 °C) were used. Result gross calorific value was calculated from stated result composition.

SMU

Measured on Gas Chromatograph Varian 3 800, with using Porapack and molsieve packed columns, 2 1mL sample loops, TCD and FID detectors, 90 °C. All measurements were done in automatic way. Before entering sample loops all gas mixtures went through a mass flow controller.

All calibration standards were made gravimetrically according ISO 6142 and 6143, impurities of parent gases were estimated at NMI except methane, nitrogen, CO₂, that were checked on hydrocarbons, CO, CO₂, N₂ by SMU on GC.

All runs in first, third, fifth measurement sequence had rising molar fraction, second, fourth, sixth processed in reverse order. All calibration standards in previous tables were used at each run. Uncertainty of response consisted from figure characterised 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.

NIST

The sample was analyzed using a research grade HP 5890 gas chromatograph equipped with flame ionization and thermal conductivity detectors. The components were separated using a 9.14m x 3.2mm capillary packed with SP-1700 on 80/100 mesh. The column was operated at 40 °C for 8 minutes then temperature programmed to 105 °C at 30 °C/minute and held. The thermal conductivity detector was maintained at 150 °C and operated on low sensitivity. The helium column carrier flow rate was 20 mL/minute with a helium make-up flow of 30 mL/min. The samples were injected onto the column via a 6-port stainless steel gas sampling valve equipped with a 0.5 mL sample loop. The C3 through C6 were also analyzed using a 25m x 0.53mm PLOT column coated with aluminum oxide/potassium chloride. The column was isothermal for 3 minutes at 45 °C then temperature programmed to 45 °C at 7 °C/min then to 135 °C at 10°C/min then to 180 °C at 20 °C/min and held for 5 minutes. The helium was analyzed using a 1.8 m by 3.2 mm column packed with Molesieve 5A and operated at 40 °C. The nitrogen carrier flow was set at 20 mL/min with a detector make-up flow of 30 °C to the TCD operated at 150 °C on low sensitivity.

Used heating values for the hydrocarbons from the document GPA 2145-00 (2000 revision) at 60 °F. Multiplied the heating value of specific compound by the concentration, summed all values for total.

Annex B: Evaluation of uncertainty

NMi VSL

Ordinary least squares (OLS) is used as technique for evaluating the calibration curve. A linear model is used for *iso*-butane (low calorific mixture), *iso*-pentane, *n*-pentane, and *neo*-pentane. In all other cases a quadratic model has been used. The uncertainty of the calibration standards (*Primary Standard gas Mixtures, PSMs*) is added to the uncertainty from assigning a value to the key comparison gas mixtures. The uncertainty of the PSMs includes all relevant components of uncertainty from e.g.

- gravimetry (mass pieces, weighing, calibration of the balance buoyancy correction, molar masses)
- impurity of the parent gases
- instability
- verification

The uncertainty of the gravimetric preparation of the standards used was evaluated according to Alink and Van der Veen⁷. The uncertainty in the impurities present in all pure components and mixtures, that are used to prepare the standards are stored in purity tables. When a mixture is prepared, the uncertainty of the components is automatically calculated from the uncertainty of the gravimetric preparation and the uncertainties of the components present in the mother mixtures.

All new prepared standards are verified for their composition against existing (gravimetrically prepared) standards. This verification is a check of the gravimetric preparation process, which includes determination of errors due to leakage of air into the cylinder, leakage of gas from the cylinder valve during filling, escape of gas from the cylinder, absorption of components on the internal surface of the cylinder. Only when no significant difference between the analysed and the gravimetric composition is found, the cylinder is approved as a new standard. Several selected cylinders covering the concentration ranges of all constituents in the natural gas standards are used for long term stability testing. During these tests no instability has been detected for any of the components component. Because it is difficult or impossible to discern between these different uncertainty contributions, the standard deviation of the results of the stability measurements for a cylinder having a similar mole fraction was chosen to cover these uncertainties.

NMIJ

Bracketing has been used as technique for performing the calibration and evaluating the results.

VNIIM

Uncertainty of content of measured components, methane and calorific value was calculated according to ISO 6974⁸, ISO 6976⁹, and 'Guide to the expression of uncertainty in measurement'.

⁷ A. Alink and A.M.H. van der Veen, Uncertainty Calculations for the preparation of primary gas mixtures, *Metrologia*, **37** (2000) , pp. 641-650.

⁸ ISO 6974-3:2000, Natural gas - Determination of composition with defined uncertainty by gas chromatography - Part 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C8 using two packed columns

NRCCRM

The uncertainty of gravimetric methods for every component are listed in the tables below:

Uncertainties for each component in the low calorific mixture

Component	x (% , mol/mol)	Uncertainty of gravimetric method(%)
Nitrogen	12.0	0.1
Carbon dioxide	4.0	0.2
Helium	0.50	0.5
Ethane	0.75	0.5
Propane	0.30	0.5
iso-Butane	0.20	1.0
n-Butane	0.20	1.0
iso-Pentane	0.050	2.5
n-Pentane	0.050	2.5
Neo-Pentane	0.050	3.0
Hexane	0.050	3.0
Methane	81.55(balance)	0.1

Uncertainties for each component in the high calorific mixture

Component	x (% , mol/mol)	Uncertainty of gravimetric method(%)
Nitrogen	1.20	0.5
Carbon dioxide	0.80	0.5
Ethane	11.00	0.2
Propane	4.50	0.2
iso-Butane	0.10	1.0
n-Butane	0.10	1.0
iso-Pentane	0.035	2.5
n-Pentane	0.035	2.5
Neo-Pentane	0.050	3.0
Hexane	0.020	3.0
Methane	82.16(balance)	0.1

The expanded uncertainties are combined with the relative standard uncertainty of gravimetric methods u_c and the uncertainty of GC methods S . The confidence interval is 95% and a coverage factor k is 2. The calculation equation is:

$$U = k \sqrt{\left(\frac{S}{\sqrt{n}}\right)^2 + u_c^2}$$

where: $k = 2$, the coverage factor,
 S ---- the relative standard deviation of components determined in GC methods,
 $n = 6$, the number of experiment replications,
 u_c ---- the relative standard uncertainty of gravimetric methods.

⁹ ISO 6976: 1995, Natural gas - Calculation of calorific values, density, relative density and Wobbe index from composition, 45 p.

NPL

For each CCQM mixture, calibration took place using the appropriate set of three standards, allowing coverage of the nominal concentration of each species. At least seven repeat analyses were performed and the first of these was rejected, to eliminate any possible 'carry-over' effects from the previous standards. Data analysis took place by a generalised least squares method, performed using XGenline (a software program developed at NPL). The use of a three-point calibration curve necessitated the use of a linear function.

The uncertainties assigned to the concentration of the components in the calibration standards were determined from the uncertainties in both the gravimetric technique and the purity analysis of the components. These, along with the standard deviation of each analytical measurement were entered into XGenline and the uncertainty of the unknown calculated (strictly following the GUM procedure).

The uncertainty for each analysis, $u(x_{ij})$, was normalised by use of equation 1 and the final (mean) value, $u(y_i)$, then generated by equation 2.

$$u(y_{ij}) = y_{ij} \sqrt{\frac{(1 - 2x_{ij})u^2(x_{ij})}{x_{ij}^2} + \sum_{i=1}^{i=n} u^2(x_{ij})} \quad \text{Equation 1}$$

$$u(y_i)^2 = \frac{1}{n^2} \sum_{j=1}^{j=n} u(y_{ij})^2 \quad \text{Equation 2}$$

Where $u(x_{ij})$ is the uncertainty of the j^{th} individual analytical result, $u(y_{ij})$ is the normalised uncertainty of this and $u(y_i)$ is the final normalised uncertainty assigned to a set of n individual analytical results.

BAM

The uncertainty of the grav. prepared standards is the combined uncertainty of the following uncertainty sources:

- Uncertainty of the balances (Volland / Sartorius) $U_{(\text{bal.V})}$ / $U_{(\text{bal.S})}$
- Uncertainty of the impurities of the pure gases $U_{(\text{imp.})}$
- Uncertainty of the main component of the pure gases $U_{(\text{pure gas})}$
- Residual-uncertainty of non-recovery errors related to the gas cylinder and to the component gas $U_{(\text{imp./pure gas})}$

The uncertainty of the analysis is the combined uncertainty of three uncertainty sources:

- Uncertainty of the grav. prepared standards U_{Standard}
- Standard deviation (GC-Analysis) U_{GC}
- Residual-uncertainty of non-recovery errors U_{residual}

SMU

The data were processed in accordance to ISO 6143. At B_least these models of analytical curves were used:

Nitrogen	TCD	2-nd polynomial
Carbon dioxide	TCD	linear

Ethane	FID	2-polynomial
Propane	FID	2-polynomial
<i>iso</i> -Butane	FID	linear
<i>n</i> -Butane	FID	linear
<i>iso</i> -Pentane	FID	linear
<i>n</i> -Pentane	FID	linear
<i>neo</i> -Pentane	FID	linear (<i>n</i> -pentane calibration)
<i>n</i> -Hexane	FID	linear
Methane	FID	2-polynomial

With least square weighted regression (both x and y) for all particular results were found standard uncertainties $u(x_j)$. For each day the average \bar{x}_i was calculated (8). Its standard deviation (3) is combination from standard deviation of the mean (type A) (1) and from standard deviation (type B) (2).

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

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

$$u(\bar{x}_i) = \sqrt{u_A(\bar{x}_i)^2 + u_B(x_i)^2} \quad (3)$$

Following estimation of result uncertainty keeps "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.

$$s_R = \sqrt{s_{\bar{x}}^2 + s_r \frac{n-1}{n}} \quad (4)$$

$$s_r = \sqrt{\frac{\sum_{i=1}^p u(\bar{x}_i)^2}{p}} \quad (5)$$

$$s_{\bar{x}} = \frac{\max(\Delta x)}{\sqrt{3}} \quad (6)$$

$$\Delta x = \bar{x}_1 - \bar{x}_2 \quad (7)$$

$$\bar{x}_i = \frac{\sum_{j=1}^n x_j}{n} \quad (8)$$

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

As final standard uncertainty we assigned to the result (9) $\max(s_R \text{ or } s_r)$

p - number of days (3)

n - number of measurements in 1 day

Expanded uncertainty of gross calorific value followed uncertainties assigned to all components molar fractions. All estimations of uncertainties were derived from mathematical formulas stated at ISO 6976 and there were (except that from estimated uncertainty of

data of molar calorific value from table 3 of ISO standard, we assigned to all $u(H_i) = 0,5$ found negligible in comparison with that from composition determination.

NIST

Nineteen standards were used to calibrate the instruments. They were gravimetrically prepared primary standards. Standards were used to bracket the concentration of the sample, but not all standards contained every compound. All of the pure components used to prepare the standards were analysed for impurities prior to use. The estimated uncertainty of the concentrations of each component is ≤ 0.1 relative with a coverage factor of 2.

The estimated uncertainties (calculated as %) used are as follows:

1. The estimated uncertainty in the preparation of gravimetric primary standards (the purity of reagents, the uncertainty in the weights and the resolution of the balance used to prepare the standards) of (U_s).
2. The estimated uncertainty in the determination of the component peak area response (U_{r1} through U_{rn}) from replicate injections of the sample and standard for each of the collected ratios.

Annex C: Calorific value

One laboratory (VNIIM) reported for one of the cylinders (BAM-062, low calorific mixture) an experimental value for the calorific value. This annex describes briefly the establishment of the reference value, and the method used to determine the calorific value experimentally.

The enthalpy of combustion on a molar basis is given as [12]

$$\bar{H}^0(t_1) = \sum_{j=1}^N x_j \bar{H}_j^0(t_1) \quad (18)$$

where $\bar{H}^0(t_1)$ denotes the ideal molar calorific value, $\bar{H}_j^0(t_1)$ the ideal molar calorific value of component j , and x_j the amount of substances fraction of component j . The combined standard uncertainty associated with $\bar{H}^0(t_1)$ follows from applying the uncertainty propagation formula of the GUM to equation (18) [3]. Assuming independence among the enthalpies and amount of substances fractions, the expression for the standard uncertainty of $\bar{H}^0(t_1)$ becomes

$$u^2(\bar{H}^0(t_1)) = \sum_{j=1}^N x_j^2 u^2(\bar{H}_j^0(t_1)) + \sum_{j=1}^N (\bar{H}_j^0(t_1))^2 u^2(x_j) \quad (19)$$

According to the international standard [12], the repeatability is computed from

$$\Delta H_{mix}^0 = \left\{ \sum_{j=1}^N [\Delta x_j (H_j^0 - H_{mix}^0)]^2 \right\}^{\frac{1}{2}} \quad (20)$$

This expression is also valid for the calculation of the uncertainty associated with $\bar{H}^0(t_1)$ under the condition that all amount of substance fractions are known, that is, their sum adds up to unity. In practice, this requirement can be interpreted that the sum of all amount of substance fractions should not deviate significantly from unity. As for the mixtures used in this project this condition is met, the latter approach can be used.

One laboratory submitted an experimentally determined calorific value. The comparison with the calculated reference value is shown in table 28. The way of presenting the results is identical with that of the composition (see main text of this report).

Table 28: Experimental and calculated values for calorific value versus reference value

Laboratory	Cylinder	Ref. Value	u	Rep. Value	U	k	D	u(D)	Remarks
VNIIM	BAM-062	31804	10	31846	41	2	42	23	
VNIIM	BAM-062	31804	10	31818	60	1.96	14	32	Experimental

Description of the method

Determination of heat of combustion a natural gas sample by means of the calorimeter method was performed with the calorimeter that is a part of the state primary standard for the unit of combustion energy (GET 16-96).

The standard comprises an isoperibol water calorimeter, a temperature measuring set-up and an assembly for preparing and dosing gases. The procedure of combustion and the calorimeter itself are based on the principles introduced by Rossini and Pilcher [13,14].

Design and operation

The isoperibol classic calorimeter consists of two nested cans with an air gap between, outer bath (jacket) with water constant temperature.

The inner can is filled with distilled water and contains: a reaction vessel with a steel burner, heat exchanger, constant speed stirrer, heater for warming up the water to a starting temperature and Hewlett-Packard quartz thermometer with the resolution of 0,0001 °C (readings of temperature are taken every 30 seconds). The inner can rests on three plastic legs on the bottom of the outer can, the gap between the inner and outer cans being kept constant.

In the course of a run of measurements the outer bath (jacket) is temperature controlled at the level of $(27,435 \pm 0,001)$ °C. While preparing and carrying out experiments the temperature inside the room is kept at the level of $(25,0 \pm 0,1)$ °C.

The assembly for preparing and dosing gases consists of a gas humidifying system, a unit for gas temperature control and a dose-meter device. For a dose-meter the constant volume spiral made of a teflon tube (7 mm in diameter and 13 m in length) is used. The spiral is located inside a separate thermostat where the temperature is kept at the level of $(25,0 \pm 0,1)$ °C. In the same thermostat there are coil pipes intended for thermostating the gases before feeding them into a burner.

An inner volume of the spiral has been determined with the gravimetric method and is equal to $(506,20 \pm 0,11)$ cm³, where 0,11 cm³ is the confidence limit (error) of the result obtained for three single measurements. Before the experiment, for an hour, the spiral is blown through with the gas to be burnt from a cylinder. Then the gas pressure inside the spiral is equal to barometric pressure. While carrying out the combustion experiment a combustible gas is being expelled from the spiral by a stream of argon.

Thus, as distinguished from works [13,14], the gas volume was used for calculation of a specific heat of combustion on a volumetric basis rather than the mass of a burnt gas.

Gas runs

Combustion of the gas sample takes place inside the reaction vessel submerged in the water in the inner can. After outlet from the dose-meter, the combustible gas is mixed with argon and then with oxygen of ultra high purity and after that fed to the burner through an arm of the vessel. On the one hand, the argon acts as a moderator to lift the flame off the tip preventing decomposition of the sample, heat transfer up the arm and carbon build-up on the tip. On the other hand, the argon is added so that its presence in combustion products might compensate change of a volume of reaction products. The second feed from the oxygen supplier goes to the base of the reaction vessel through the second arm to provide an oxygen rich atmosphere.

The design of the metal burner differs very much from that of the burners used by Rossini and Pilcher [13,14]. It work within the combustible gas flow range of (1.8-3.0) l/h is stable.

Two stainless steel electrodes act as a spark gap just above the tip of the burner.

To create the conditions under which the measurements of the superior heat of combustion of gas are carried out in accordance with the definition of this quantity, it was necessary to provide a complete condensation of reaction water vapour and eliminate the evaporation of the condensate.

The calculation shows that to do this requires, on the one hand, that the total oxygen (primary and secondary) supplied into the burner should be preliminary saturated with water vapour at the temperature of 25 °C and on the other hand, it is necessary to add a dry argon the flow of which is determined by calculation from the oxidation reaction in such a manner that its presence in the reaction products might compensate a change in the volume of reaction products. On combustion of methane according to this procedure the following water balance takes place:

A summary gas stream is supplied into the burner:

$$G_{\Sigma \text{ entering}} = G_{CH_4} + G_{\Sigma O_2, \text{ enter}} + G_{Ar} = 2,3 + 6,8 + 2,3 = 11,4 \text{ l/hour}$$

A water vapour stream is fed along with the above gas stream:

$$G_{H_2O, \text{ entering}} = a * G_{\Sigma O_2, \text{ enter}} = 0,02304 * 6,8 = 0,1567 \text{ g/hour,}$$

where $a = 0,02304 \text{ g/l}$ is the density of a dry saturated vapour at 25 °C.

The flow combustion products is:

$$G_{\Sigma \text{ leaving}} = G_{CO_2} + G_{\Sigma O_2, \text{ exceed}} + G_{Ar} = 2,3 + 2,2 + 2,3 = 6,8 \text{ l/hour}$$

Along with it a stream of water vapour is brought out:

$$G_{H_2O, \text{ leaving}} = a * G_{\Sigma \text{ leaving}} = 0,02304 * 6,8 = 0,1567 \text{ g/hour}$$

To saturate both the primary and the secondary (fat) oxygen with water vapour, were barbotised through special vessels filled in with the water heated to the temperature of (40-50) °C, then they were passed through the coil pipes of the dose-meter thermostat.

An excess of oxygen as well as a relationship between the primary and secondary oxygen were chosen in such a way, that they were near the recommended ones [14]. Flow rates for all gases are given in Table 29 (both for conditions of the calibration by burning methane and the case of combustion of a low calorific mixture) where the corresponding flow rates are indicated for other gases as well.

Table 29

Gas supplied	Gas flow rate for the calibration by burning methane, l/h	Gas flow rate for the case of low calorific mixture combustion, l/h
Non-dried combustible gas	2.3	2.3
Primary oxygen, O ₂ , saturated at 25 °C	1.1	1.0
Secondary oxygen, O _{2fat} , saturated at 25 °C	5.7	4.8
Argon, Ar, dry	2.3	1.9

Calorimeter calibration

Calibration of the calorimeter is realized by burning a high purity methane (99,95 %), the superior heat of combustion of which (HCH₄) according to ISO 6976:95 is equal to 37,10 MJ/m³ (95% confidence limit of approximately ±0,05 MJ/m³) under the standard conditions for combustion, p=101,325 kPa, T=298,16 K, and standard conditions for volume measurements, p=101,325 kPa, T=293,16 K.

The calorimetric experiment consist of three periods:

1. in a fore-period that lasts 10 minutes, an increase of temperature from a starting value 24,30 °C up to value 24,36 °C takes place due to a heat stream both from the jacket and the stirrer friction;
2. the main-period is divided into two stages: stage 1 with the period of combustion that lasts 14 minutes and within which the temperature reaches the value of 25,61 °C, and stage 2 with the subsequent period of thermal equilibrium re-establishment, which lasts 6,5 minutes and when the temperature value becomes equal to 25,64 °C. Over the main-period the calorimeter temperature increases approximately by 1,28 °C, the average point of the main-period being near 25,00 °C;
3. the final-period lasting 10 minutes is characterized by inflows of heat that are the same as those in the fore-period, the temperature increasing from 25,64 °C up to 25,67 °C.

An energy equivalent of the calorimeter, (W), is calculated from (1):

$$W = \frac{H_{CH_4} * V_{gas}}{\Delta t_{corr}} + \Delta W \quad (1)$$

where H_{CH_4} - is the superior heat of high purity methane combustion equal to 37,10 MJ/m³; V_{gas} is the gas volume under the standard conditions, (p=101,325 kPa; T=293,16 K), which is equal to $V_{gas}=V * F$, where: V is the volume of the spiral, equal to 506,2 cm³; F is the coefficient used to bring the gas volume to the standard conditions.

It is calculated from equation (2):

$$F = \frac{p}{1013,25} * \frac{273,15 + 20}{273,15 + 25} \quad (2)$$

Δt_{corr} is the corrected temperature rise, °C;

ΔW is the heat capacity of one-half the water formed in methane combustion. It is determined from equation (3):

$$\Delta W = 0,5 * m_{water} * C_{p, water} = p / 1013,25 * 1,56 \text{ J/K} \quad (3),$$

p is the barometric pressure, gPa.

When carrying out the combustion experiment, to bring the volume of the gas burnt to the standard conditions an electronic barometer is used for measuring the barometric pressure with the uncertainty of 20 Pa and the temperature of the dose-meter thermostat, which is established to be equal to 25 °C (or 298,16 K), is checked up.

An average value of the energy equivalent is determined from a series of calorimetric experiments of methane combustion. Each series includes six experiments.

Corrections

The value obtained for the energy equivalent provides the possibility to determine the heat quantity related to the average temperature of experiment, which is equal to 25 °C.

We have analyzed and estimated possible corrections, which can be introduced when carrying out the combustion experiment.

1. The correction for ignition energy estimated in the idle experiment is negligible because the spark discharge time does not exceed 1-2 seconds.
2. The correction for heat introduced into the calorimeter by the gas current flow, is negligible due to the fact that the room temperature, the temperature of gases coming from the thermostat, and the average temperature of the experiment are close to 25 °C, and their deviations do not exceed 0,1 °C.
3. The correction for water vapours entering and leaving the burner, is negligible due to provision for their mass balance.
4. The correction for reduction of the reaction enthalpy to 25 °C does not exist because the average temperature of the experiment is close to 25 °C.

Uncertainty of the Energy Equivalent Value

The uncertainty of the energy equivalent measurement is estimated according to [3] and is presented in table 30.

Table 30: Procedure for Calculation of the Energy Equivalent Measurement Uncertainty of the Calorimeter with a Gas Burner

Name	Equation according to [3]	Value
1	2	3
Result of the i-th observation, J/K	W_i	15175.71 15200.53 15181.03 15201.90 15199.46 15157.81
Number of observations	n	6
Arithmetic mean of the result of observations, J/K	$\bar{W} = (\sum W_i) / n$	15186.07
Type A relative standard uncertainty	$u_A = \sqrt{(\sum (\bar{W} - W_i)^2) / n(n-1)} / \bar{W}$	$5 \cdot 10^{-4}$
Type B relative standard uncertainty components from measurement of the following quantities:	$u_{iB} = \frac{\Theta_i}{\sqrt{3}}$	
1 standard value of methane heat of combustion;		$5.8 \cdot 10^{-4}$
2 barometric pressure;		$1.2 \cdot 10^{-4}$
3 gas temperature in the dose-meter;		$2.0 \cdot 10^{-4}$
4 volume of the spiral;		
5 temperature rise in the calorimeter		$1.2 \cdot 10^{-4}$

calorimeter		$0.5 \cdot 10^{-4}$
Type B relative standard uncertainty	$u_B = \sqrt{\frac{\sum_{i=1}^5 \Theta_i^2}{3}}$	$6.3 \cdot 10^{-4}$
Relative combined standard uncertainty	$u_C = \sqrt{u_A^2 + u_B^2}$	$8.1 \cdot 10^{-4}$
Estimation of the effective number of the degrees of freedom	$\nu = (n-1) \left[1 + \frac{u_B^2}{u_A^2} \right]^2$	33.5
Confidence level	P	0.99
Coverage factor	$t_n = t(P, \nu)$	2.576
Relative expanded uncertainty	$U_p = t_n * u_C$	$20.9 \cdot 10^{-4}$
Expanded uncertainty, J/K		31.74
Energy equivalent of the calorimeter, J/K	\bar{W}	15186.07

Thus, the energy equivalent of the calorimeter is equal to 15186,07 J/K, the expanded uncertainty being equal to 31, 74 J/K.

Combustion of Natural Gas Sample with a Low Calorific Mixture

The procedure of the calorimetric experiments on natural gas combustion resembles the calibration experiments as much as possible. The reference flow-rate of natural gas was taken the same as in calibration and was equal to 2,3 l/hour. Proceeding from the known reference gas mixture composition, some changes were introduced into the flow-rates of the other gases providing for the water balance. (They are presented in Table 29)

Due to a lower combustion heat of the mixture in comparison to methane, the start of temperature measurements (the first point of the fore-period) was shifted to the value 24,39 °C. Hence, the fore-period was within the temperature interval from 24,39 °C to 24,44 °C, the main period - from 24,44 °C to 25,58 °C, and the final-period from 25,58 °C to 25,61 °C. The corrected temperature rise was equal to ≈ 1 °C.

The superior heat of combustion was calculated by the equation:

$$H_s = \frac{\bar{W} * \Delta t_{corr}}{V * F} \quad (5)$$

The measurement results are presented in Table 31.

Table 31: Procedure for Calculation of the Heat of Combustion Measurement Uncertainty of the Low-Caloric Mixture of a Natural Gas Sample

Name	Equation according to [3]	Value
1	2	3
Result of the i-th observation, MJ/m ³	H _i	31.770
		31.834
		31.875
		31.813

Name	Equation according to [3]	Value
1	2	3
		31.793 31.824
Number of observations	n	6
Arithmetic mean of the result of observations, J/K	$\bar{H} = (\sum H_i) / n$	31.818
Type A relative standard uncertainty	$u_A = \sqrt{(\sum (\bar{H} - H_i)^2) / n(n-1) / \bar{H}}$	$5 \cdot 10^{-4}$
Type B relative standard uncertainty components from measurement of the following quantities: 1. energy equivalent of the calorimeter; 2. barometric pressure; 3. gas temperature in the dose-meter; 4. temperature rise *		$8.1 \cdot 10^{-4}$ $1.2 \cdot 10^{-4}$ $2.0 \cdot 10^{-4}$ $0.6 \cdot 10^{-4}$
Type B relative standard uncertainty	$u_B = \sqrt{\sum_1^4 u_{B,i}^2}$	$8.5 \cdot 10^{-4}$
Relative combined standard uncertainty	$u_C = \sqrt{u_A^2 + u_B^2}$	$9.8 \cdot 10^{-4}$
Estimation of the effective number of the degrees of freedom	$\nu = (n-1) [1 + \frac{u_B^2}{u_A^2}]^2$	75.7
Confidence level	P	0.95
Coverage factor	$t_n = t(P, \nu)$	1.96
Relative expanded uncertainty	$U_p = t_n \cdot u_C$	$19.2 \cdot 10^{-4}$
Expanded uncertainty, MJ/m ³		0.06
Superior volumetric heat of combustion, MJ/m ³	\bar{H} [298,15 K, 101,325 kPa; V(293,15 K, 101,325 kPa)]	31.82

*When estimating the Type B uncertainty, the dose-meter volume measurement uncertainty is not taken into account because it has been already accounted for in the energy equivalent standard uncertainty value.

Results (table 32):

The value of the superior volumetric heat of combustion of natural gas (low-calorific gas mixture) at standard conditions of combustion (298,15 K; 101,325 kPa) and volume measurements (293, 15 K; 101,325 kPa) is equal to 31,82 MJ/m³.

The combined standard uncertainty is equal to 0,03 MJ/m³.

The expanded uncertainty is equal to 0,06 MJ/m³.

Table 32: Results (low-calorific gas mixture) Gross calorific value (kJ/m³, p=101325 Pa, T=298,15 K; volume: p=101325 Pa, T=293,15K)

Measurement	Date (dd/mm/yy)	Result (kJ/m ³)	Standard uncertainty (%)
1	25.12.2001	31770	
2	26.12.2001	31834	
3	27.12.2001	31875	
4	29.12.2001	31813	
5	03.01.2002	31793	
6	04.01.2002	31824	
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Parameter		Result (kJ/m ³)	Expanded Uncertainty (kJ/m ³)
Gross calorific value		31818	60
			Coverage factor
			1.96

References

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