International Comparison

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Final Report CCQM P49 – Natural gas types IV and V

Field

Amount of substance

Subject

Comparison in the field of natural gas analysis

Participants

CSIRO-NML (AU), BAM[1] (DE), NMi VSL[1] (NL), GUM (PO)

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 C_6 (hexane) to complement and extent the earlier key comparisons in this area (CCQM-K1e-g) [1]. The mixtures in CCQM-K1 contained only components up to C_4 (butane). The compositions of the mixtures used in this key comparison have chosen to be typical for respectively low and high calorific value mixtures.

This comparison has been conducted in parallel to CCQM-K16. The participants have expressed their interest to participate, but not in a formal key comparison.

[1] BAM and NMi VSL organised this comparison.

Participants

Table 1 lists the participants in this key comparison.

Table 1: List of participants

Acronym	Country	Institute
CSIRO-NML	AU	CSIRO National Metrology Laboratory
BAM	DE	Bundesanstalt für Materialforschung und –prüfung, Berlin, Germany
NMi VSL	NL	NMi Van Swinden Laboratorium B.V., Delft, the Netherlands
GUM	PO	Central Office of Measures, Physical Chemistry Division

Measurement standards

The same types of mixtures have been used as for CCQM-K16 [2]. Two mixtures have been submitted, one with a low calorific value, and one with a high calorific value. Table 2 gives 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
iso-Butane	0.20	0.10
n-Butane	0.20	0.10
iso-Pentane	0.050	0.035
n-Pentane	0.050	0.035
neo-Pentane	0.050	0.050
n-Hexane	0.050	0.020
Methane	81.85 (balance)	82.16 (balance)

Schedule

The same schedule as for the CCQM-K16 has been used. The schedule of this comparison was as follows [2]:

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

Laboratory reports received until September 2002 have been accepted.

Measurement protocol

The same protocol as for the CCQM-K16 has been used. The only exception concerns the components to be measured: it was up to the participating laboratory to decide on what parameters results would be submitted.

Measurement equation

The same model as for the CCQM-K16 has been used [2]. For the calculation of degrees of equivalence, the same procedure has been followed as in the CCQM-K16. For degrees of equivalence across the comparisons (CCQM-PXX and CCQM-K16), the same models apply as for the CCQM-K16 [2], as the mixtures have been made in parallel [3].

Degrees of equivalence

In the figures 1-23, the degrees of equivalence for all participating laboratories are given in % (mol/mol). 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 expanded uncertainties using $k = 2$.

The results of CCQM-K16 are included in the graphs for comparison. The participants in CCQM-K16 were NRCCRM (CR), BAM (DE), NMIJ (JP), NMi VSL (NL), VNIIM (RU), SMU (SK), NPL (UK), and NIST (US) [2].

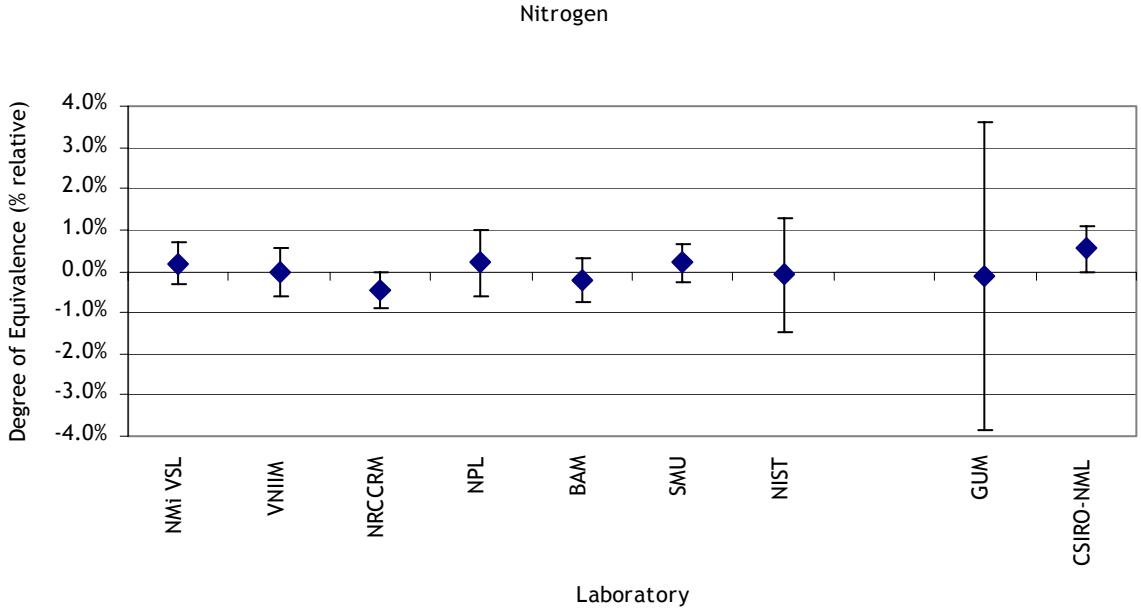

Figure 1: Degrees of equivalence for nitrogen (low calorific mixture)

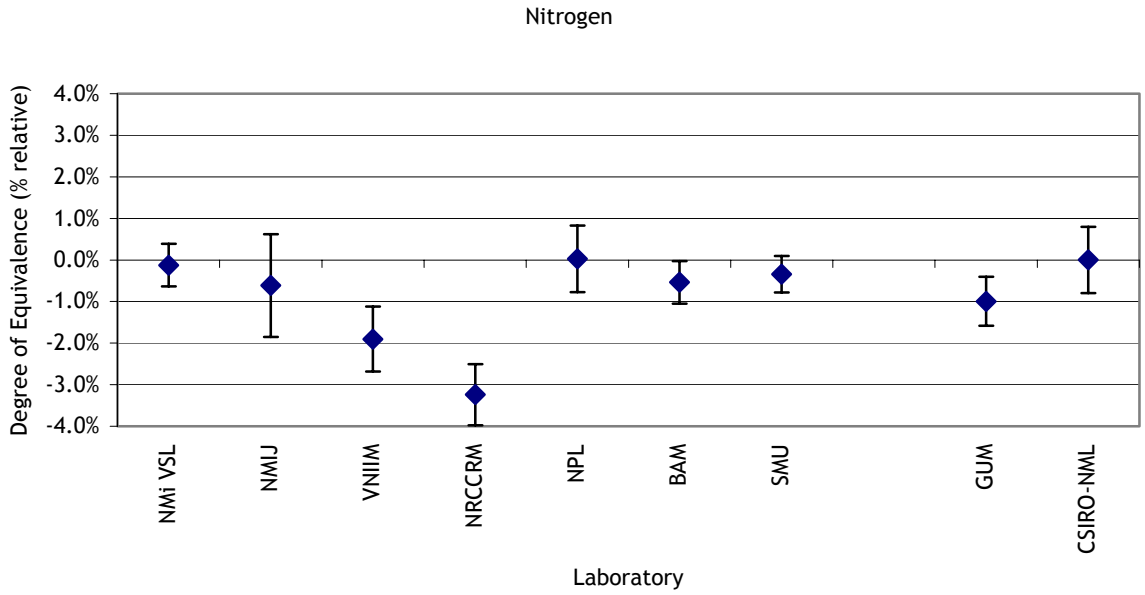

Figure 2: Degrees of equivalence for nitrogen (high calorific mixture)

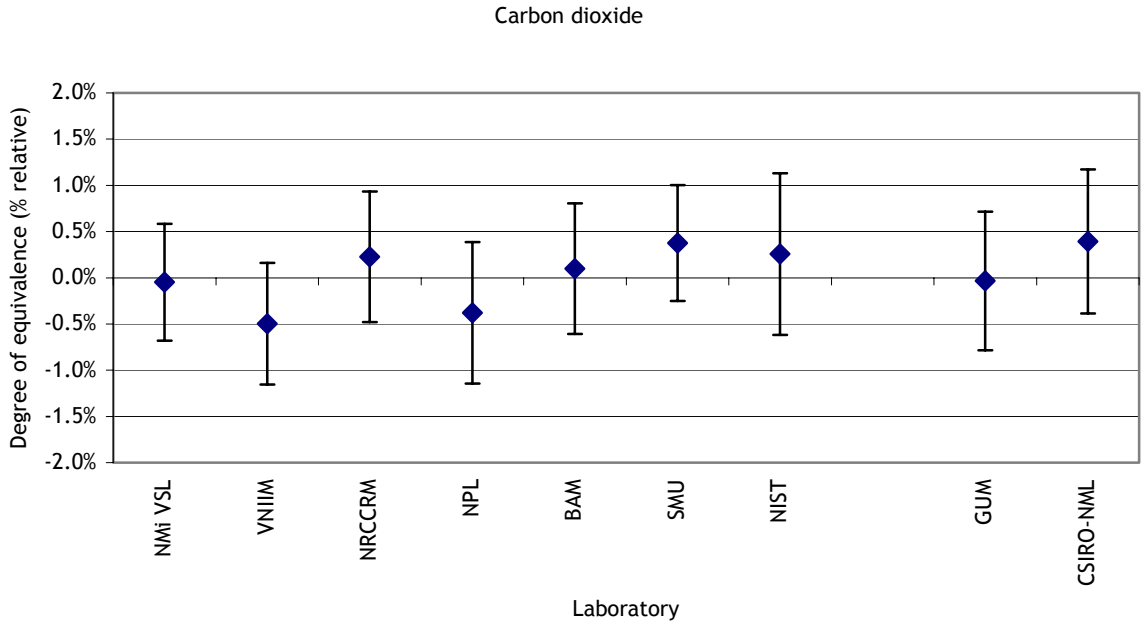

Figure 3: Degrees of equivalence for carbon dioxide (low calorific mixture)

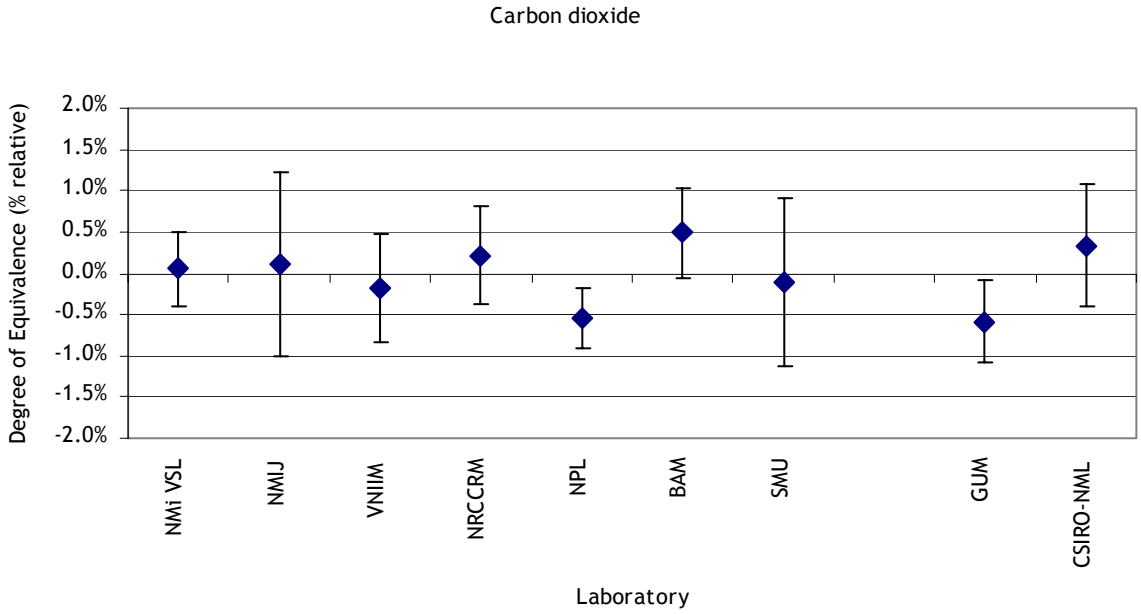

Figure 4: Degrees of equivalence for carbon dioxide (high calorific mixture)

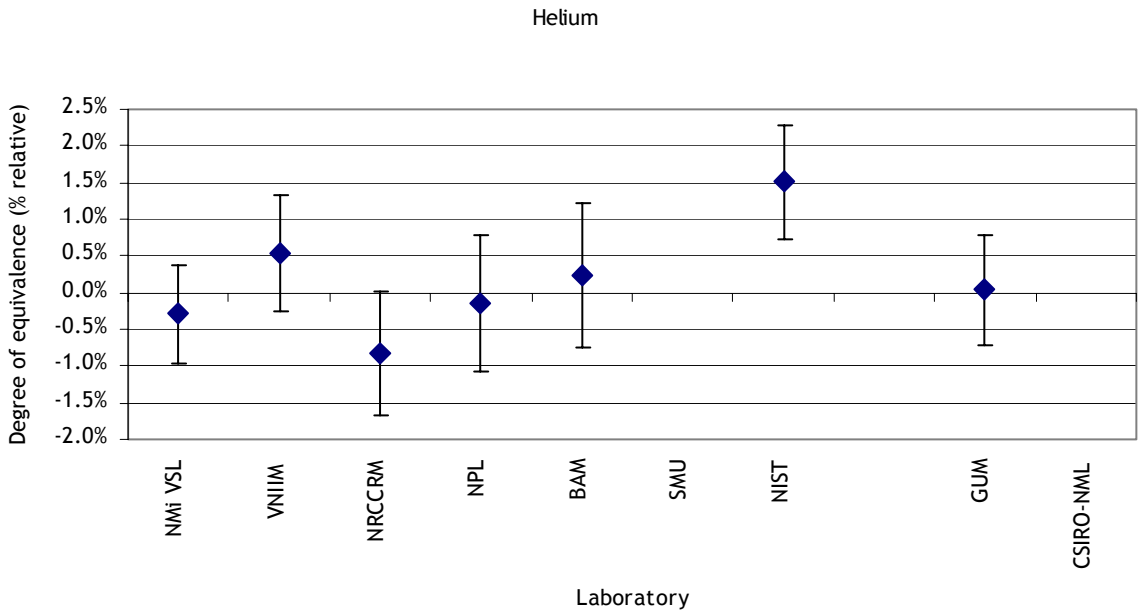

Figure 5: Degrees of equivalence for helium (low calorific mixture)

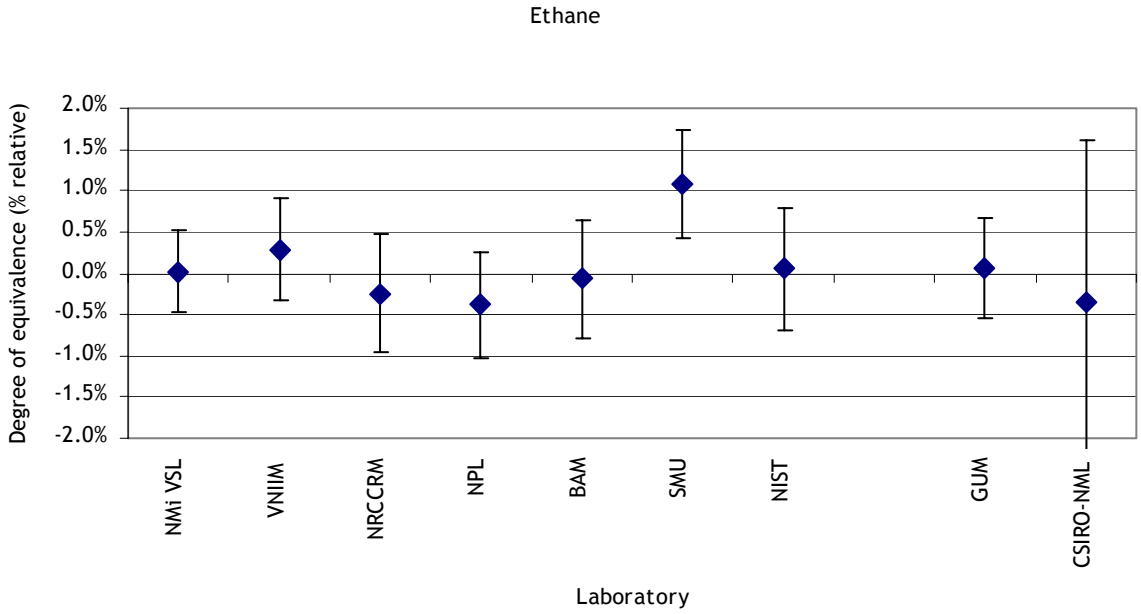

Figure 6: Degrees of equivalence for ethane (low calorific mixture)

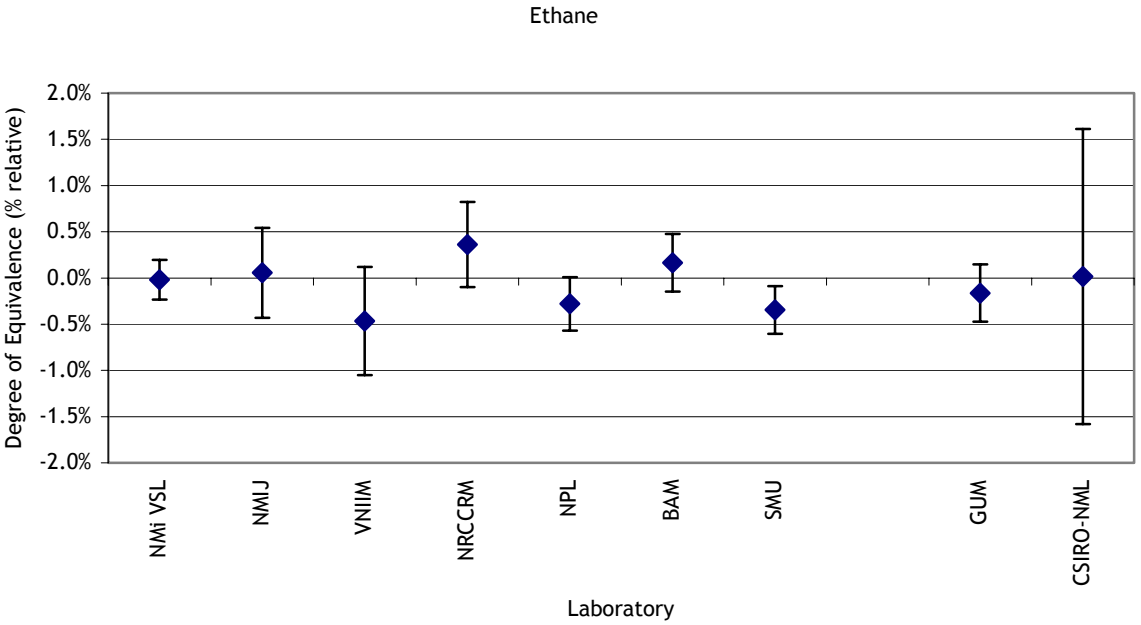

Figure 7: Degrees of equivalence for ethane (high calorific mixture)

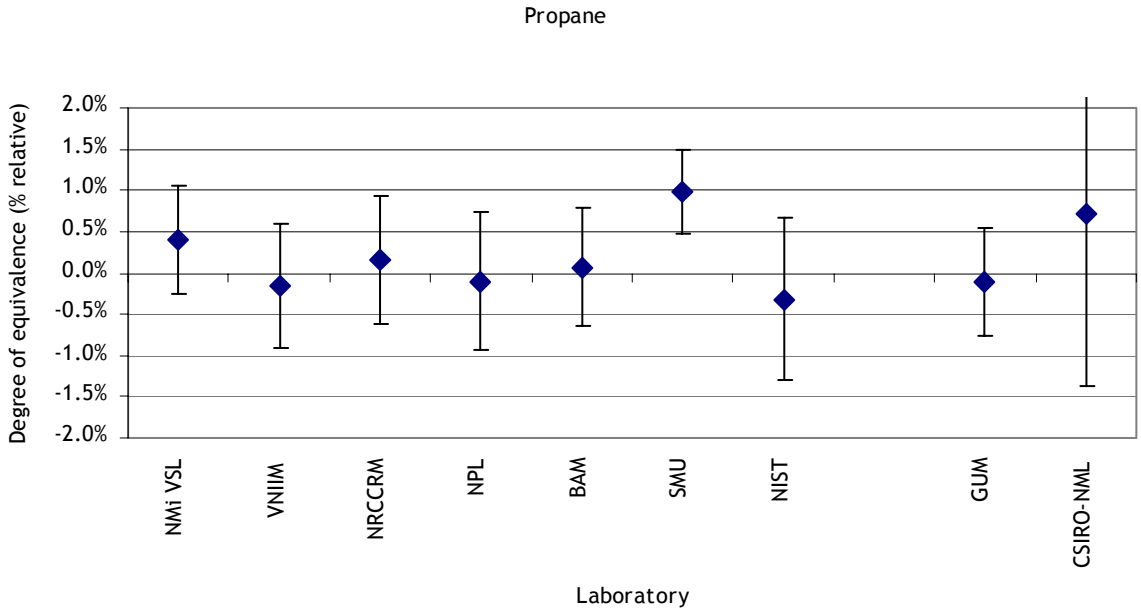

Figure 8: Degrees of equivalence for propane (low calorific mixture)

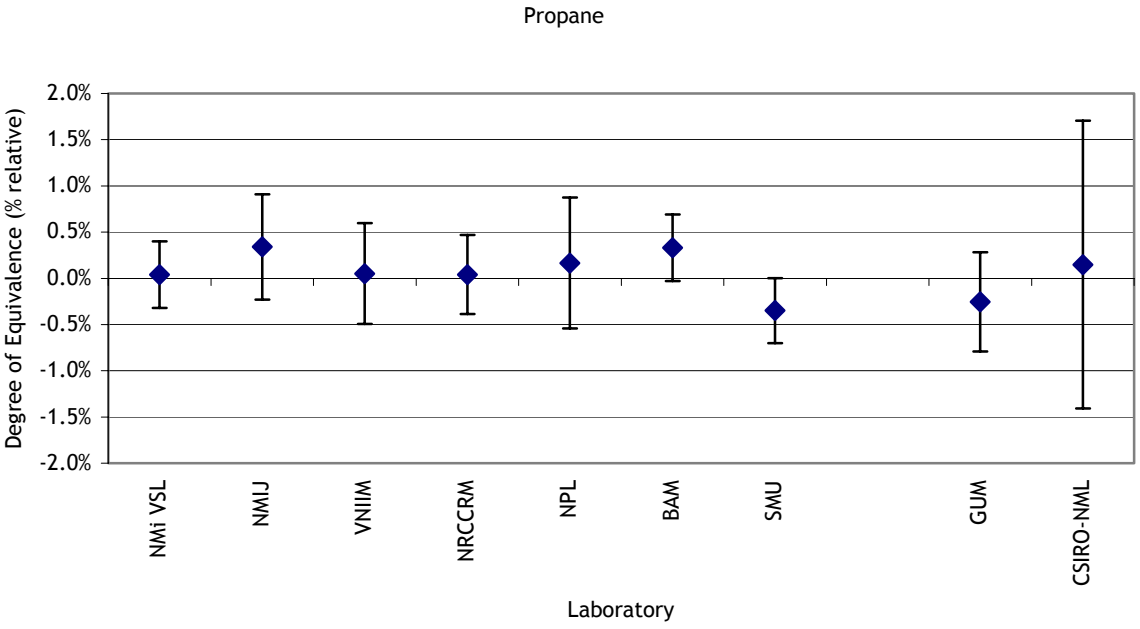

Figure 9: Degrees of equivalence for propane (high calorific mixture)

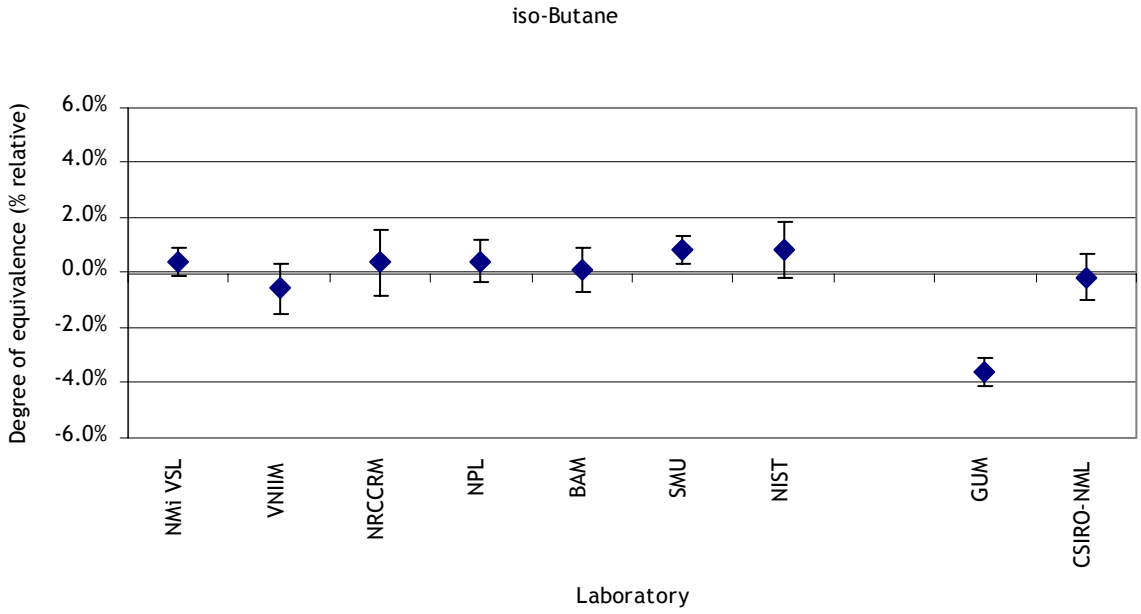

Figure 10: Degrees of equivalence for *iso*-butane (low calorific mixture)

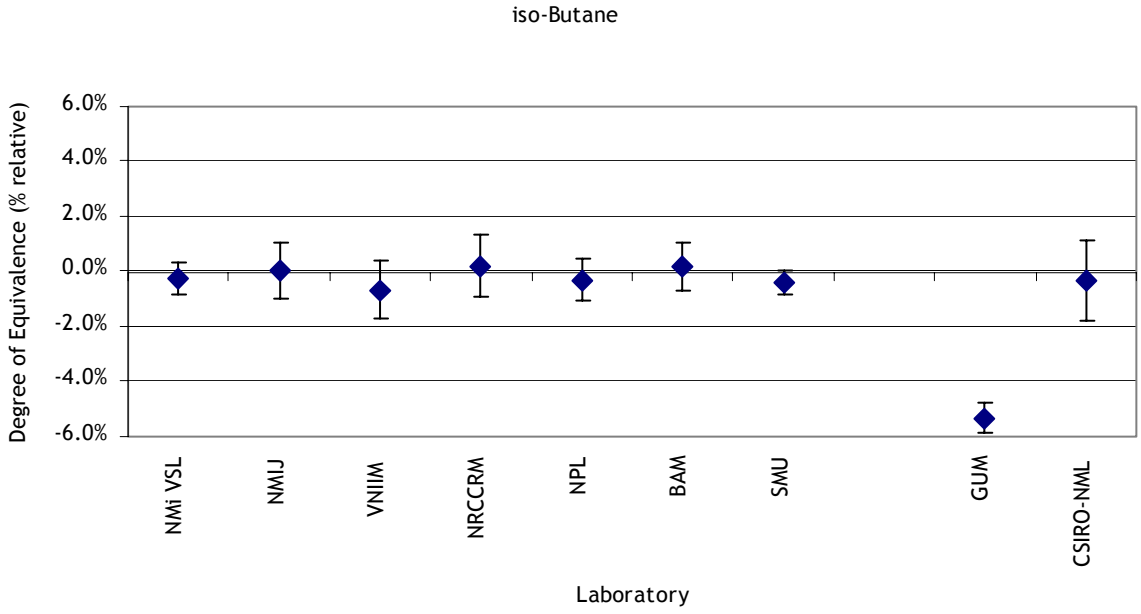

Figure 11: Degrees of equivalence for *iso*-butane (high calorific mixture)

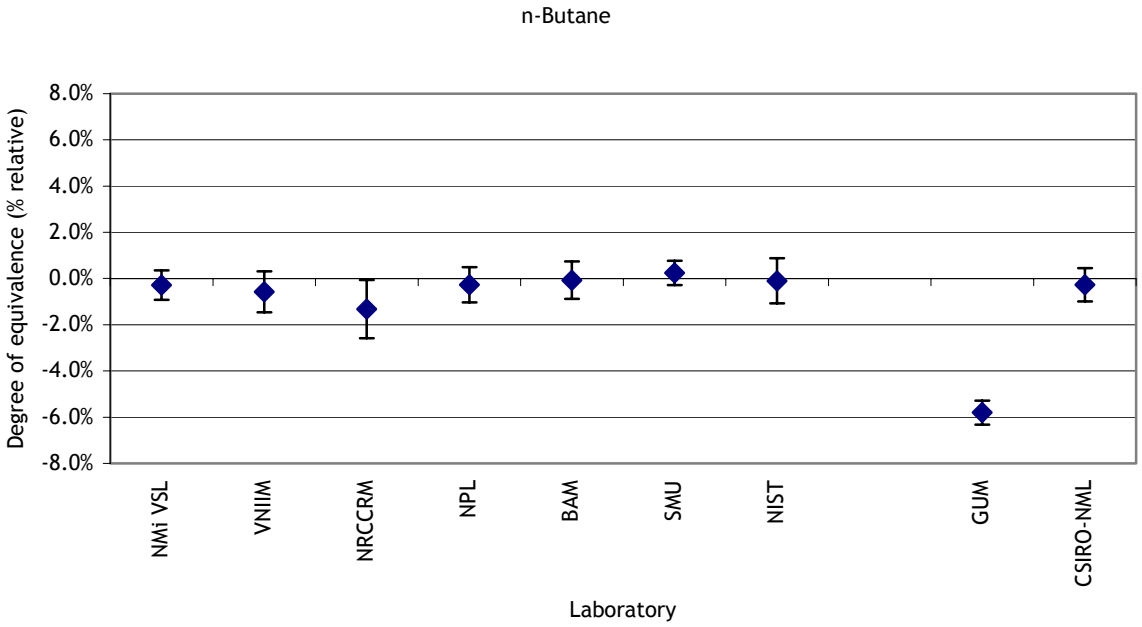

Figure 12: Degrees of equivalence for *n*-butane (low calorific mixture)

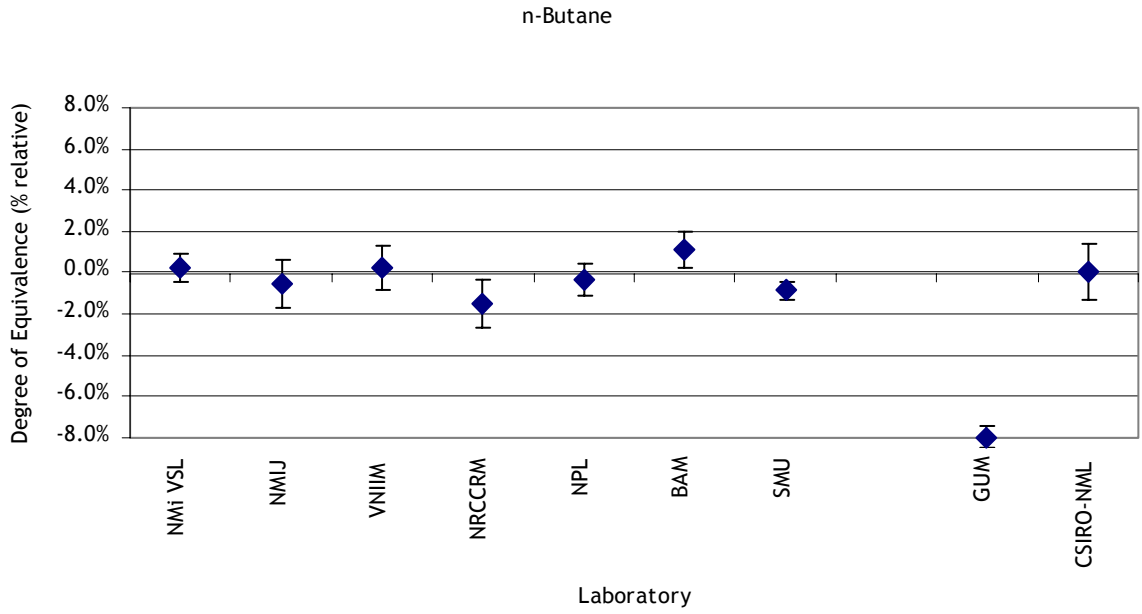

Figure 13: Degrees of equivalence for *n*-butane (high calorific mixture)

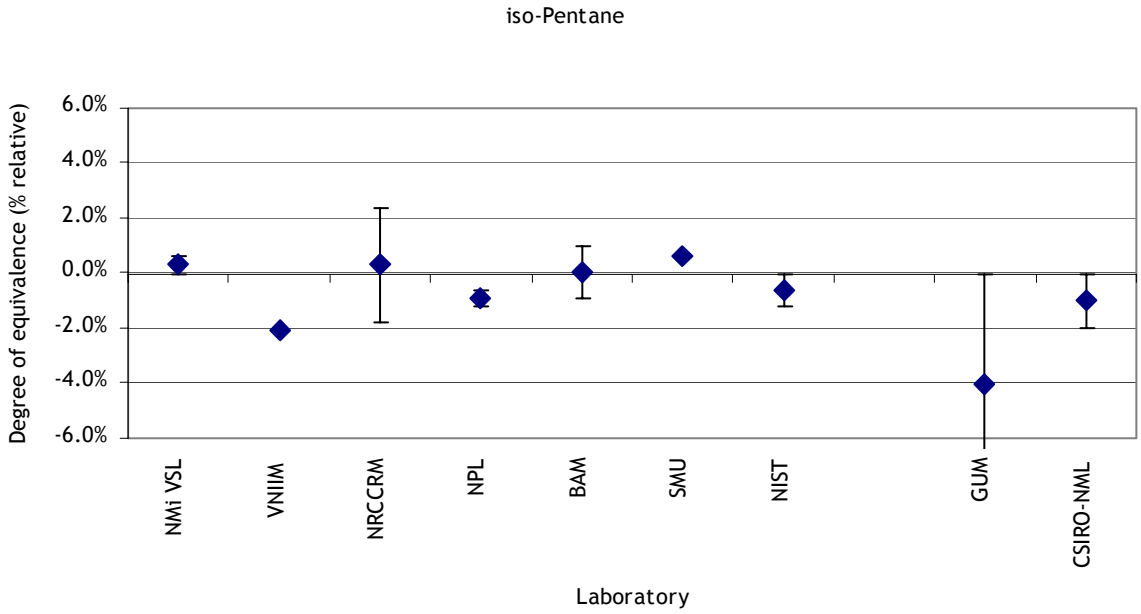

Figure 14: Degrees of equivalence for *iso*-pentane (low calorific mixture)

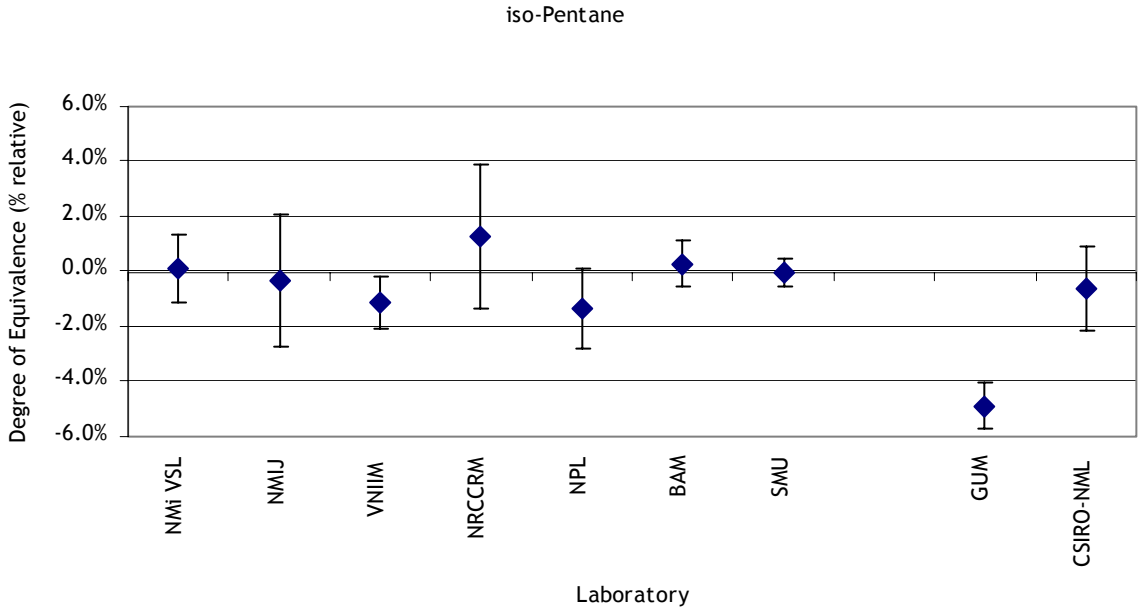

Figure 15: Degrees of equivalence for *iso*-pentane (high calorific mixture)

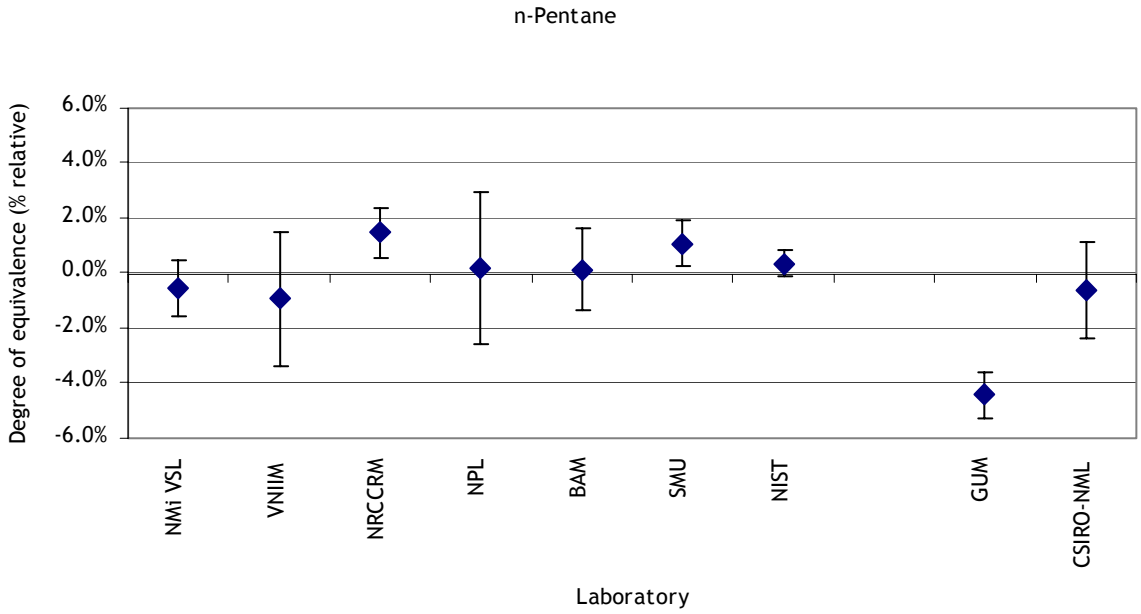

Figure 16: Degrees of equivalence for *n*-pentane (low calorific mixture)

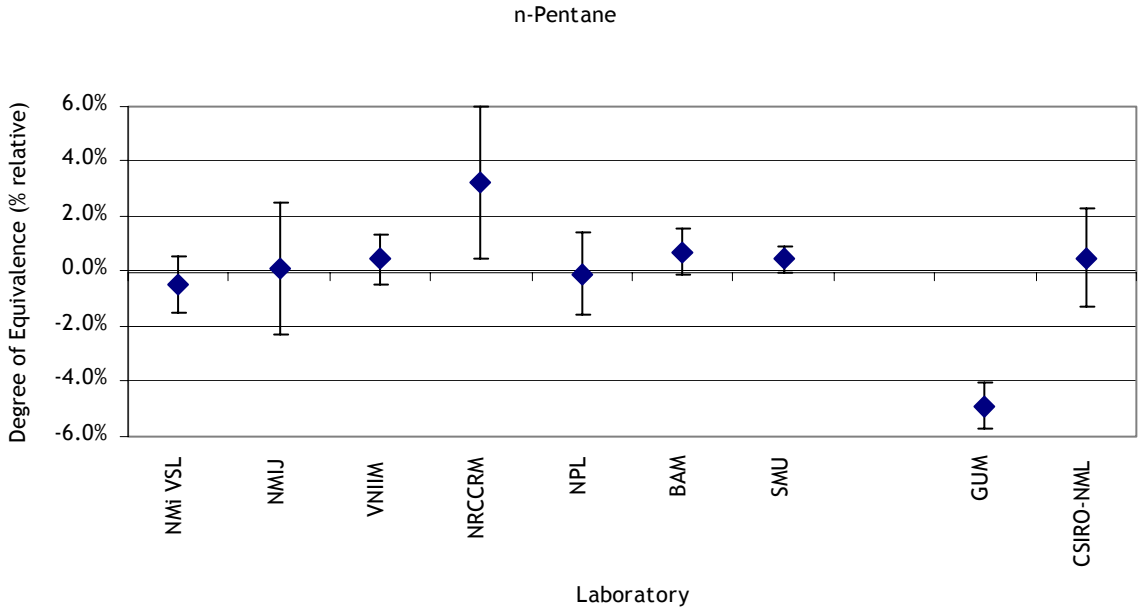

Figure 17: Degrees of equivalence for *n*-pentane (high calorific mixture)

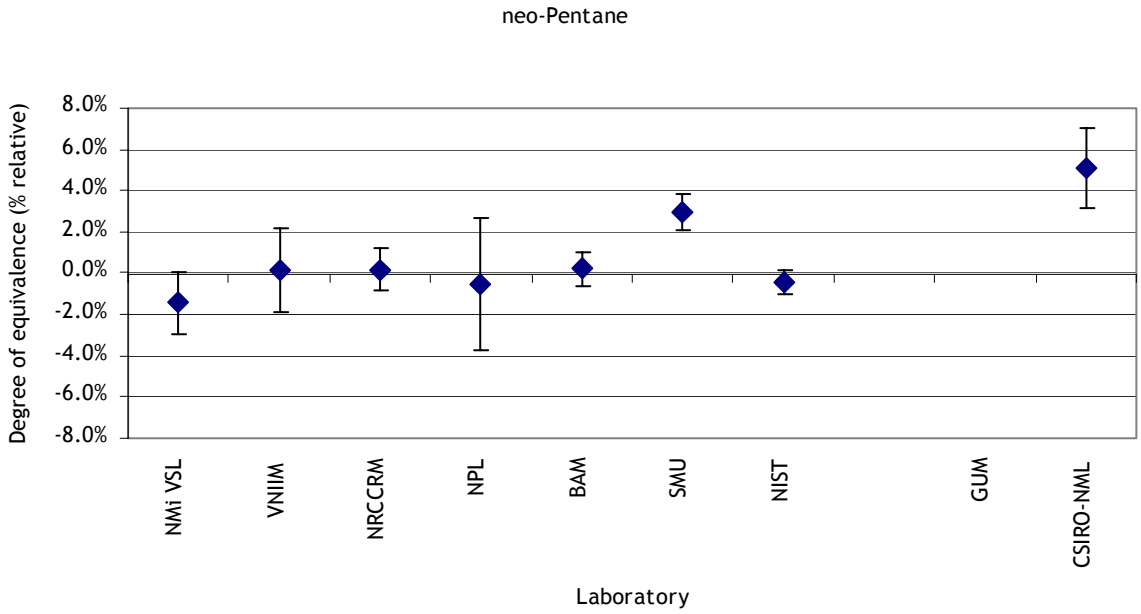

Figure 18: Degrees of equivalence for *neo*-pentane (low calorific mixture)

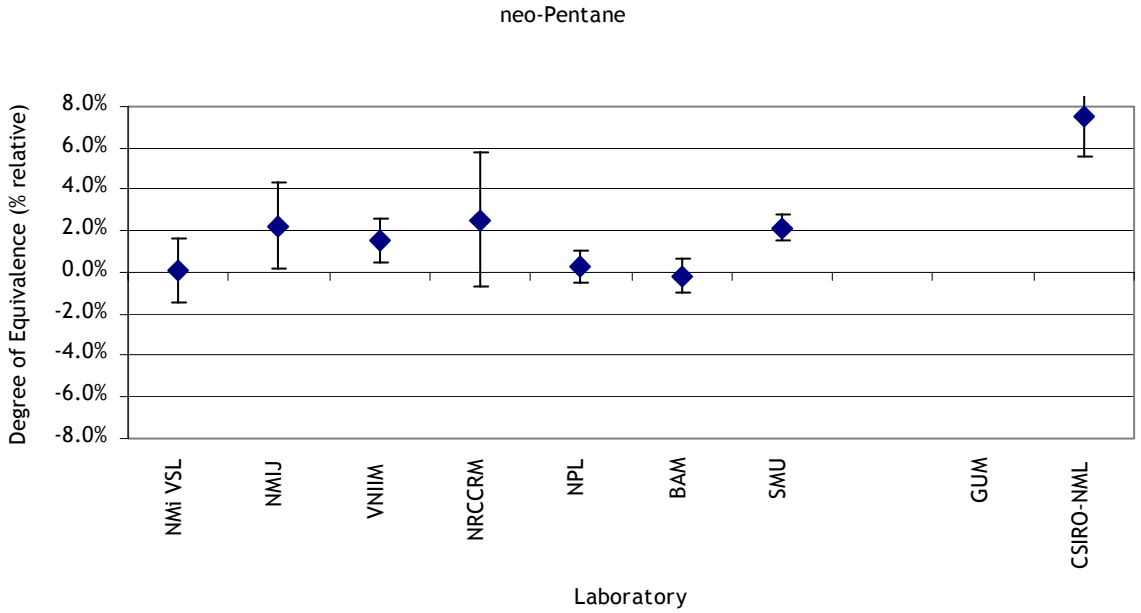

Figure 19: Degrees of equivalence for *neo*-pentane (high calorific mixture)

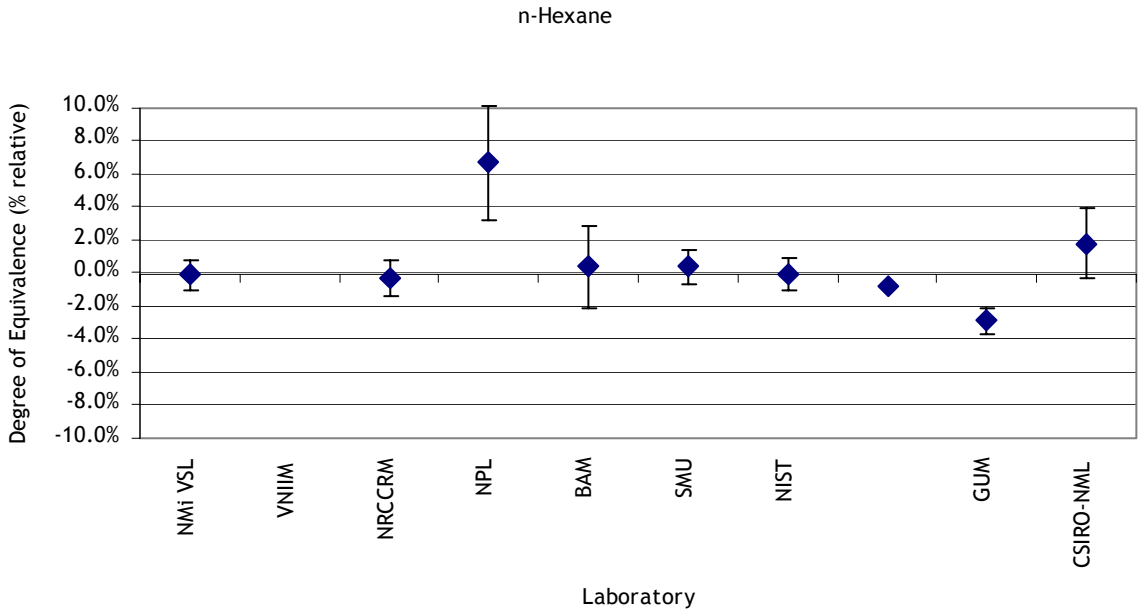

Figure 20: Degrees of equivalence for *n*-hexane (low calorific mixture)

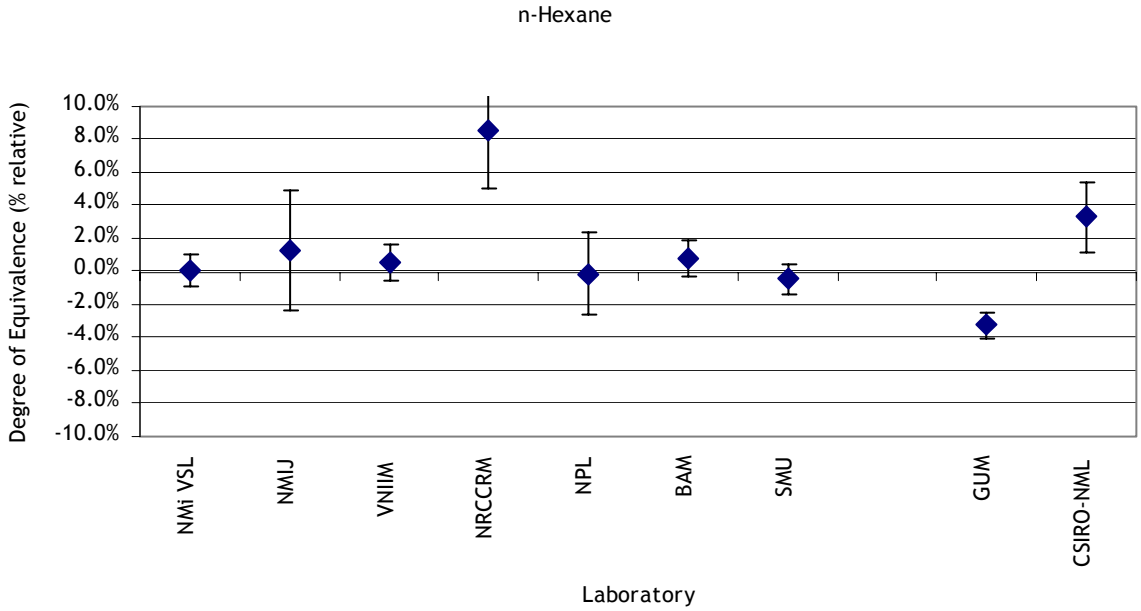

Figure 21: Degrees of equivalence for *n*-hexane (high calorific mixture)

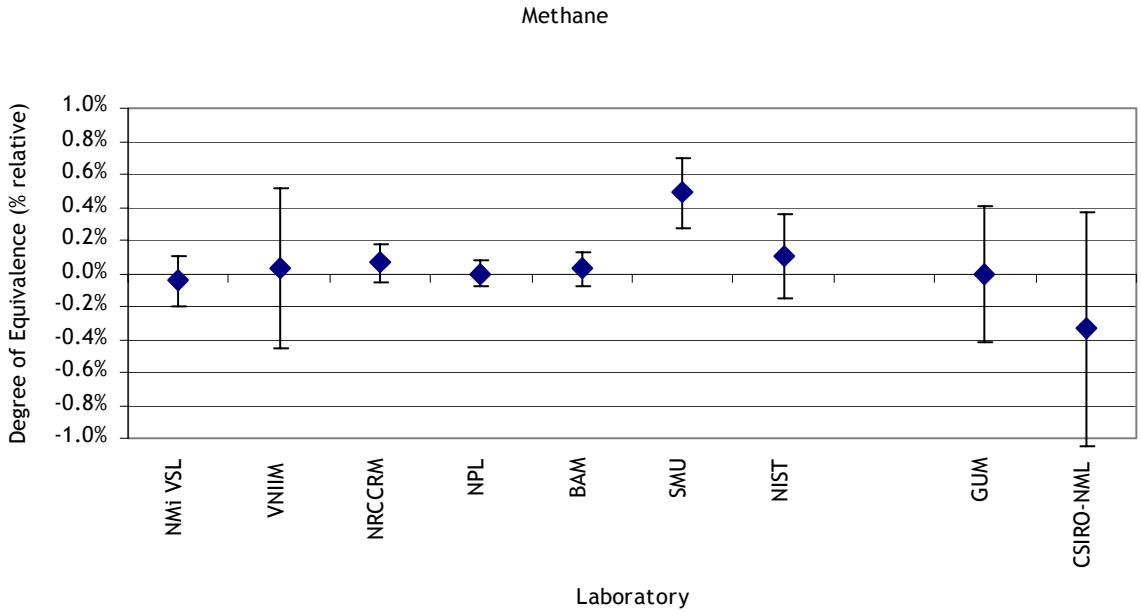

Figure 22: Degrees of equivalence for methane (low calorific mixture)

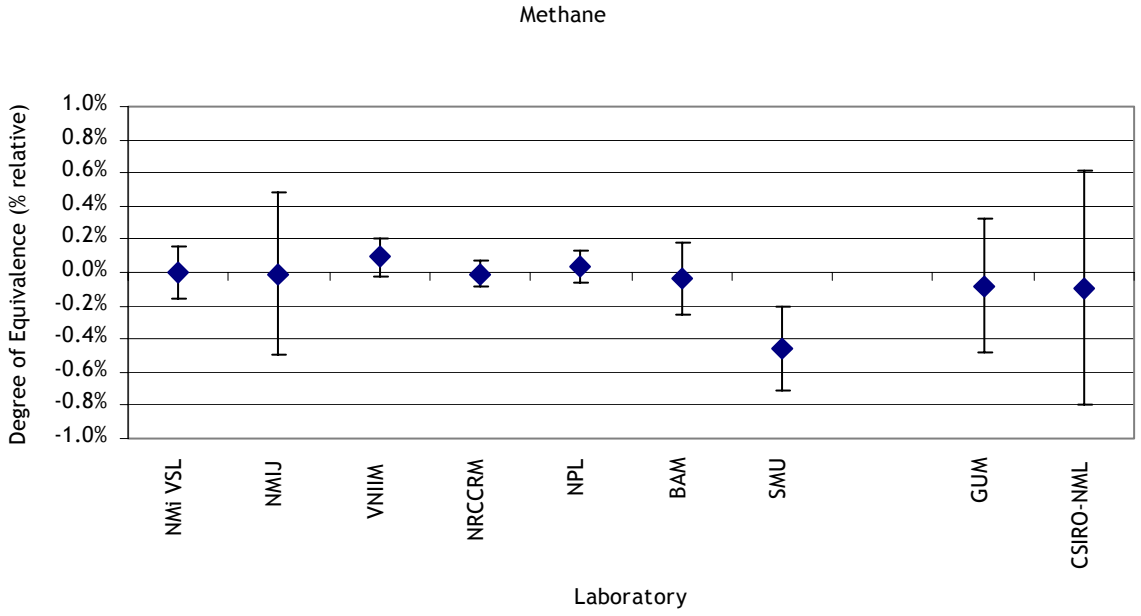

Figure 23: Degrees of equivalence for methane (high calorific mixture)

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 confidence[2] (10^{-2} mol/mol)

Table 3: 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	$U(\Delta x)$
GUM	BAM-008	12.0841	0.0007	0.0240	0.0240	12.07	0.45	2	-0.014	-0.12%	2	0.453
CSIRO-NML	BAM-026	12.2176	0.0007	0.0240	0.0240	12.284	0.06	2.5	0.066	0.54%	2	0.068

Table 4: 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	$U(\Delta x)$
GUM	VSL129379	1.2050	0.0001	0.0019	0.0019	1.193	0.006	2	-0.0120	-1.00%	2	0.0071
CSIRO-NML	VSL129347	1.2050	0.0001	0.0019	0.0019	1.205	0.011	2.5	0.0000	0.00%	2	0.0096

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

Table 5: 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	$U(\Delta x)$
GUM	BAM-008	4.0014	0.0005	0.012	0.012	4.000	0.018	2	0.00	-0.03%	2	0.03
CSIRO-NML	BAM-026	4.0770	0.0005	0.012	0.012	4.093	0.026	2.5	0.02	0.39%	2	0.03

Table 6: 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	$U(\Delta x)$
GUM	VSL129379	0.80290	0.00006	0.00080	0.00080	0.7982	0.0036	2	-0.0047	-0.59%	2	0.0039
CSIRO-NML	VSL129347	0.80480	0.00007	0.00080	0.00080	0.8075	0.0071	2.5	0.0027	0.34%	2	0.0059

Table 7: 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	$U(\Delta x)$
GUM	BAM-008	0.5079	0.0002	0.0015	0.0015	0.5081	0.002	2	0.0002	0.04%	2	0.0038
CSIRO-NML	BAM-026	0.5086	0.0002	0.0015	0.0015							

Table 8: 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	$U(\Delta x)$
GUM	BAM-008	0.7486	0.0002	0.0015	0.0015	0.749	0.003	2	0.0005	0.07%	2	0.0046
CSIRO-NML	BAM-026	0.7496	0.0002	0.0015	0.0015	0.747	0.018	2.5	-0.0026	-0.35%	2	0.0147

Table 9: 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	$U(\Delta x)$
GUM	VSL129379	11.0480	0.0008	0.0044	0.0045	11.03	0.03	2	-0.018	-0.16%	2	0.034
CSIRO-NML	VSL129347	11.0383	0.0009	0.0044	0.0045	11.04	0.22	2.5	0.002	0.02%	2	0.176

Table 10: 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	$U(\Delta x)$
GUM	BAM-008	0.2913	0.0001	0.0006	0.0006	0.291	0.002	2	-0.0003	-0.11%	2	0.0019
CSIRO-NML	BAM-026	0.2917	0.0001	0.0006	0.0006	0.2938	0.0075	2.5	0.0021	0.72%	2	0.0061

Table 11: 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	$U(\Delta x)$
GUM	VSL129379	4.5064	0.0004	0.0045	0.0045	4.495	0.022	2	-0.011	-0.25%	2	0.024
CSIRO-NML	VSL129347	4.5053	0.0004	0.0045	0.0045	4.512	0.087	2.5	0.007	0.15%	2	0.070

Table 12: 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	$U(\Delta x)$
GUM	BAM-008	0.2001	0.0002	0.0004	0.0004	0.1929	0.0007	2	-0.0072	-3.61%	2	0.0011
CSIRO-NML	BAM-026	0.2000	0.0002	0.0004	0.0004	0.1997	0.0018	2.5	-0.0003	-0.16%	2	0.0017

Table 13: 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	$U(\Delta x)$
GUM	VSL129379	0.10098	0.00001	0.00016	0.00016	0.0956	0.0004	2	-0.0054	-5.31%	2	0.0005
CSIRO-NML	VSL129347	0.10013	0.00001	0.00016	0.00016	0.0998	0.0018	2.5	-0.0003	-0.33%	2	0.0015

Table 14: 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	$U(\Delta x)$
GUM	BAM-008	0.2006	0.0001	0.0004	0.0004	0.1890	0.0007	2	-0.0116	-5.80%	2	0.0010
CSIRO-NML	BAM-026	0.2005	0.0001	0.0004	0.0004	0.2000	0.0015	2.5	-0.0005	-0.27%	2	0.0014

Table 15: 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	$U(\Delta x)$
GUM	VSL129379	0.10000	0.00005	0.00017	0.00018	0.0921	0.0004	2	-0.007952	-7.95%	2	0.0005
CSIRO-NML	VSL129347	0.10085	0.00005	0.00017	0.00018	0.1009	0.0017	2.5	5E-05	0.05%	2	0.0014

Table 16: 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	$U(\Delta x)$
GUM	BAM-008	0.0502	0.0001	0.0001	0.0002	0.0482	0.0004	2	-0.0020	-4.06%	2	0.0005
CSIRO -NML	BAM-026	0.0495	0.0001	0.0001	0.0002	0.0490	0.0005	2.5	-0.0005	-0.99%	2	0.0005

Table 17: 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	$U(\Delta x)$
GUM	VSL129379	0.03491	0.00001	0.00006	0.00006	0.0332	0.00027	2	-0.0017	-4.89%	2	0.0003
CSIRO-NML	VSL129347	0.03469	0.00001	0.00006	0.00006	0.0345	0.0007	2.5	-0.0002	-0.59%	2	0.0005

Table 18: 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	$U(\Delta x)$
GUM	BAM-008	0.0490	0.0001	0.0001	0.0002	0.04680	0.00040	2	-0.0022	-4.43%	2	0.0005
CSIRO-NML	BAM-026	0.0513	0.0001	0.0001	0.0002	0.05098	0.00057	2.5	-0.0003	-0.60%	2	0.0006

Table 19: 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	$U(\Delta x)$
GUM	VSL129379	0.03491	0.00001	0.00004	0.00004	0.0332	0.00028	2	-0.0017	-4.90%	2	0.0003
CSIRO-NML	VSL129347	0.03473	0.00001	0.00004	0.00004	0.0349	0.00076	2.5	0.0002	0.49%	2	0.0006

Table 20: 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	$U(\Delta x)$
GUM	BAM-008	0.0497	0.0001	0.0001	0.0001							
CSIRO-NML	BAM-026	0.0498	0.0001	0.0001	0.0001	0.0523	0.0013	2.5	0.0025	5.10%	2	0.0011

Table 21: 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	$U(\Delta x)$
GUM	VSL129379	0.05052	0.00004	0.00007	0.00009							
CSIRO-NML	VSL129347	0.04993	0.00004	0.00008	0.00009	0.0537	0.0012	2.5	0.0038	7.56%	2	0.0010

Table 22: 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	$U(\Delta x)$
GUM	BAM-008	0.0503	0.0001	0.0002	0.0002	0.04890	0.00039	2	-0.0014	-2.86%	2	0.0005
CSIRO-NML	BAM-026	0.0493	0.0001	0.0002	0.0002	0.05019	0.00068	2.5	0.0009	1.78%	2	0.0007

Table 23: 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	$U(\Delta x)$
GUM	VSL129379	0.019944	0.000003	0.000030	0.000030	0.01930	0.00014	2	-0.0006	-3.23%	2	0.0002
CSIRO-NML	VSL129347	0.019884	0.000003	0.000030	0.000030	0.02054	0.00052	2.5	0.0007	3.30%	2	0.0004

Table 24: 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	$U(\Delta x)$
GUM	BAM-008	81.7659	0.0027	0.0820	0.0820	81.76	0.37	2	-0.006	-0.01%	2	0.40
CSIRO-NML	BAM-026	81.5543	0.0027	0.0820	0.0820	81.28	0.75	2.5	-0.274	-0.34%	2	0.62

Table 25: 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	$U(\Delta x)$
GUM	VSL129379	82.0957	0.0010	0.0329	0.0329	82.03	0.33	2	-0.066	-0.08%	2	0.33
CSIRO-NML	VSL129347	82.1057	0.0010	0.0328	0.0329	82.03	0.72	2.5	-0.076	-0.09%	2	0.58

Discussion of results

For nitrogen, GUM reports a value differing more than the expanded uncertainty of the difference between measured and reference value for nitrogen (–1.00% relative) for the high calorific mixture. All other values for nitrogen agree within 1%, and the observed deviations are smaller than their associated expanded uncertainties. All results for carbon dioxide agree well with the reference value and are within 1%, with the exception of the result of GUM on the high calorific mixture, where the observed deviation is larger than its associated expanded uncertainty. Helium is measured by laboratory J only, and the result agrees well with the reference value. The results of both laboratories for ethane and propane agree within 1% with the reference value for both mixtures.

GUM reports values deviating more than 1% and more than the associated expanded uncertainty from the reference value for iso-butane (low calorific mixture: –3.61%; high calorific mixture: –5.31% relative), n-butane (low calorific mixture: –5.80%; high calorific mixture: –7.95% relative), iso-pentane (low calorific mixture: –4.06%; high calorific mixture: –4.89% relative), n-pentane (low calorific mixture: –4.43%; high calorific mixture: –4.90% relative) and n-hexane (low calorific mixture: –2.86%; high calorific mixture: –3.23% relative). The laboratory does not report a value for neo-pentane.

CSIRO-NML reports values differing more than the expanded uncertainty of the difference between measured and reference value for neo-pentane (low calorific mixture: 5.10%; high calorific mixture: 7.56% relative) and n-hexane (low calorific mixture: 1.78%; high calorific mixture: 3.30% relative). All other results agree within 1% relative with the reference value.

Discussion and conclusions

For most parameters, the results of laboratories J and K agree within 1% relative with the reference value. GUM has some problems in measuring the butanes and higher hydrocarbons, whereas CSIRO-NML has some problems with neo-pentane and n-hexane only.

References

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

[2] Van der Veen A.M.H., Heine H.-J., Brinkmann F.N.C., Ziel P.R., Wang Lin Zhen, Kato K., Kustikov Y.A., Musil S., Milton M.J.T., Guenther F.R., "International Key Comparison CCQM-K16 – Natural Gas types IV and V", Final Report, April 2004

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

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

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Annex A: Methods of measurement

GUM

Instruments used for measurement:

I Varian Star 3600 gas chromatograph with 2 independent channels (only FID is common for both):
Channel A with packed column (Molsieve 13X, Hayesep C), FID and TCD
Channel B with capillary column (Plot Fused Silica CP-A1203/KCl, 50 m, 0.53 ID), FID
II Unicam 610 gas chromatograph with 2 independent channels, software 4880.
Channel A with packed column with Molesieve protected by a Porapack backflush column, TCD
Channel B used Porapack: backflush and analysis columns, FID

For analyses of helium nitrogen was used as carrier gas. For rest analyses helium was carrier gas.

CSIRO-NML

The concentrations of each natural gas component were determined by conventional gas chromatography using a Varian 3800 gas chromatograph equipped with both TCD and FID detectors.

All natural gas components were separated using a Hayesep R (80/100 mesh, 12'x 1/8" SS) column with helium as the carrier gas. The column was temperature programmed using the following method:

Temperature(°C)	Rate(°C/min.)	Hold time(min.)	Total time (min.)
30		5	5
150	40	8	16
100	40	7.75	25
150	40	18.75	45
220	20	9.5	58

The nitrogen and carbon dioxide components were determined using the TCD detector. All hydrocarbon components (C_1 – C_6) were determined using the FID detector.

Data collection and processing were performed with Varian Star-5.5 software.

Calibration Standards:
Two calibration standards were used, one containing low calorific value natural gas, and the second containing a high calorific value natural gas mixture. The natural gas calibration standards were prepared in our laboratory from very high purity commercial gases with the concentrations of the natural gas components determined gravimetrically.

Prior to calibration standard preparation, the impurity and composition of the high purity commercial gases were determined. Impurities including hydrogen, oxygen, nitrogen and carbon monoxide were determined using a Varian 3800 GC equipped with a pulse discharge helium ionisation detector (PDHID) using Unibeads and Molsieve 5A (60/80, 5' x 1/8" SS) columns. All hydrocarbon impurities were determined on a PLOT fused silica (Al_2O_3/KCl 50m x 0.53mm ID) column attached to a FID detector. Carbon dioxide impurities were determined on a Varian 3400 GC using a Hayesep N (80/100, 2m x 1/8" SS) column attached to a methanizer and FID detector.
Calibration of GC for CCQM samples was perfomed using a single point for each sample.

Annex B: Evaluation of uncertainty

GUM

The calibration procedure depended on the number of available standards – for some of the components we used 1 point calibration with 3 standards, for the others bracketing with 3 PSM. The sample and standard were measured one by one, repeated 6 or 10 times. This method eliminated the influence of temperature and atmospheric pressure.

CSIRO-NML

For each natural gas component we established two types of uncertainty:

- Gravimetric uncertainty
- Analytical uncertainty

The Gravimetric uncertainty contributions include:

- Balance uncertainty
- Cylinder buoyancy
- Cylinder expansion
- Tare mass uncertainty
- Tare mass buoyancy
- Standard mass buoyancy
- Impurity of gases

The analytical uncertainty contributions include:

- Uncertainty of sample measurement

The total standard uncertainty of measurement was determined using the mathematical model:

$$Cx = Cs * Rx / Rs$$

Where:

- Cx = concentration of sample
- Cs = concentration of standard
- Rx = average response of GC for sample
- Rs = average response of GC for standard