International Comparison CCQM K23b – Natural gas type II

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Field

Amount of substance

Subject

Comparison in the field of natural gas analysis

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Introduction

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 per unit of volume or mass 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. In most cases, the calorific value and other thermodynamical properties are calculated from composition data.

At the highest metrological level, natural gas standards are commonly prepared gravimetrically as PSMs (Primary Standard Mixtures). This international key comparison is a repeat of CCQM-K1e-g. The mixtures concerned contain nitrogen, carbon dioxide and the alkanes up to butane. The only difference with CCQM-K1e-g is the addition of *iso*-butane to the list. This part of the comparison concerns the type II natural gas. The results on the types I and III natural gas are reported elsewhere [1].

Participants

Table 1 lists the participants in this key comparison.

Table 1: List of participants

Acronym	Country	Institute
NMIA	AU	National Metrology Institute of Australia, Lindfield, Australia
INMETRO	BR	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, Xerém RJ, Brasil
NIM	CN	National Institute of Metrology, Beijing, PR China
BAM	DE	Bundesanstalt für Materialforschung und –prüfung, Berlin, Germany
CMI	CZ	Ceský metrologický institute, Brno, Czech Republic
CEM	ES	Centro Espanol de Metrologia, Madrid, Spain

Acronym	Country	Institute
BNM-LNE	FR	BNM-LNE, Centre Métrologie et Instrumentation, Paris, France
OMH	HU	National Office of Measures, Budapest, Hungary
KRISS	KR	Korea Research Institute of Standards and Science, Daejon, South-Korea
CENAM	MX	Centro Nacional de Metrologia, Queretaro, Mexico
NMIJ	JP	National Metrology Institute of Japan, Tsukuba, Japan
NMi VSL	NL	NMi Van Swinden Laboratorium B.V., Delft, the Netherlands
GUM	PO	Central Office of Measures, Warsaw, Poland
IPQ	PT	Instituto Português da Qualidade, Monte de Caparica, Portugal
VNIIM	RU	D.I. Mendeleyev Institute for Metrology, St. Petersburg, Russia
SMU	SK	Slovak Institute of Metrology, Bratislava, Slovak Republic
NPL	UK	National Physical Laboratory, Teddington, Middlesex, United Kingdom

Measurement standards

A suite of mixtures of type II has been prepared for this comparison. Table 2 shows the nominal composition of the mixture used (expressed as amount of substance fractions).

Table 2: Nominal composition of the mixtures

Component	Mixture II x (10^{-2} mol mol^{-1})
Nitrogen	7
Carbon dioxide	3
Ethane	9.4
Propane	3.4
n-Butane	1
iso-Butane	0.8
Methane	75.4

The mixtures have been prepared gravimetrically and subsequently verified.

The preparation of the mixtures has been carried out using the normal procedure for the preparation of gas mixtures [6]. The following gases were used: methane (5.5), ethane (5.0), n-butane (3.5) and iso-butane (3.5) from Scott Specialty Gases, Nitrogen (6.0) from Air Products, Carbon dioxide (5.2) from AGA, and propane (3.5) from Air Liquide. All gases were directly introduced in the final mixture. The final mixture had a pressure of approximately 7 MPa.

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, and ethane) and GC/FID (propane, iso-butane, and n-butane).

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 also 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 addressing which components have been included in the evaluation, and what is their quantitative impact on the uncertainty of the results reported.

Schedule

The schedule of this key comparison was as follows:

Until March 2005	Preparation of the gas mixtures
July 2005	Shipment of distribution cylinders to participating laboratories
August 2005	Start of comparison
January 15, 2006	Close of comparison
January 15, 2006	Cylinders and reports due to coordinating laboratory

LNE withdrew from this part of the key comparison. It indicated that the timetable was not acceptable.

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

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

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

$$u^2_{i,prep} = u^2_{i,grav} + u^2_{i,purity} + u^2_{i,stab} + u^2_{i,nr} . \tag{2}$$

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

$$\Delta x_{i,nr} = 0, \tag{3}$$

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

$$\Delta x_{i,stab} = 0, \tag{4}$$

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 theory 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

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity}, \tag{5}$$

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

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2 . \tag{6}$$

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]

$$\left| x_{i,prep} - x_{i,ver} \right| \le 2\sqrt{u_{i,prep}^2 + u_{i,ver}^2} . \tag{7}$$

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]. All mixtures prepared in this key comparison satisfy for all components the condition given in equation (7).

The reference value of mixture *i* in a key comparison[1] can be defined as

$$x_{i,ref} = \left\langle x_{i,ref} \right\rangle + \delta x_{i,ref}, \tag{8}$$

where

$$x_{i,ref} = x_{i,prep} + \Delta x_{i,ver} . \tag{9}$$

Since the amount of substance fraction from preparation is used as the basis, the expectation of the correction $<\Delta x_{i,ver}>$ 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

$$x_{i,ref} = \left\langle x_{i,prep} \right\rangle + \delta x_{i,prep} + \delta \Delta x_{i,ver} . \tag{10}$$

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

$$\Delta x_{i,ver} = 0, \tag{11}$$

that is, there is no correction from the verification. The verification experiments have demonstrated that within the uncertainty of these measurements, the gravimetric values of the key comparison mixtures agreed with older measurement standards.

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

$$u_{i,ref}^2 = u_{i,prep}^2 + u_{i,ver}^2 . \tag{12}$$

The values for $u_{\mathrm{i,ver}}$ are given in the tables containing the results of this key comparison.

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[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].

Measurement methods

The measurement methods used by the participants are described in annex A of this report. A summary of the calibration methods, dates of measurement and reporting, and the way in which metrological traceability is established is given in table 3.

Table 3: Summary of calibration methods and metrological traceability

Laboratory	Measurements	Calibration	Traceability
NMIA	10-09-2005	Bracketing	Own standards
IPQ	29-09-2005	ISO 6143	NPL + NMi VSL
NIM	06-12-2005	Single point	Own standards
NMi VSL	09-09-2005	OLS[2]	Own standards
CMI	21-09-2005	OLS	Own standards + NMi VSL
NMIJ	22-12-2005	ISO 6143	Own standards
CENAM	21-12-2005	ISO 6143	Own standards
CEM	20-10-2005	ISO 6143	NMi VSL
KRISS	27-09-2005	Bracketing	Own standards
VNIIM	05-12-2005	Bracketing	Own standards
OMH	03-10-2005	Matching	Own standard
BAM	21-09-2005	Bracketing	Own standards
INMETRO	17-10-2005	OLS	NMi VSL
NPL	07-09-2005	Bracketing	Own standards
SMU	13-12-2005	ISO 6143	Own standards
GUM	05-01-2006	ISO 6143	Own standards

Supported CMC claims

At the CCQM GAWG meeting in Sèvres in 2004, the following expert opinion concerning the type of CMC[3] claims was agreed. The results of this key comparison (CCQM-K23abc) can be used for supporting claims for the following components and ranges (see table 4).

Table 4: Components and ranges supported by CCQM-K23

Component	Ranges x (mmol mol^{-1})
Nitrogen	10 – 200
Carbon dioxide	1 – 50
Ethane	10 – 200
Propane	1 – 50
n-Butane	0.5 – 15
iso-Butane	0.5 – 15
Methane	700 – 980

These ranges apply only when the NMI has participated in this key comparison for all three mixtures. CMCs for unsaturated components up to C_4 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 to the measurement methods used in this key comparison.

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[2] OLS = ordinary least squares

[3] CMC = calibration and measurement capability

When the measurement capability is delivered as a gas mixture in a cylinder, the *dew point* of the mixture is relevant. The dew point is a function of the composition of the mixture, the pressure in the cylinder and the temperature. The composition of the mixture and the pressure of the final mixture shall be chosen such that at 0°C, all components of the gas mixture are still in the gas phase, that is, no condensation takes place. In practice, this requirement may for a given composition have implications for the maximum pressure of the final mixture.

When CMC claims outside the ranges specified above need be evaluated, for the components specified the ranges can of course extrapolate the ranges. It is important to emphasise that in particular when extrapolating to lower amount-of-substance fractions, the uncertainty at these levels can be greater than the uncertainties reported with the results in the key comparison. A critical examination of the uncertainty evaluation is therefore an essential part of the reviewing process. The NMI submitting the claim should -as appropriate- provide evidence (results from, e.g., validation studies) to support the extended ranges and the claimed uncertainties. The participation in the key comparison may however be a suitable basis for underpinning such CMC claims.

Degrees of equivalence

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

$$\Delta x_i = D_i = x_i - x_{\mathrm{KCRV}}, \tag{13}$$

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*. [4] Appreciating the special conditions in gas analysis, it can be expressed as

$$\Delta x_i = D_i = x_i - x_{i,ref}. \tag{14}$$

The standard uncertainty of D_i can be expressed as

$$u^2(\Delta x_i) = +u^2_{i,lab} + u^2_{i,prep} + u^2_{i,ver}, \tag{15}$$

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]

$$D_{ij} = D_i - D_j, \tag{16}$$

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

$$u^2(D_{ij}) = +u^2_{i,lab} + u^2_{i,prep} + u^2_{i,ver} + u^2_{j,lab} + u^2_{j,prep} + u^2_{j,ver}. \tag{17}$$

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 1-7, 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 labora-

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

tory results, the expanded uncertainty (stated at a confidence level of 95%) from the laboratory was divided by the reported coverage factor.

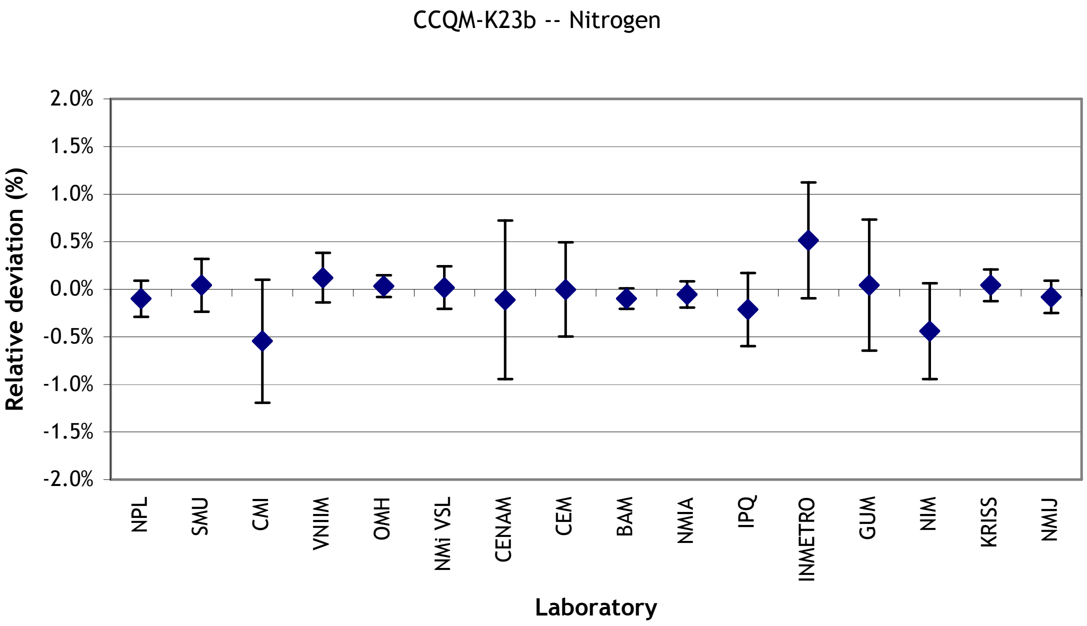

Figure 1: Degrees of equivalence for nitrogen (mixture II)

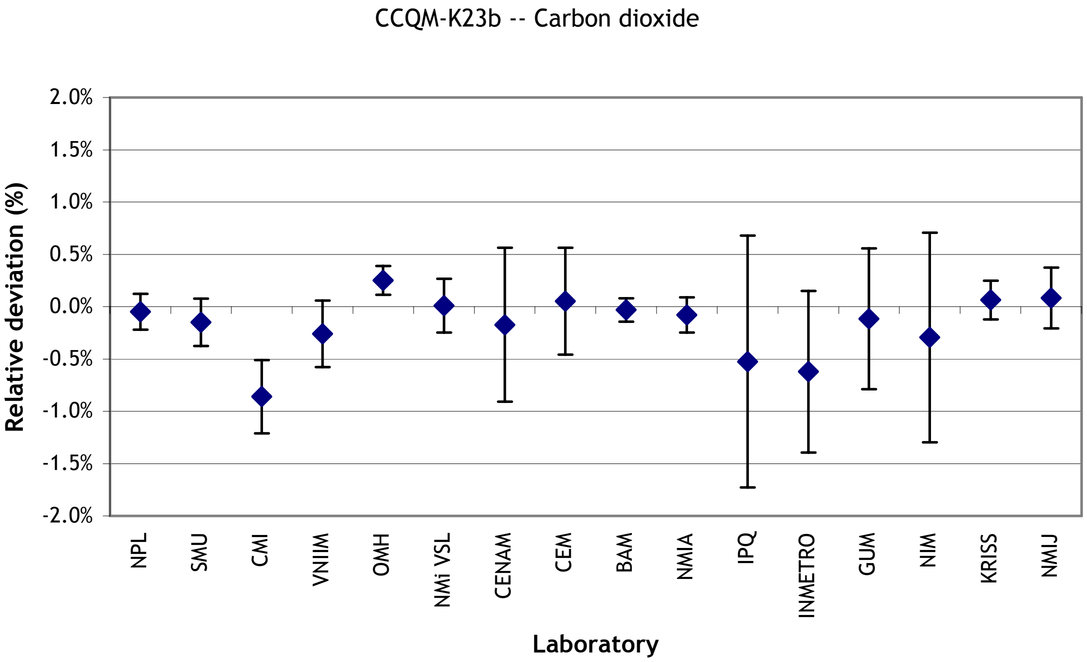

Figure 2: Degrees of equivalence for carbon dioxide (mixture II)

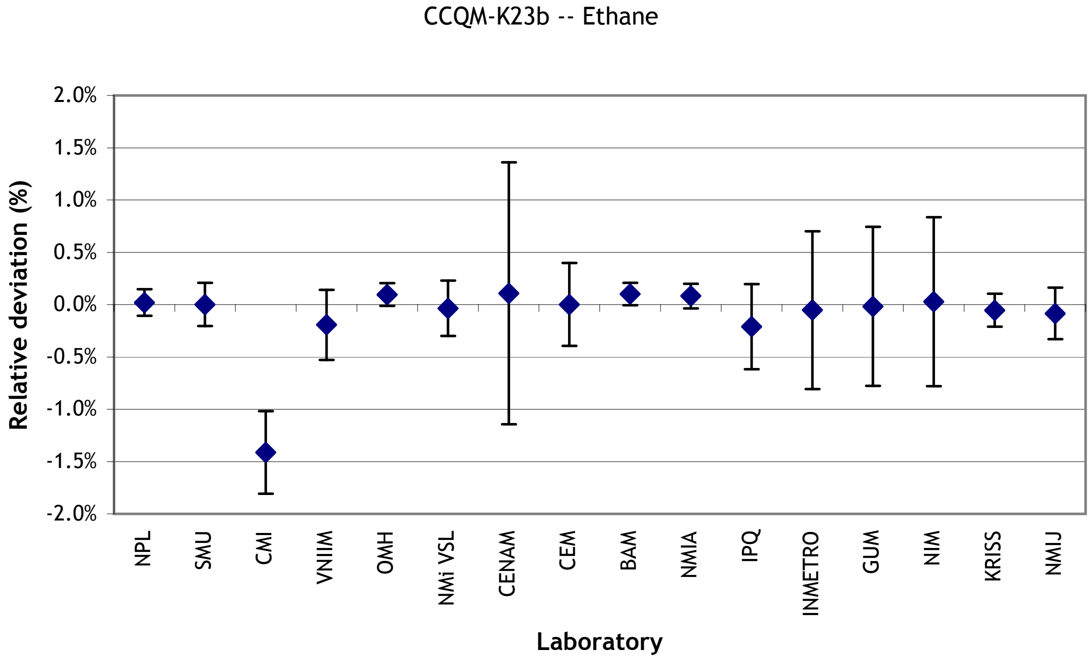

Figure 3: Degrees of equivalence for ethane (mixture II)

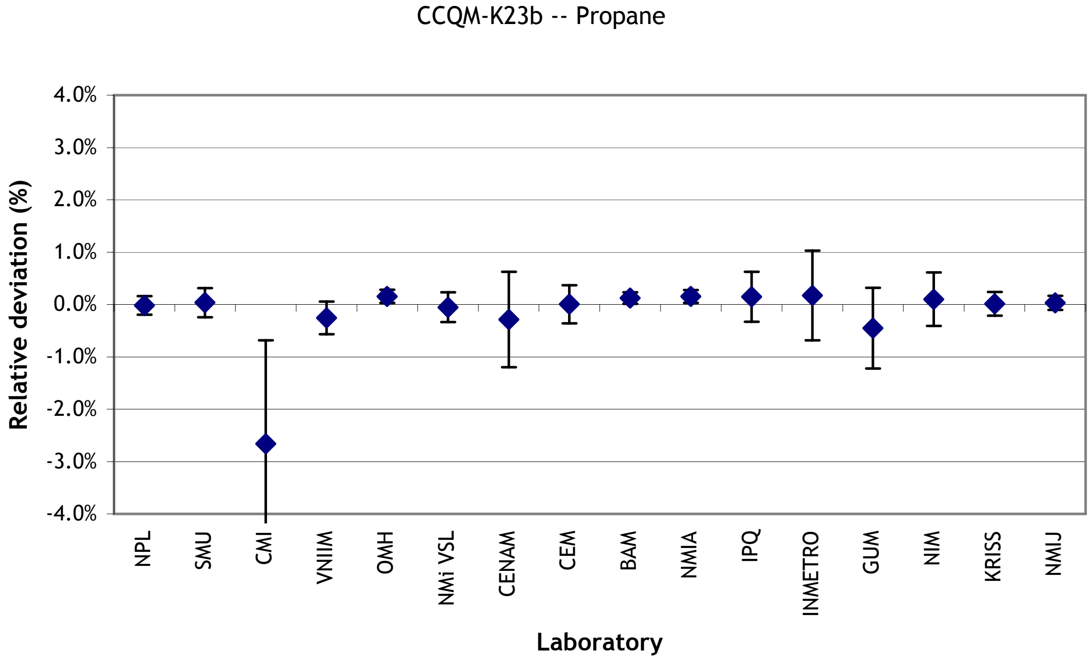

Figure 4: Degrees of equivalence for propane (mixture II)

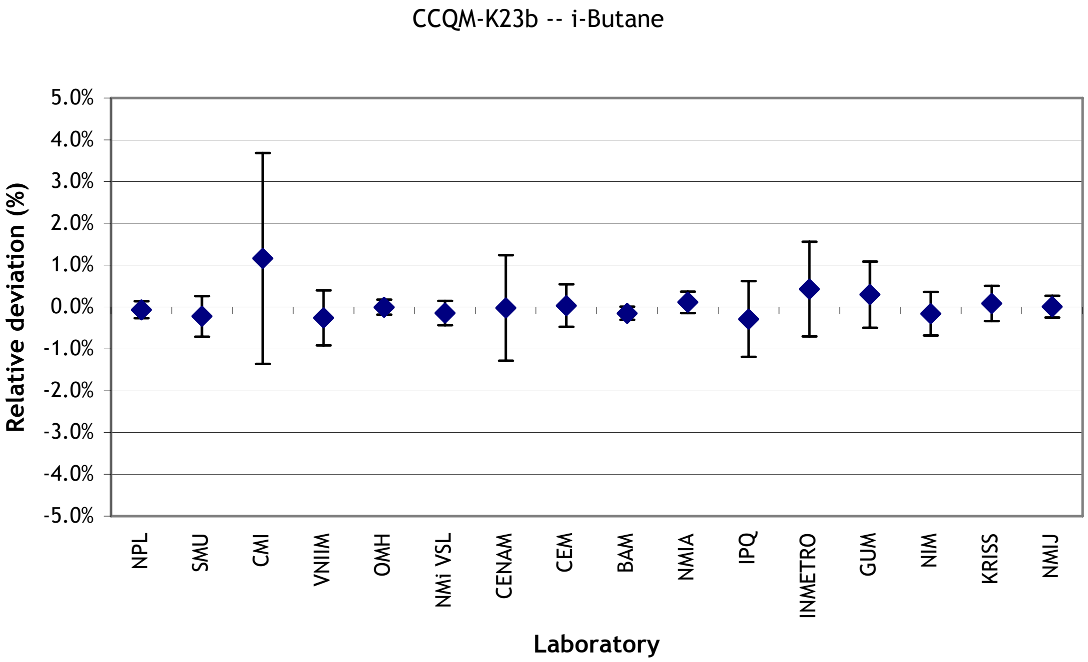

Figure 5: Degrees of equivalence for *iso*-butane (mixture II)

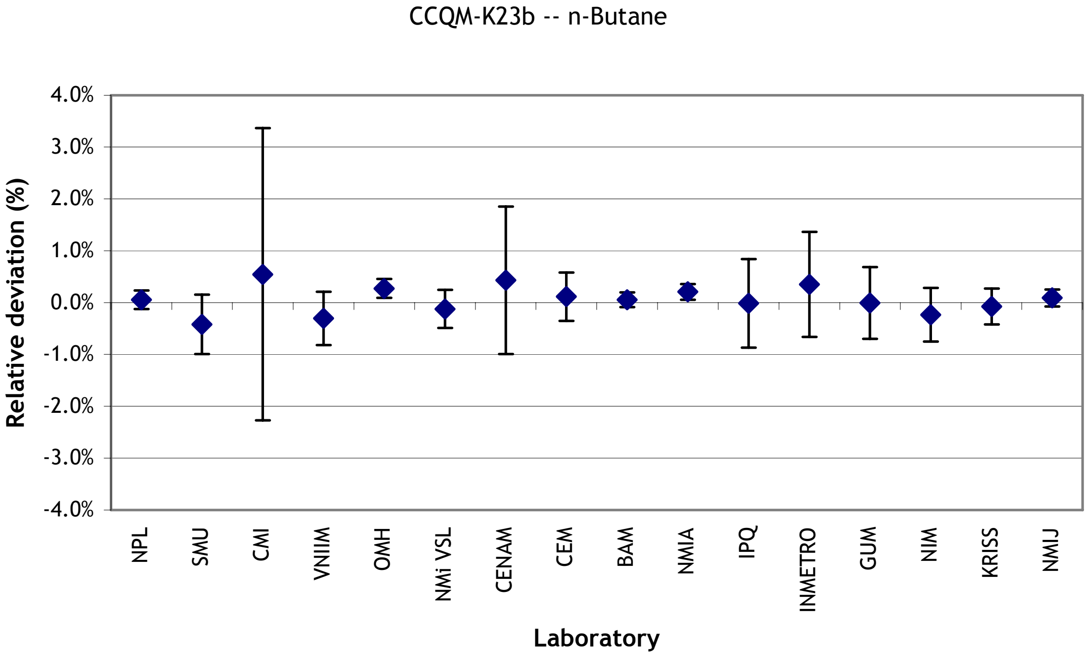

Figure 6: Degrees of equivalence for *n*-butane (mixture II)

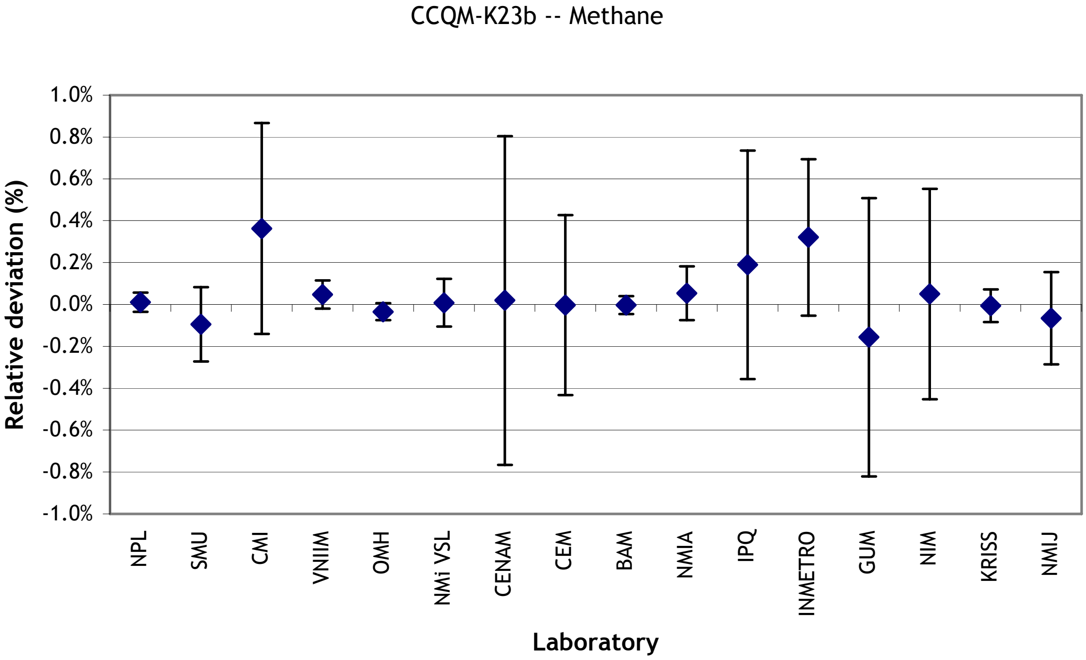

Figure 7: Degrees of equivalence for methane (mixture II)

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)
k	assigned coverage factor for degree of equivalence
$U(\Delta x)$	Expanded uncertainty of difference Δx, at 95% level of confidence[5] (10^{-2} mol/mol)

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[5] As defined in the MRA [4], a degree of equivalence is given by Δx and U(Δx).

Table 5: Results for nitrogen, mixture II

Laboratory	**Cylinder**	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL205170	7.00807	0.00095	0.00350	0.00363	7.0012	0.0112	2	-0.007	2	0.013
SMU	VSL200238	7.02641	0.00096	0.00350	0.00363	7.0294	0.018	2	0.003	2	0.019
CMI	VSL200229	7.04538	0.00095	0.00350	0.00363	7.007	0.045	2	-0.038	2	0.046
VNIIM	VSL302766	7.11231	0.00095	0.00350	0.00363	7.121	0.017	2	0.009	2	0.018
OMH	VSL202794	7.06610	0.00094	0.00350	0.00363	7.0685	0.0078	4.53	0.002	2	0.008
NMi VSL	VSL133436	7.03273	0.00096	0.00350	0.00363	7.034	0.014	2	0.001	2	0.016
CENAM	VSL302704	6.89662	0.00094	0.00350	0.00363	6.889	0.057	2	-0.008	2	0.057
CEM	VSL200231	6.99485	0.00094	0.00350	0.00363	6.9947	0.034	2	0.000	2	0.035
BAM	VSL200239	7.02572	0.00095	0.00350	0.00363	7.01894	0.00211	2	-0.007	2	0.008
NMIA	VSL200246	7.01675	0.00094	0.00350	0.00363	7.013	0.007	2.18	-0.004	2	0.010
IPQ	VSL200241	7.01193	0.00095	0.00350	0.00363	6.997	0.026	2	-0.015	2	0.027
INMETRO	VSL200236	7.00103	0.00094	0.00350	0.00363	7.037	0.042	2	0.036	2	0.043
GUM	VSL200237	7.03594	0.00095	0.00350	0.00363	7.039	0.048	2	0.003	2	0.049
NIM	VSL305182	6.99373	0.00097	0.00350	0.00363	6.963	0.0345	2	-0.031	2	0.035
KRISS	VSL200230	7.02403	0.00095	0.00350	0.00363	7.027	0.009	2	0.003	2	0.012
NMIJ	VSL200248	7.02637	0.00095	0.00350	0.00363	7.0208	0.0094	2	-0.006	2	0.012

Table 6: Results for carbon dioxide, mixture II

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL205170	2.99416	0.00059	0.00150	0.00161	2.9927	0.0040	2	-0.0015	2	0.0051
SMU	VSL200238	3.01141	0.00060	0.00151	0.00162	3.0069	0.0060	2	-0.0045	2	0.0068
CMI	VSL200229	3.00282	0.00059	0.00150	0.00161	2.9770	0.0100	2	-0.0258	2	0.0105
VNIIM	VSL302766	3.01583	0.00059	0.00151	0.00162	3.0080	0.0090	2	-0.0078	2	0.0096
OMH	VSL202794	3.02991	0.00059	0.00151	0.00162	3.0375	0.0060	4.53	0.0076	2	0.0042
NMi VSL	VSL133436	2.99375	0.00060	0.00150	0.00161	2.9940	0.0070	2	0.0002	2	0.0077
CENAM	VSL302704	3.01822	0.00059	0.00151	0.00162	3.0130	0.0220	2	-0.0052	2	0.0222
CEM	VSL200231	3.00721	0.00058	0.00150	0.00161	3.0088	0.0150	2	0.0016	2	0.0153
BAM	VSL200239	3.00688	0.00059	0.00150	0.00161	3.0060	0.0009	2	-0.0009	2	0.0034
NMIA	VSL200246	3.01568	0.00059	0.00151	0.00162	3.0133	0.0043	2.18	-0.0024	2	0.0051
IPQ	VSL200241	3.00379	0.00059	0.00150	0.00161	2.9880	0.0360	2	-0.0158	2	0.0361
INMETRO	VSL200236	3.00469	0.00059	0.00150	0.00161	2.9860	0.0230	2	-0.0187	2	0.0232
GUM	VSL200237	3.00749	0.00059	0.00150	0.00162	3.0040	0.0200	2	-0.0035	2	0.0203
NIM	VSL305182	3.01088	0.00060	0.00151	0.00162	3.0020	0.0300	2	-0.0089	2	0.0302
KRISS	VSL200230	3.00711	0.00059	0.00150	0.00161	3.0090	0.0045	2	0.0019	2	0.0056
NMIJ	VSL200248	3.01222	0.00059	0.00151	0.00162	3.0147	0.0081	2	0.0025	2	0.0088

Table 7: Results for ethane, mixture II

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL205170	9.41761	0.00102	0.00471	0.00482	9.4194	0.0072	2	0.0018	2	0.0120
SMU	VSL200238	9.41386	0.00102	0.00471	0.00482	9.4140	0.0170	2	0.0001	2	0.0195
CMI	VSL200229	9.42315	0.00101	0.00471	0.00482	9.2900	0.0360	2	-0.1332	2	0.0373
VNIIM	VSL302766	9.40419	0.00101	0.00470	0.00481	9.3860	0.0300	2	-0.0182	2	0.0315
OMH	VSL202794	9.37970	0.00101	0.00469	0.00480	9.3887	0.0038	2.11	0.0090	2	0.0102
NMi VSL	VSL133436	9.41842	0.00103	0.00471	0.00482	9.4150	0.0230	2	-0.0034	2	0.0249
CENAM	VSL302704	9.60958	0.00102	0.00480	0.00491	9.6200	0.1200	2	0.0104	2	0.1204
CEM	VSL200231	9.39533	0.00101	0.00470	0.00480	9.3954	0.0360	2	0.0001	2	0.0373
BAM	VSL200239	9.40663	0.00101	0.00470	0.00481	9.4162	0.0028	2	0.0096	2	0.0100
NMIA	VSL200246	9.40837	0.00101	0.00470	0.00481	9.4160	0.0060	2.18	0.0076	2	0.0111
IPQ	VSL200241	9.41178	0.00102	0.00471	0.00481	9.3920	0.0370	2	-0.0198	2	0.0382
INMETRO	VSL200236	9.37697	0.00101	0.00469	0.00480	9.3720	0.0700	2	-0.0050	2	0.0707
GUM	VSL200237	9.29267	0.00102	0.00465	0.00476	9.2910	0.0700	2	-0.0017	2	0.0706
NIM	VSL305182	9.40450	0.00103	0.00470	0.00481	9.4070	0.0753	2	0.0025	2	0.0759
KRISS	VSL200230	9.41509	0.00101	0.00471	0.00482	9.4100	0.0113	2	-0.0051	2	0.0148
NMIJ	VSL200248	9.43195	0.00102	0.00472	0.00482	9.4240	0.0210	2	-0.0080	2	0.0231

Table 8: Results for propane, mixture II

Laboratory	**Cylinder**	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL205170	3.40658	0.00060	0.00170	0.00181	3.4059	0.0048	2	-0.0007	2	0.0060
SMU	VSL200238	3.40056	0.00061	0.00170	0.00181	3.4017	0.0087	2	0.0011	2	0.0094
CMI	VSL200229	3.39542	0.00060	0.00170	0.00180	3.3050	0.0670	2	-0.0904	2	0.0671
VNIIM	VSL302766	3.39774	0.00060	0.00170	0.00180	3.3890	0.0100	2	-0.0087	2	0.0106
OMH	VSL202794	3.40861	0.00060	0.00170	0.00181	3.4139	0.0031	2.87	0.0053	2	0.0042
NMi VSL	VSL133436	3.39578	0.00061	0.00170	0.00180	3.3940	0.0090	2	-0.0018	2	0.0097
CENAM	VSL302704	3.42494	0.00060	0.00171	0.00181	3.4150	0.0310	2	-0.0099	2	0.0312
CEM	VSL200231	3.46047	0.00060	0.00173	0.00183	3.4606	0.0120	2	0.0001	2	0.0125
BAM	VSL200239	3.39859	0.00060	0.00170	0.00180	3.4027	0.0010	2	0.0041	2	0.0037
NMIA	VSL200246	3.40258	0.00060	0.00170	0.00180	3.4078	0.0023	2.18	0.0052	2	0.0042
IPQ	VSL200241	3.43192	0.00060	0.00172	0.00182	3.4370	0.0160	2	0.0051	2	0.0164
INMETRO	VSL200236	3.41119	0.00060	0.00171	0.00181	3.4170	0.0290	2	0.0058	2	0.0292
GUM	VSL200237	3.41239	0.00061	0.00171	0.00181	3.3970	0.0260	2	-0.0154	2	0.0263
NIM	VSL305182	3.40859	0.00061	0.00170	0.00181	3.4120	0.0171	2	0.0034	2	0.0175
KRISS	VSL200230	3.39951	0.00060	0.00170	0.00180	3.4000	0.0068	2	0.0005	2	0.0077
NMIJ	VSL200248	3.40150	0.00060	0.00170	0.00180	3.4025	0.0027	2	0.0010	2	0.0045

Table 9: Results for *iso*-butane, mixture II

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL205170	0.799604	0.000436	0.000400	0.000591	0.79907	0.00109	2	-0.0005	2	0.0016
SMU	VSL200238	0.796694	0.000439	0.000398	0.000592	0.79490	0.00370	2	-0.0018	2	0.0039
CMI	VSL200229	0.793793	0.000434	0.000397	0.000588	0.80300	0.02000	2	0.0092	2	0.0200
VNIIM	VSL302766	0.781058	0.000435	0.000391	0.000585	0.77900	0.00500	2	-0.0021	2	0.0051
OMH	VSL202794	0.801447	0.000431	0.000401	0.000589	0.80140	0.00100	2.37	0.0000	2	0.0014
NMi VSL	VSL133436	0.797880	0.000441	0.000399	0.000595	0.79670	0.00200	2	-0.0012	2	0.0023
CENAM	VSL302704	0.796186	0.000432	0.000398	0.000587	0.79600	0.01000	2	-0.0002	2	0.0101
CEM	VSL200231	0.784835	0.000430	0.000392	0.000582	0.78510	0.00380	2	0.0003	2	0.0040
BAM	VSL200239	0.797899	0.000434	0.000399	0.000589	0.79670	0.00040	2	-0.0012	2	0.0012
NMIA	VSL200246	0.800407	0.000432	0.000400	0.000589	0.80130	0.00180	2.18	0.0009	2	0.0020
IPQ	VSL200241	0.797190	0.000436	0.000399	0.000590	0.79490	0.00710	2	-0.0023	2	0.0072
INMETRO	VSL200236	0.799879	0.000433	0.000400	0.000589	0.80330	0.00900	2	0.0034	2	0.0091
GUM	VSL200237	0.798744	0.000438	0.000399	0.000593	0.80110	0.00620	2	0.0024	2	0.0063
NIM	VSL305182	0.788257	0.000444	0.000394	0.000594	0.78700	0.00390	2	-0.0013	2	0.0041
KRISS	VSL200230	0.801922	0.000434	0.000401	0.000591	0.80260	0.00313	2	0.0007	2	0.0033
NMIJ	VSL200248	0.798739	0.000436	0.000399	0.000591	0.79880	0.00168	2	0.0001	2	0.0021

Table 10: Results for *n*-butane, mixture II

Laboratory	**Cylinder**	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL205170	0.992473	0.000436	0.000496	0.000661	0.99302	0.00119	2	0.0005	2	0.0018
SMU	VSL200238	0.999205	0.000440	0.000500	0.000665	0.99500	0.00560	2	-0.0042	2	0.0058
CMI	VSL200229	0.995562	0.000435	0.000498	0.000661	1.00100	0.02800	2	0.0054	2	0.0280
VNIIM	VSL302766	1.004048	0.000436	0.000502	0.000665	1.00100	0.00500	2	-0.0030	2	0.0052
OMH	VSL202794	0.984699	0.000432	0.000492	0.000655	0.98740	0.00180	2.87	0.0027	2	0.0018
NMi VSL	VSL133436	0.997206	0.000442	0.000499	0.000666	0.99600	0.00340	2	-0.0012	2	0.0037
CENAM	VSL302704	0.988737	0.000433	0.000494	0.000657	0.99300	0.01400	2	0.0043	2	0.0141
CEM	VSL200231	0.980479	0.000431	0.000490	0.000653	0.98160	0.00440	2	0.0011	2	0.0046
BAM	VSL200239	1.002064	0.000435	0.000501	0.000663	1.00261	0.00050	2	0.0005	2	0.0014
NMIA	VSL200246	0.996129	0.000433	0.000498	0.000660	0.99820	0.00080	2.18	0.0021	2	0.0015
IPQ	VSL200241	0.995839	0.000437	0.000498	0.000662	0.99570	0.00840	2	-0.0001	2	0.0085
INMETRO	VSL200236	0.997503	0.000434	0.000499	0.000661	1.00100	0.01000	2	0.0035	2	0.0101
GUM	VSL200237	1.004261	0.000439	0.000502	0.000667	1.00420	0.00680	2	-0.0001	2	0.0069
NIM	VSL305182	0.998365	0.000445	0.000499	0.000669	0.99600	0.00500	2	-0.0024	2	0.0052
KRISS	VSL200230	0.997362	0.000435	0.000499	0.000662	0.99660	0.00319	2	-0.0008	2	0.0035
NMIJ	VSL200248	0.997976	0.000437	0.000499	0.000664	0.99888	0.00096	2	0.0009	2	0.0016

Table 11: Results for methane, mixture II

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL205170	75.3811	0.0020	0.0151	0.0152	75.3890	0.0166	2	0.008	2	0.035
SMU	VSL200238	75.3514	0.0020	0.0151	0.0152	75.2800	0.1300	2	-0.071	2	0.134
CMI	VSL200229	75.3435	0.0019	0.0151	0.0152	75.6170	0.3780	2	0.274	2	0.379
VNIIM	VSL302766	75.2844	0.0020	0.0151	0.0152	75.3200	0.0400	2	0.036	2	0.050
OMH	VSL202794	75.3291	0.0019	0.0151	0.0152	75.3027	0.0040	3.31	-0.026	2	0.030
NMi VSL	VSL133436	75.3638	0.0020	0.0151	0.0152	75.3700	0.0800	2	0.006	2	0.086
CENAM	VSL302704	75.2653	0.0019	0.0151	0.0152	75.2800	0.5900	2	0.015	2	0.591
CEM	VSL200231	75.3764	0.0019	0.0151	0.0152	75.3740	0.2140	2	-0.002	3	0.324
BAM	VSL200239	75.3618	0.0019	0.0151	0.0152	75.3595	0.0113	2	-0.002	2	0.032
NMIA	VSL200246	75.3597	0.0019	0.0151	0.0152	75.4000	0.1000	2.18	0.040	2	0.097
IPQ	VSL200241	75.3471	0.0020	0.0151	0.0152	75.4900	0.4100	2	0.143	2	0.411
INMETRO	VSL200236	75.4083	0.0019	0.0151	0.0152	75.6500	0.2800	2	0.242	2	0.282
GUM	VSL200237	75.4481	0.0020	0.0151	0.0152	75.3300	0.5000	2	-0.118	2	0.501
NIM	VSL305182	75.3953	0.0020	0.0151	0.0152	75.4330	0.3772	2	0.038	2	0.378
KRISS	VSL200230	75.3546	0.0019	0.0151	0.0152	75.3500	0.0497	2	-0.005	2	0.058
NMIJ	VSL200248	75.3308	0.0020	0.0151	0.0152	75.2814	0.1630	2	-0.049	2	0.166

Discussion of results

The reported results for nitrogen (figure 1) agree with the KCRV within 0.5% relative. In all cases, the departure from the KCRV is smaller than the associated expanded uncertainty. For carbon dioxide (figure 2), most results agree with the KCRV within 0.5% relative. The only NMIs with a larger departure are IPQ, INMETRO, and CMI, and in case of CMI the departure from the KCRV is greater than the associated expanded uncertainty. The departure from the KCRV for OHM is also greater than the associated expanded uncertainty.

For all but one, the reported results for ethane (figure 3) agree with the KCRV within 0.5% relative. The only exception is CMI, and the deviation from the KCRV is also greater than the associated expanded uncertainty. The same applies to propane (figure 4), *i*–butane and *n*–butane (figures 5 and 6 respectively). In the case of propane and *n*–butane, the deviation from the KCRV for OMH, BAM and NMIA is greater than the associated expanded uncertainty. In the case of *n*–butane the deviation of the result of NMIA and OMH from the KCRV also exceeds the associated expanded uncertainty.

The reported results for methane finally (figure 7) agree with the KCRV within 0.4% relative, and are all within the stated uncertainties consistent with the KCRV. For most of the NMIs, this agreement is much better, 0.1% relative.

Conclusions

The agreement of the results in this key comparison is very good. For all parameters, with a few exceptions, the results agree within 0.5% (or better) with the key comparison reference value. For methane, the results are generally within 0.1% (or better) of the KCRV.

Most of the NMIs that did not participate in CCQM-K1e-g do very well in this key comparison. In some cases, the uncertainties claimed are quite large in comparison with the NMIs for which this comparison is a true ‘repeat’, but the observed differences with the KCRV usually reflect that these claims are realistic.

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CCQM-K23b

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Annex A: Measurement Reports

Measurement Report from BAM

Reference Method

For the determination of:
Nitrogen (N_2), Carbon Dioxide (CO_2), Ethane (C_2H_6), Propane (C_3H_8),
n-Butane (n-C_4H_{10}), 2-Methyl-Propane (i-C_4H_{10}), and Methane (CH_4).

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 N_2, CO_2, C_2H_6, C_3H_8, n-C_4H_{10}, I-C_4H_{10} and CH_4.
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 C_3H_8, n-C_4H_{10} and I-C_4H_{10}.
Carrier Gas: Helium
Columns: Capillary column, 50 m x 0,32 µm LP-SIL-8-CB
Oven Temperature: 50 °C to 150 °C
Detector: FID
Data Collection: Total Chrom Workstation

Calibration Standards:

All standards were prepared individually according to ISO 6142
”Gas analysis - Preparation of calibration gases - Gravimetric Method”.

Depending on the concentration of the components, standards were prepared individually from pure gases or from pre-mixtures which were individually prepared from pure gases.

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.

Composition of calibrants may be reported in the following format:

BAM 6028-050808

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*)) (k=2) **%$_{rel}$**
Nitrogen	6,6583	0,05
Carbon dioxide	2,8466	0,05
Ethane	8,8876	0,09

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*)) (k=2) **%$_{rel}$**
Propane	3,2294	0,10
iso-Butane	0,80434	0,12
n-Butane	0,98565	0,12
(any relevant impurities)		
Methane	Balance (76,58806)	0,025

C49331-050507

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*)) (k=2) **%$_{rel}$**
Nitrogen	7,5703	0,04
Carbon dioxide	3,2365	0,05
Ethane	9,3690	0,09
Propane	3,4001	0,10
iso-Butane	0,81847	0,12
n-Butane	1,00434	0,12
(any relevant impurities)		
Methane	Balance (74,60126)	0,025

C49360-050608

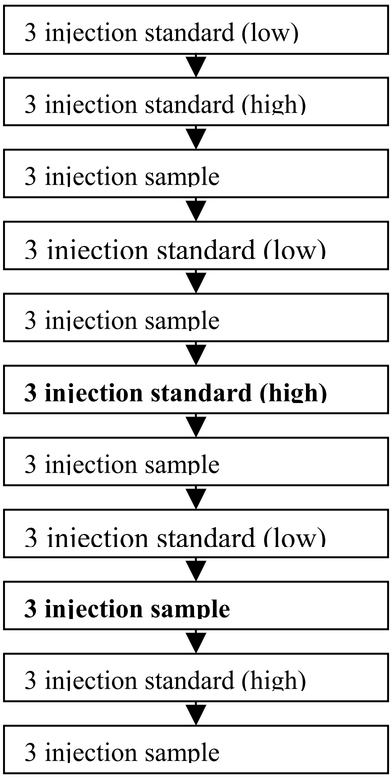
Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*)) (k=2) **%$_{rel}$**
Nitrogen	7,4032	0,04
Carbon dioxide	3,1650	0,04
Ethane	9,8955	0,08
Propane	3,5932	0,08
iso-Butane	0,79930	0,12
n-Butane	1,02413	0,12
(any relevant impurities)		
Methane	Balance (74,11979)	0,025

Instrument Calibration:

Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.)[6]:

For the instrument calibration the bracketing technique was used. The fraction of the current used standards deviated no more than +10%rel. and -10%rel. respectively from those of the sample.

Measurement sequence



Sample handling:

After heating (50 to 55 °C) the cylinder for 8 hours, the cylinder were rolled about 16 hours before analysis was started.

Each cylinder was equipped with a pressure regulator that was purged three times by sequential evacuation and pressurisation with the gas mixture used.

Continous flow (2 – 3ml/min) through the sample loop.

Evaluation of measurement uncertainty

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

- Uncertainty of the balances (Voland / Sartorius) $U_{(bal.V)}$ / $U_{(bal.S)}$
- Uncertainty of the impurities of the pure gases $U_{(imp.)}$
- Uncertainty of the main component of the pure gases $U_{(pure\ gas)}$

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[6] Please state in particular the calibration model, its coefficients, and the uncertainty data (if necessary, as covariance matrix)

- 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 four uncertainty sources:

- Uncertainty of the grav. prepared calibration gas $U_{\text{cal gas}}$
- Standard deviation (GC-Sample) $U_{\text{GC(sample)}}$
- Standard deviation (GC-Calibration) $U_{\text{GC(analysis)}}$

Residual-uncertainty of non-recovery errors U_{residual}

Measurement Report from CEM

Reference Method:

GC Agilent 6890 N,
TCD detector, 150 ºC,
Columns: porapack, molsieve
Carrier Gas: He

Calibration Standards:

The Standards were prepared by NMi VSL according to ISO 6142, analysed and verified according to ISO 6143.

Component	Assigned value(x)	Standard uncertainty ($u(x)$)
Nitrogen	7,506 x 10^{-2}	0,0125 x 10^{-2}
Carbon dioxide	3,158 x 10^{-2}	0,0045 x 10^{-2}
Ethane	9,435 x 10^{-2}	0,014 x 10^{-2}
Propane	3,524 x 10^{-2}	0,006 x 10^{-2}
iso-Butane	1,113 x 10^{-2}	0,0025 x 10^{-2}
n-Butane	1,099 x 10^{-2}	0,0025 x 10^{-2}
Methane	74,16 x 10^{-2}	0,04 x 10^{-2}
(any relevant impurities)		

Component	Assigned value(x)	Standard uncertainty ($u(x)$)
Nitrogen	5,506 x 10^{-2}	0,008 x 10^{-2}
Carbon dioxide	2,009 x 10^{-2}	0,003 x 10^{-2}
Ethane	6,072 x 10^{-2}	0,009 x 10^{-2}
Propane	2,188 x 10^{-2}	0,004 x 10^{-2}
iso-Butane	0,6034 x 10^{-2}	0,0014 x 10^{-2}
n-Butane	0,5932 x 10^{-2}	0,0014 x 10^{-2}
Methane	83,03 x 10^{-2}	0,045 x 10^{-2}
(any relevant impurities)		

Component	Assigned value(x)	Standard uncertainty ($u(x)$)
Nitrogen	3,495 x 10^{-2}	0,006 x 10^{-2}
Carbon dioxide	0,8004 x 10^{-2}	0,00175 x 10^{-2}
Ethane	2,818 x 10^{-2}	0,004 x 10^{-2}
Propane	0,7989 x 10^{-2}	0,0014 x 10^{-2}
iso-Butane	0,1513 x 10^{-2}	0,00035 x 10^{-2}
n-Butane	0,1486 x 10^{-2}	0,00035 x 10^{-2}
Methane	91,79 x 10^{-2}	0,045 x 10^{-2}
(any relevant impurities)		

Instrument Calibration:

Linear regression with 3 standards (calibration curve).

The measurement sequence were: standard/sample/standard/standard

7 times each cylinder

The temperature was controlled and 20,5 ºC ± 0,5 ºC. The injection was at ambient pressure. We reject always the first measurement of each cylinder for each component. The integration parameters are different for each component.

Sample handling:

How were the cylinders treated after arrival (e.g. stabilized) and how were samples transferred to the instrument? (automatic, high pressure, mass-flow controller, dilution etc).:

We left for a few days to condition the cylinders to the laboratory temperature.

We have homogenised the cylinders before each analysis rolling them.

We use an automatic sampler to transfer the mixtures to the GC.

The gas outlet was 2 bar

Evaluation of measurement uncertainty

Please describe briefly how the uncertainty of measurement associated with the final result has been evaluated. Please address only the main components of uncertainty addressed in the uncertainty of the calibrants, sample handling, calibration of the equipment, and the measurement. If deemed useful, raw measurement data can be given as well in this section.

The uncertainty evaluation was performed using B_LEAST program.

We use the linear fit regression

The uncertainty sources were:

- ☐ Standard uncertainty
- ☐ Instrument deviation
- ☐ Uncertainty fit regression

After obtaining the results the concentrations were standarized.

Measurement Report from CENAM

Reference Method

Natural Gas Analyzer of Separation System (6890 Gas Chromatograph; with TCD, FID and set of switching valves), including data collection and processor. Regulator of low pressure in the outlet of cylinder, with SS tubing of 1/16”. Col. 1 Packed column, Wasson Model, Molecular Sieve. Col.2 Capillary Column; Wasson Model, Nominal length: 60 m, Nominal diameter: 0,32 mm Nominal film thickness: 3.0 µm.
Oven Program: 40ºC; 4 min; 5 ºC/min140 ºC.
He flow: 26.9 mL/min and 1.0 mL/min
Reference He flow: 30 mL/min
Make up: Helium
FID temperature: 250 ºC
TCD temperature: 150 ºC

The concentration was calculated by interpolation of a calibration curve using three concentration levels of CENAM primary gas mixtures. The sample and standards were analyzed at least five times each by triplicate.

Calibration Standards

The calibration standards for the measurements were primary standards (primary standard mixtures, PSMs). The method used for the preparation of PSMs was the gravimetric method following the guidelines of the ISO/DIS 6142. The procedure for weighing was a Borda weighing scheme (RTRTRTR). The parent gases were in all cases at least 3.0 of purity and 5.0 for balance. Their uncertainties were calculated by type B evaluation or/and type A evaluation.

The instrument for weighing was a Mettler balance model PR10003 (10 kg capacity and 1 mg resolution) and sets of weights class E2 (serial number 520779750101, from 1 to 5 kg – 4 pieces) and E2 (serial number 41003979, from 1 mg to 1 kg – 25 pieces) according to the R 111 of OIML, all of them traceable to SI by CENAM´s Standards.

The value concentration and associated uncertainty of the primary standard mixtures used to quantify the sample are the following:

Mixture II Standards

Cylinder Number	Component	Assigned Value (cmol/mol)	Standard uncertainty (cmol/mol)
FF31087	Nitrogen	6,3225	0,0023
	Carbon dioxide	2,6988	0,0014
	Ethane	10,31472	0,00053
	Propane	3,73472	0,00093
	Iso-Butane	0,72051	0,00041
	n-Butane	1,1003	0,0018
	Methane	75,1077	0,0083
CAL-010686	Nitrogen	6,9817	0,0021
	Carbon dioxide	2,9989	0,0014

	Ethane	9,46798	0,00050
	Propane	3,19714	0,00081
	Iso-Butane	0,80032	0,00035
	n-Butane	0,9996	0,0014
	Methane	75,5536	0,0074
FF31062	Nitrogen	7,7027	0,0021
	Carbon dioxide	3,3394	0,0013
	Ethane	8,42130	0,00045
	Propane	3,28361	0,00083
	Iso-Butane	0,88134	0,00035
	n-Butane	0,8976	0,0013
	Methane	75,4733	0,0072

Instrument Calibration:

The calibration procedure was according to ISO 6143 using B_Least program software for multipoint Calibration. It was used 3 concentration levels in the following sequence: Std$_2$SmStd$_1$SmStd$_3$…

Sample Handling:

Sample and standards were rolled and left to environmental temperature 24h before analysis. Between cylinder and GC was used a configuration system made of SS lines of 1/16 inch OD with a valve and one low pressure regulator to avoid contamination of air in tubing walls and interference between sample and standards.

Uncertainty:

The main sources of uncertainty considered to estimate the combined standard uncertainty are derived from the:

Model used for evaluating measurement uncertainty:

$$C = \mu + \delta_T + \delta_s + \delta_m$$

The combined uncertainty has three contributions:

a) Reproducibility and Repeatability.

The combined effect (δ_T) of the reproducibility and repeatability was evaluated by the statistical method of analysis of variance.

b) Mathematical model effect (δ_m).

This component corresponds to the estimated uncertainty which come from the B_Least program software for multipoint Calibration.

c) Performance instrument (δ_s)

Variability observed using a Primary Standard Mixture as a sample control.

Coverage factor: k=2

Expanded uncertainty: It was obtained by the product of the combined standard uncertainty and a factor of 2 and it was calculated according to the “Guide to the Expression of Uncertainty in Measurement, BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (1995)”

Measurement Report from CMI

Reference Method:

GC/TCD,
Microchromatograph HP P200,
System of sample automatically injection - input pressure of gas: 1 bar

Calibration Standards:

Primary reference material – NMi, NL

Certified reference materials – Linde Praha, CZ, prepared by ISO 6142, since May 2005 – own CMI preparation:

There were prepared two CMI gas mixtures for calibration:

1st:

Component	Assigned value(x) . 10^{-2} mol/mol	Standard uncertainty (u(x)) . 10^{-2} mol/mol
Nitrogen	7,177	0,013
Carbon dioxide	2,990	0,0014
Ethane	9,407	0,005
Propane	3,335	0,0018
Methane	77,09	0,12

2nd:

iso-Butane	0,793	0,0024
n-Butane	1,008	0,0034
Methane	98,20	0,11

Top level of calibrants – NMi gas mixture:

Component	Assigned value(x) . 10^{-2} mol/mol	Standard uncertainty (u(x)) . 10^{-2} mol/mol
Nitrogen	3,033	0,006
Carbon dioxide	0,999	0,002
Ethane	0,999	0,002
Propane	0,5006	0,0013
iso-Butane	0,2016	0,0008
n-Butane	0,2988	0,0008
(any relevant impurities)		
Methane	93,97	0,125

Instrument Calibration:

Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.)[7]:

---

[7] Please state in particular the calibration model, its coefficients, and the uncertainty data (if necessary, as covariance matrix)

Temperature of column, gas flow and pressure are stabilised and controlled by GC

Calibration is based on a measurement of standards, after stabilisation of parameters is measured standard: six times – values of peak areas of components should be very closely.

For measured area (average) is saved certified value of concentration.

The calibration was provide as two-point calibration (NMi and CMI CRMs given above) with following check of area peaks by another standard gas mixture with close concentration of component

Used model is linear regression

The range of standards are: (mol %)

methane	80	99,9
ethane	0,4	10
Propane	0,1	3,5
n-butane	0,01	1
i-butane	0,01	1
CO2	0,05	3
Nitrogen	0,1	20

Sample handling:
Automatic injection

Evaluation of measurement uncertainty
Considered sources of uncertainty budget are: standard combine uncertainty:

- uncertainty of repeatability (analytical measurement) - standard deviation
- uncertainty of gravimetrically prepared standard (PRM, CRM)
- uncertainty of calibration (as relative standard deviation)

combination: $u_c(i) = \sqrt{u^2{}_{s,PRM}(i) + u^2_{odch.}(i) + u^2_{s,opak.}(i)}$

Measurement Report from GUM

Reference Method:

Varian Star 3600 gas chromatograph with two 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

Calibration Standards:

GUM standards were prepared by gravimetric method according to ISO 6142. All the standards were prepared from separate pre–mixtures. The cylinders were evacuated on turbo molecular pump, filled up and weighted on the verification balance (balance with damping and projection device for reflection range). The standards were prepared in steel and aluminium (with coated layers) cylinders. The purity of pure gases used for preparation was taken from the certificates of producer.

The cylinder number 6721_2

Component	Assigned value(x)	Standard uncertainty ($u(x)$)
Nitrogen	0,0405	0,00005
Carbon dioxide	0,01028	0,00002
Ethane	0,03022	0,00005
Propane	0,01003	0,00002
iso-Butane	0,002003	0,000007
n-Butane	0,002005	0,000007
(any relevant impurities)		
Methane	0,9050	0,0007

The cylinder number 2107_1

Component	Assigned value(x)	Standard uncertainty ($u(x)$)
Nitrogen	0,1027	0,0001
Carbon dioxide	0,02083	0,00003
Ethane	0,05731	0,00005
Propane	0,0170	0,00009
iso-Butane	0,004202	0,000011
n-Butane	0,012921	0,000033
(any relevant impurities)		
Methane	0,7851	0,0003

The cylinder number 2108_1

Component	Assigned value(x)	Standard uncertainty ($u(x)$)
Nitrogen	0,07418	0,00007
Carbon dioxide	0,02441	0,00003
Ethane	0,07795	0,00005
Propane	0,03664	0,00011
iso-Butane	0,007816	0,000020
n-Butane	0,009744	0,000024
(any relevant impurities)		
Methane	0,7693	0,0003

The cylinder number 2002_1

Component	Assigned value(x)	Standard uncertainty ($u(x)$)
Nitrogen	0,0704	0,00007
Carbon dioxide	0,02992	0,00003

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*))
Ethane	0,09253	0,00006
Propane	0,03406	0,00011
iso-Butane	0,008012	0,000021
n-Butane	0,009934	0,000025
(any relevant impurities)		
Methane	0,7551	0,0003

The cylinder number 2110_1

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*))
Nitrogen	0,0499	0,00007
Carbon dioxide	0,03519	0,00003
Ethane	0,13627	0,00007
Propane	0,0394	0,0001
iso-Butane	0,006064	0,000016
n-Butane	0,011906	0,000031
(any relevant impurities)		
Methane	0,7213	0,0003

The cylinder number 2115_1

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*))
Nitrogen	0,0901	0,00009
Carbon dioxide	0,039999	0,00003
Ethane	0,10964	0,00006
Propane	0,0491	0,0001
iso-Butane	0,012008	0,000030
n-Butane	0,004949	0,000013
(any relevant impurities)		
Methane	0,6942	0,0003

The cylinder number 0274_2

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*))
Nitrogen	0,1333	0,0002
Carbon dioxide	0,005044	0,00001
Ethane	0,02980	0,00005
Propane	0,005011	0,00001
iso-Butane	0,000988	0,000003
n-Butane	0,000993	0,000004
(any relevant impurities)		
Methane	0,8249	0,0006

The cylinder number 0287_2

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*))
Nitrogen	0,0866	0,00009
Carbon dioxide	0,008458	0,00001
Ethane	0,02679	0,00005
Propane	0,00823	0,00001
iso-Butane	0,001481	0,000005
n-Butane	0,001540	0,000005
(any relevant impurities)		
Methane	0,8669	0,0007

Instrument Calibration:

The measurement was done as calibration curve procedure. Each couple of one standard and one sample was measured during one day and their ratio was calculated. The measurements were repeated between 5 and 10 times. The calibration curve was calculated from ratios by the software B_least.exe. The value of the sample concentration was calculated from curve equation. The sample and the standard were measured one by one to eliminate the influence of temperature and atmospheric pressure. Thus neither the temperature nor the pressure correction was taken into calculation.

Sample handling:

The cylinders were stabilized in room temperature before measurements. The samples were transferred to the instrument by low-pressure line under atmospheric pressure and automatically dozed.

Evaluation of measurement uncertainty

The final uncertainty, calculated according to ISO 6143, consists of the following components:

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

Measurement Report from INMETRO

Reference Method:

A GC specifically set up for natural gas analysis was used:

Varian CP-3800 (ISO 6974 configuration) equipped with both TCD and FID detectors. The nitrogen, carbon dioxide and methane were determined using the TCD detector the other components were determined using FID detector.

Carrier gas: Helium.

Columns: 1.5 m x 1/8” ultimetal Molsieve 13X 80/100
0.5 m x 1/8” ultimetal Hayesep T 80/100
0.5 m x 1/8” ultimetal Hayesep Q 80/100
60 m x 0.25 mm CP-Sil 5 CB

Data collection was performed using Star Chromatography Workstation 6.3

Calibration Standards:

It was used four standards to calibrate the GC. They were prepared according International Standard ISO 6142:2001 by NMi-VSL.

PRM ML 6679

Component	Assigned value(x) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Nitrogen	4,970	0,0085
Carbon dioxide	6,975	0,0105
Ethane	4,992	0,009
Propane	2,981	0,006
iso-Butane	0,5008	0,00014
n-Butane	0,4912	0,00014
Methane	78,98	0,10

PRM ML 6800

Component	Assigned value(x) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Nitrogen	7,041	0,013
Carbon dioxide	3,072	0,006
Ethane	3,004	0,005
Propane	1,991	0,005
iso-Butane	0,2990	0,0008
n-Butane	0,1987	0,0006
Methane	83,99	0,11

PRM ML 6873

Component	Assigned value(x) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Nitrogen	1,004	0,003
Carbon dioxide	4,984	0,009
Ethane	2,004	0,0004
Propane	0,9992	0,0020
iso-Butane	0,0992	0,0003
n-Butane	0,0996	0,0003
Methane	89,96	0,12

PRM ML 6847

Component	Assigned value(x) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Nitrogen	2,977	0,006
Carbon dioxide	0,9980	0,0020
Ethane	0,9990	0,0020
Propane	0,4981	0,0012
iso-Butane	0,2013	0,0005
n-Butane	0,2950	0,0015
Methane	92,72	0,12

Instrument Calibration:

The standards used were described in topic above. Temperature and pressure correction were not take into calculation. The measurement sequence was injection of the standards and then injection of the sample.

Sample handling:

After arrival in the lab the cylinder was stabilised at room temperature (21ºC and humidity of 55%) before measurements.
The standards and sample were transferred directly to the GC automatically using a system composed three valves, pressure regulator and flowmeter.

Evaluation of measurement uncertainty

The uncertainty of the unknown sample was calculated according to ISO GUM. Three sources of uncertainty were considered:

- Uncertainty of the standards (certificate – type B)
- Standard deviation (analysis – type A)
- Calibration curve (type A)

Measurement Report from IPQ

Reference Method:

A Gas Chromatograph was used for natural gas analyses.
GC: HP 6890
Columns: 20 % Sebaconitrile on PAW, 80/100 Mesh, 2 ft, 6 inch coil of 0,125 inch OD Stainless
25 % DC-200 on PAW, 80/100 Mesh, 15 ft, 6 inch coil of 0,125 inch OD Stainless
Porapak Q, 80/100 Mesh, 6 ft, 6 inch coil of 0,125 inch OD Stainless
Molecular Sieve 13x, 45/60 Mesh, 10 ft, 6 inch coil of 0,125 inch OD Stainless
Molecular Sieve 13x, 45/60 Mesh, 4 ft, 6 inch coil of 0,125 inch OD Stainless
Detector: 2 Thermal Conductivity Detectors (TCD)
Valves: System of four valves
Sample introduction: Multi position gas sampling valves, injection at 2 bar pressure.
Oven Temperature: 70 ºC, isothermal
Carrier: N_2 and He
Data Collection: HP integrator 3396 Series III and Agilent Chemstation Plus

A Non Dispersive Infrared Analyser (NDIR - Uras 4) was used for CO_2 analyses.
Sample introduction: Multi position gas sampling valves, injection at 2 bar pressure.
Data Collection: Software Sira version 2.0

Calibration Standards:

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

	NPL		NMi			
	NG002	**NG005**	**0540E**	**0541E**	**0542E**	**0543E**
N_2 (%)	12,004±0,072	1,2059±0,0072	7,493±0,022	4,978±0,015	10,05±0,03	2,532±0,010
CO_2(%)	3,992±0,024	0,8096±0,0049	1,004±0,004	2,010±0,007	0,5009±0,0020	0,2029±0,0010
C_2H_6 (%)	0,7529±0,0045	11,039±0,007	9,99±0,03	7,522±0,023	2,514±0,009	5,012±0,017
C_3H_8 (%)	0,3009±0,0018	4,4874±0,027	2,984±0,010	1,999±0,007	0,4985±0,0022	1,005±0,004
n-C_4H_{10} (%)	0,2002±0,0012	0,1011±0,0006	0,689±0,003	0,4959±0,0024	0,0995±0,0006	0,2996±0,0015
i-C_4H_{10} (%)	0,1989±0,0012	0,1001±0,0006	0,4999±0,0024	0,698±0,003	0,0996±0,0006	0,2998±0,0015
CH_4 (%)	81,848±0,25	82,116±0,25	77,04±0,19	81,30±0,20	85,94±0,21	89,95±0,22
He (%)	0,5030±0,005	-	0,1026±0,0005	0,4022±0,0020	0,2014±0,0010	0,3029±0,0015
neo-C_5H_{12} (%)	0,04927±0,00049	0,04989±0,00050	-	-	-	-
i-C_5H_{12} (%)	0,04944±0,00044	0,03489±0,00031	0,0999±0,0009	0,2933±0,0024	0,0490±0,0005	0,1998±0,0017
n-C_5H_{12} (%)	0,05063±0,00046	0,03485±0,00031	0,0996±0,0009	0,2987±0,0024	0,0488±0,0005	0,1982±0,0017
n-C_6H_{14} (%)	0,04972±0,00044	0,02002±0,00018	-	-	-	-

Instrument Calibration:

The calibration instrument was done according to ISO 6143. We have used the B_Least program to fit the best model for data handling. All components of mixture have a goodness of fit less than 2 using a linear function.
For Nitrogen (N_2) were used a set of six PSM (from NMi and NPL) and to the others components were used a set of four PSM (from NMi).

Sample handling:

After arrival the cylinder was stored at ambient temperature in a storage room.
The sample was transferred to the instrument through an auto-sampler.

Evaluation of measurement uncertainty

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

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

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

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

Measurement Report from KRISS

Reference Method:

Instruments:

- Gas-Chromatographs(GC, HP 6890) with FID detectors for the determination of hydrocarbons and TCD detectors for the determination of nitrogen and carbon dioxide.

Working principles:

- Gas-Chromatography
- One-point comparison between reference and sample gases.
- The reference gases as calibration standard were prepared by gravimetry through the standard operational procedure of gas CRM in KRISS.

Type of configuration:

- A MFC and a quick connector were assisted for the quick change of cylinders and maintaining the constant flow rate.
- Fig. of the configuration;

Data collection:

- One-point comparison between reference and sample gases.
- GC signal was integrated as an area value for each peak.

2 Calibration Standards:

Preparation method:

- Four reference cylinders were prepared through the standard operational procedure of gas CRM.
- Assay analysis was also carried out through the determination of impurity components in the pure gases used.

Purity analyses:

- Purity of Ethane, Propane, iso-Butane and n-Butane,

Ethane gas		Propane gas		iso-Butane gas		n-Butane gas	
Impurity	Concentration, umol/mol	Impurity	Concentration, umol/mol	Impurity	Concentration, umol/mol	Impurity	Concentration, umol/mol
CH4	0.02	CH4	0.81	CH4	<0.5	CH4	<0.5
H2	<0.5	H2	<0.5	H2	<0.5	H2	<0.5
O2	2.5	O2	1.3	O2	24.5	O2	45
CO	0.07	CO	0.06	CO	2.4	CO	1.3
CO2	0.25	CO2	9.5	CO2	19.2	CO2	4.8
N2	10.9	N2	31.3	N2	123	N2	254
C2H2	<0.025	C2H2	0.03	C2H2	0.28	C2H2	<0.025
C2H4	0.9	C2H6	143	C2H6	42.9	C2H6	0.45

Ethane gas		Propane gas		iso-Butane gas		n-Butane gas	
Impurity	Concentration, umol/mol	Impurity	Concentration, umol/mol	Impurity	Concentration, umol/mol	Impurity	Concentration, umol/mol
C3H8	1.1	C2H4	<0.025	C2H4	0.28	C2H4	0.28
C3H6	298	c-C3H6	4.2	C3H8	132.3	C3H8	89.7
iso-C4H10	<0.013	C3H6	298	C3H6	0.21	C3H6	0.87
n-C4H10	0.57	iso-C4H10	9.4	n-C4H10	104.7	i-C4H10	842
Unkn. C5	0.7	n-C4H10	0.3	Unkn.C5	4.7	i-C5H12	0.28
<C6	<0.1	Unkn. C5	0.28	<C6	<0.1	n-C5H12	15.4
H2O	27	<C6	<0.1	H2O	43	<c6	<0.1
		H2O	43			H2O	25.9

- Purity of Methane, Carbon dioxide and Nitrogen;

Methane gas		Carbon dioxide gas		Nitrogen gas	
Impurity	Concentration, umol/mol	Impurity	Concentration, umol/mol	Impurity	Concentration, umol/mol
H2	<0.5	H2	<0.05	H2	<0.05
O2	1.4	CO	<0.1	CO	<0.1
CO	<0.05	CH4	0.99	CH4	0.0013
CO2	0.11	CO2	-	CO2	<0.01
N2	13.1	Ar	<1	Ar	<0.35
C2H2	<0.025	O2	2.43	O2	0.35
C2H6	0.51	N2	4.11	N2	-
C2H4	<0.025	NMHC	45.1	NMHC	<0.1
C3H8	0.18	H2O	5	H2O	1.2
C3H6	<0.013				
iso-C4H10	0.6				
n-C4H10	0.006				
n-C5H12	0.11				
<C6	<0.1				
H2O	11.2				

Certified value and Uncertainty of reference standard:

- Cylinder No., ME2201 and ME5598;

Component	ME2201		ME5598	
	Assigned value, mol/mol	Expanded uncertainty % relative(CL, 95%, k=2)	Assigned value, mol/mol	Expanded uncertainty % relative(CL, 95%, k=2)
Nitrogen	0.07024	0.12	0.06970	0.13
Carbon dioxide	0.03029	0.15	0.03131	0.15
Ethane	0.09367	0.11	0.09494	0.12
Propane	0.03352	0.17	0.03387	0.18
iso-Butane	0.00800	0.38	0.00785	0.39
n-Butane	0.01017	0.31	0.00993	0.33
Methane	0.7541	0.06	0.7523	0.06

- Cylinder No., ME0400 and ME0466;

Component	ME0400		ME0466	
	Assigned value, % mol/mol	Expanded uncertainty % relative(CL, 95%, k=2)	Assigned value, % mol/mol	Expanded uncertainty % relative(CL, 95%, k=2)
Nitrogen	0.07089	0.12	0.07013	0.12
Carbon dioxide	0.03148	0.15	0.03018	0.15
Ethane	0.09317	0.11	0.09578	0.11
Propane	0.03333	0.17	0.03440	0.17
iso-Butane	0.00797	0.38	0.00787	0.39
n-Butane	0.01029	0.31	0.00998	0.32
Methane	0.7528	0.061	0.7516	0.062

Instrument Calibration:

- In-situ calibration
- The GC response of the gases was obtained by, so-called, A-B-A' method with a calibration standard and a sample; at first, the response of calibration standard, at second, the response of sample, at last, the response of calibration standard again were obtained.
- After averaging two response values of calibration standard, the concentration of sample gas was calculated as a result by direct comparison between two response values and the concentration value of standard.

Sample handling:

- After receiving the sample cylinders, we stored it at the working Lab. of room temperature.

Evaluation of measurement uncertainty

- As an example, the evaluation procedure for propane is described below;

(1) Model equation:

$C_x = C_x^0 \text{ x } f_{std}$

where, C_x is concentration of propane in sample gas as a measurand,

C_x^0 is concentration of propane in sample gas with a variation due to reproducibility.

f_{std} is a factor, 1 with a variation due to uncertainty of calibration standard.

(2) Standard uncertainties of input variables:

1) Standard uncertainty of C_x^0 ; $u(C_x^0)$,

- The average concentration of propane and reproducibility of the determination were obtained from the measurement data same as the previous result table and listed below;

No.	Results mol/mol
1	0.03404
2	0.03400
3	0.03400
4	0.03397
Average	0.03400
Standard Deviation	0.000030
Standard uncertainty	0.000015

- $u(C_x^0)$ is 0.000015 mol/mol obtained by the evaluation of type A.

2) Standard uncertainty of f_{std} ; $u(f_{std})$,

- f_{std}=1.
- The concentration of propane in standard gas of ME2201 was 0.003352 mol/mol and standard uncertainty was 0.000026 mol/mol obtained from the certificate.
- Therefore, $u(f_{std})$ was 0.000029/0.03352=0.00087 obtained by the evaluation of type B.

(3) Combined standard uncertainty, $u(C_x)$,

- With uncertainty propagation rule, sensitivity coefficient including probability distribution and method of evaluation are summarized below;

Quantity		Standard uncertainty				
Symbol	Value	Symbol	Value	Sensitivity coefficient	Probability distribution	Method of evaluation
C_x^0	0.03400 mol/mol	$u(C_x^0)$	0.000015 mol/mol	1	t	A
f_{std}	1	$u(f_{std})$	0.00087	0.034 mol/mol	Normal	B

-$u^2(C_x) = (1 \text{ x } 0.000015)^2 + (0.034 \text{ x } 0.00087)^2$

-$u(C_x) = 0.000033$ mol/mol

(4) Expanded uncertainty, U

-At the level of confidence with 95% and normal distribution, coverage factor, k=2 was assumed.

- U = 2 x 0.000033 = 0.000066 mol/mol
- U(% relative) = 0.000066/0.0034 x 100 = 0.20 %

(5) Results

- Measurand, the concentration of Propane (C_x);

C_x = 0.03400 ± 0.000066 mol/mol (level of confidence, 95 %, k=2).

Measurement Report from NMi VSL

Reference Method:

One GC (specifically set up for natural gas analysis) was used in the analyses.

1. Natural Gas Analyser (NGA):

GC: HP6890 N (ISO 6974 configuration, Molsieve chanel not used)
Column: Porapak R , 3 m, 1/8 in od, 80/100 mesh.
Detectors: 1 Thermal Conductivity Detector (μ-TCD) and a Flame Ionisation Deterctor (FID) placed at the exhaust of the TCD.
Valves: 1 sampling valve with 0,25 ml sampleloop
Sample introduction: Multi position gas sampling valves, injection at ambient pressure.
Oven Temperature: temperature program: 40 °C for 12 minutes, ramp 10 °C/min to 150 °C, hold for 8 minutes.
Carrier: He
Data Collection: HP Chemstation software

The temperature program of the Porapak R column results in base-line separation of all the constituents of the samples. The TCD signal is used for the non-combustable components and for the ethane. All other hydrocarbons are analysed using the FID signal.

Calibration Standards:

All **standards** have been prepared by the **gravimetric method**, according to **ISO 6142**.
Several multi component calibration standards were used, all having methane as balance gas. Depending on the concentrations of the components, standards are prepared directly from pure gases or from so called preliminary mixtures that are prepared from the pure gases. After preparation the standards were verified against existing standards. A detailed composition of the standards is given below.

All pure gases were analysed before use by GC-FID and GC-TCD, except for methane and nitrogen. For nitrogen and methane purity analyses are only performed on selected cylinders using FT-IR and GC-DID in order to check the specifications given by the producer. The results of these purity analyses are expected to be representative for the cylinders that are not tested. The result of these analyses are combined in so called purity tables, that are used to calculate the composition and uncertainties of the gas mixtures that are prepared in the laboratory. The calculated mole fractions of the different components in a mixture therefore are not only based on the purity of the pure substances, but are also based on the presence of this component as an impurity in the other pure gases.

Instrument Calibration:

The set of standards used for a measurement and the mixtures to be analysed are connected to the gas chromatograph as described in the paragraph “sample handling” . A measurement of a cylinder consist of 5 injections that are averaged and corrected for pressure using the following equation.

$$Y' = Y \cdot \frac{P}{P_0}$$

Where Y’ is the corrected response, Y is the average response of the 5 injections, P is the average of the pressures measured when injecting the sample and P0 is the standard pressure.

The models used for the different curves are in all cases second order and unweighted regression is used.

Sample Handling:

The cylinders were let to acclimatise to laboratory conditions before analysis was started.
Each cylinder was equipped with a pressure-reducing unit set to approximately 2 bar. These pressure reducers were flushed at least 8 times before the first measurement. These flushings were distributed over a 24 hours time period. After the first measurement the connected reducers remained connected to the cylinder, until all measurements were performed. Before following measurements of the sample the pressure-reducing unit was flushed only once. Afterwards the cylinders were connected by Teflon tubing to an electronic multiple stream

selection valve. Stainless steel tubing to the sample inlet port/ sample loop of the GC connected the outlet valve of this valve. Before starting the automated analysis the Teflon tubings were flushed for 3 minutes and before injection the whole system was (pulsated) flushed for 3 minutes. Just before injection a valve positioned directly behind the stream selection valve is closed and the gas in the sample loop is allowed to reach ambient pressure after which the sample is injected.

Uncertainty:

Gravimetric preparation and impurities

The uncertainty of the gravimetric preparation of the standards used was evaluated according to Alink and Van der Veen[8]. 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.

Stability, non-recovery and leakages

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. 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.

Calibration curve and repeatability

The calibration curves where constructed using software based on ISO 6143.
As indicated, second order curves where used. Together with the uncertainty of the gravimetrical concentrations of the calibration mixtures and the repeatability of the analyses of the calibration mixtures and the sample mixture, the concentration and its accompanied uncertainty where calculated for each constituent.

Model used for evaluating measurement uncertainty:

The uncertainty of the analyses is the combined uncertainty of two uncertainty sources:

- Uncertainty of the component mole fraction in the standards, which is the combined uncertainty for the gravimetrical preparation, impurities, the stability, non recovery and leakages (X_{PSM}).
- Uncertainty of the calibration process, which is uncertainty contribution coming from the appropriateness of the calibration curve (model and its residuals) and the repeatability of the analysis ($\Delta x_{analysis}$)

Typical evaluation of the measurement uncertainty for **nitrogen**:

Quantity X_i	**Estimate** x_i *mol/mol*	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$ *% relative*	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$ *% relative*
x_{psm}	0.07034	B	Normal	0.05	1	0.05
$\Delta x_{analysis}$	0	A	Normal	0.04	1	0.08
Total:						
$x_{analysis}$	0.07034					0.10

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

Typical evaluation of the measurement uncertainty for **carbon dioxide**:

Quantity X_i	**Estimate** x_i *mol/mol*	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$ *% relative*	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$ *% relative*
x_{psm}	0.02994	B	Normal	0.06	1	0.06
$\Delta x_{analysis}$	0	A	Normal	0.05	1	0.09
Total:						
$x_{analysis}$	0.02994					0.11

Typical evaluation of the measurement uncertainty for **ethane**:

Quantity X_i	**Estimate** x_i *mol/mol*	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$ *% relative*	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$ *% relative*
x_{psm}	0.09415	B	Normal	0.09	1	0.09
$\Delta x_{analysis}$	0	A	Normal	0.07	1	0.07
Total:						
$x_{analysis}$	0.09415					0.12

Typical evaluation of the measurement uncertainty for **propane**:

Quantity X_i	**Estimate** x_i *mol/mol*	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$ *% relative*	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$ *% relative*
x_{psm}	0.03394	B	Normal	0.12	1	0.12
$\Delta x_{analysis}$	0	A	Normal	0.02	1	0.04
Total:						
$x_{analysis}$	0.03394					0.13

Typical evaluation of the measurement uncertainty for **iso-butane**:

Quantity X_i	**Estimate** x_i *mol/mol*	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$ *% relative*	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$ *% relative*
x_{psm}	0.007967	B	Normal	0.07	1	0.10
$\Delta x_{analysis}$	0	A	Normal	0.03	1	0.06
Total:						
$x_{analysis}$	0.007967					0.12

Typical evaluation of the measurement uncertainty for **n-butane**:

Quantity X_i	**Estimate** x_i *mol/mol*	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$ *% relative*	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$ *% relative*
x_{psm}	0.009960	B	Normal	0.14	1	0.14
$\Delta x_{analysis}$	0	A	Normal	0.04	1	0.08
Total:						
$x_{analysis}$	0.009960					0.17

Typical evaluation of the measurement uncertainty for **methane**:

Quantity X_i	**Estimate** x_i ***mol/mol***	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$ ***% relative***	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$ ***% relative***
x_{psm}	0.7537	B	Normal	0.04	1	0.04
$\Delta x_{analysis}$	0	A	Normal	0.03	1	0.03
Total:						
$x_{analysis}$	0.7537					0.05

Standards and their mole fractions per measured component.

N_2

Cylinder code	Gravimetric Mole fraction
VSL223555	0.002026
VSL201044	0.004022
VSL205178	0.006132
VSL203620	0.008103
VSL209604	0.011914
VSL202608	0.024950
VSL203657	0.060075
VSL209564	0.12146
VSL508606	0.016003
VSL209546	0.20018

CO_2

Cylinder code	Gravimetric Mole fraction
VSL223555	0.001992
VSL201044	0.003955
VSL205178	0.006135
VSL203620	0.008106
VSL209604	0.011941
VSL200407	0.023406
VSL203657	0.025174
VSL209546	0.060065
VSL209564	0.11975
VSL508606	0.16022
VSL202608	0.20051

C_2H_6

Cylinder code	Gravimetric Mole fraction
VSL201044	0.009995
VSL205178	0.014957
VSL202608	0.020020
VSL203620	0.029769
VSL209564	0.045671
VSL200407	0.046757

Cylinder code	Gravimetric Mole fraction
VSL209546	0.065695
VSL203657	0.079880
VSL209604	0.110020

C_3H_8

Cylinder code	Gravimetric Mole fraction
VSL201044	0.0009955
VSL202608	0.004005
VSL209604	0.005937
VSL205178	0.007924
VSL209564	0.009994
VSL209546	0.020154
VSL200407	0.028573
VSL203657	0.029923
VSL223555	0.039807
VSL203620	0.049221

i-C_4H_{10}

Cylinder code	Gravimetric Mole fraction
VSL203620	0.000303
VSL201044	0.000506
VSL209545	0.000697
VSL202608	0.001004
VSL205178	0.001475
VSL209546	0.001967
VSL209604	0.002999
VSL223555	0.005052
VSL200407	0.008002
VSL508606	0.010014

n-C_4H_{10}

Cylinder code	Gravimetric Mole fraction
VSL203620	0.0003018
VSL201044	0.0005034
VSL209545	0.0007027
VSL202608	0.0009978
VSL205178	0.0014822
VSL209546	0.0019673
VSL209604	0.0029997
VSL223555	0.0049827
VSL200407	0.0080960
VSL508606	0.0099770

CH_4

Cylinder code	Gravimetric Mole fraction
VSL508606	0.58446
VSL209546	0.64776
VSL209564	0.69561
VSL202608	0.74311
VSL203657	0.79689
VSL209604	0.84811
VSL200407	0.87971
VSL203620	0.89939
VSL223555	0.93855
VSL205178	0.96189
VSL201044	0.96908
VSL209545	0.99210

Measurement Report from NMIA

Reference Method:

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.)
60		6	6
130	15	15.83	26.50

The nitrogen, carbon dioxide, methane, and ethane concentrations were determined using the TCD detector. Hydrocarbon components (ethane, propane, iso-butane and n-butane) 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 for the K23 cylinder. The concentrations of the components in the calibration standards closely bracketed the expected concentrations of the components in the CCQM K23 cylinder. The natural gas calibration standards were prepared in our laboratory from very high purity commercial gases with the concentration of the natural gas component determined gravimetrically.

Prior to calibration standard preparation, the purity and composition of the commercial gases were determined. Single point calibrations were used to determine impurity concentrations in each gas. 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 an 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 standard 1: MD8856

Component	Assigned value(x)	Standard uncertainty ($u(x)$)
Nitrogen	65.52774	0.01309
Carbon dioxide	28.46244	0.00850
Methane	769.40347	0.03202
Ethane	88.42208	0.01177
Propane	31.35384	0.00840
iso-Butane	8.00094	0.00635
n-Butane	8.81045	0.00174
(any relevant impurities)		

Calibration standard 2: MD8859

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*))
Nitrogen	71.80555	0.01059
Carbon dioxide	29.98889	0.00684
Methane	749.36972	0.02430
Ethane	95.14780	0.00950
Propane	35.23643	0.00693
iso-Butane	7.98028	0.00515
n-Butane	10.45059	0.00098
(any relevant impurities)		

Instrument Calibration:

The K23 cylinder was run with two calibration reference cylinders containing components at concentrations that closely bracketed the expected concentrations in the K23 cylinder. A sequence of runs $AB_1AB_2CB_3C$ was used to determine the concentration of components in the sample cylinder:

- A was the first reference standard.
- B was the K23 sample cylinder.
- C was the second reference standard.

Each stage of the measurement sequence represents 27 repeat analyses of a cylinder. For calculation purposes the first 14 runs were rejected and the last 13 runs were used to determine average responses.

The first result (B_1) was obtained from a single-point average calibration using the results from the first standard. The third result (B_3) was a single-point average calibration using the results from the second standard. Single-point average results were calculated 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

The second result (B_2) was a two-point bracketed result determined from the results of standard one and standard two. Two point bracketed results were calculated using the mathematical model:

$$Cx = (C_2-C_1)*(Rx-R_1)/(R_2-R_1)+C_1$$

Where:

- Cx = concentration of sample
- C_1 = concentration of first standard
- C_2 = concentration of second standard
- Rx = average response of GC for sample
- R_1 = average response of GC for first standard
- R_2 = average response of GC for second standard

The three measurement results (B_1, B_2, B_3) were combined and averaged to produce a single table of measurement results. The sequence of runs was repeated three times, to account for instrument drift with time. Three tables of measurement results are presented for the cylinder 0246-F.

Analyses were performed in a lab with a constant temperature of 22.5˚C ± 0.2˚C. The analyses results were not corrected for variations in laboratory air pressure or temperature.

Sample handling:

On arrival the courier left the sample cylinder outside overnight at temperatures close to 0˚C. The cylinder was brought inside and gently warmed in an oven at 60˚C for 2 hours. The sample cylinder was then left to equilibrate in the measurement laboratory over the weekend. A high-purity stainless steel regulator with a maximum outlet pressure of 4 Bar was fitted to the K23 cylinder. The regulator was evacuated, purged with gas, adjusted to an outlet pressure of 3 Bar, and left to equilibrate.

The K23 cylinder and calibration reference standards were connected to a Valco valve with quick-connect fittings. The Valco valve was controlled by the GC and automatically changed the cylinder for analysis. An electronic Mass Flow Controller before the sample loop maintained a constant flow of sample through the sample loop at a rate of 10 ml/min.

Evaluation of measurement uncertainty

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

- Gravimetric uncertainty, and
- Analytical uncertainty

The Gravimetric uncertainty contributions included:

- Balance uncertainty
- Buoyancy of cylinders
- Expansion of cylinders
- Tare mass uncertainty
- Tare mass buoyancy
- Impurity of gases

The amount of each contribution to the measurement uncertainty was determined. The gravimetric uncertainty for each gas component was calculated by taking the square root of the sum of the squares of the values for each uncertainty source.

The analytical uncertainty contributions included:

- Uncertainty of sample measurement
- Uncertainty of measurement of reference gases

The analytical uncertainty was calculated by using the mathematical models for single-point and bracketed point calibrations. The standard uncertainty of the analytical response for the first standard and/or the second standard was calculated; along with the standard uncertainty for the analytical response of the test cylinder.

The combined total uncertainty was determined using the principles described in the ISO Guide 34. The uncertainty obtained from the analytical measurement was combined with the gravimetric uncertainty of the reference standards to give the total combined uncertainty.

Measurement Report from NMIJ

Reference Method:

The analysis is done by using Agilent Micro GC 3000A. The software "Cerity" was used for data collection.

Table 1. Summary of Instruments

Analyte	N_2, CH_4	CO_2, C_2H_6	C_3H_8, iso-C_4H_{10}, n-C_4H_{10}
Body	1		2
Injector type	Variable	Variable	Fixed
Main column	Molsieve	Plot U	PLOTQ
Precolumn	Plot U	PLOTQ	-
Oven temp.	85 °C	70 °C	120°C
Anarytical time for 1 injection	5.5	3.5	3
Number of injections per one cylinder	10 (Only peak areas due to last 5 injections were used.)		7 (Only peak areas due to last 5 injections were used.)

Calibration Standards:

All measurements used the calibration gas standards in Table 2. These standards were prepared by gravimetric method, according to ISO 6142:2001.

Table 2 Concentrations in calibration standards. (Units is μmol/mol).

(a) calibration standard 1

Component	Assigned value(x) (Gravimetric value)	Standard uncertainty (u(x))
Nitrogen	60767.76	3.96
Carbon dioxide	26043.71	2.60
Ethane	76548.86	4.27
Propane	29472.4	2.72
iso-Butane	7203.8	1.99
n-Butane	9197.2	2.00
(any relevant impurities)		
Methane	790766	24.9

(b) calibration standard 2

Component	Assigned value(x) (Gravimetric value)	Standard uncertainty (u(x))
Nitrogen	66631.28	4.01
Carbon dioxide	26965.95	2.64
Ethane	85074.76	4.42
Propane	30711.0	2.77
iso-Butane	6402.4	2.02
n-Butane	8407.1	2.02
(any relevant impurities)		
Methane	775807	24.5

(c) calibration standard 3

Component	Assigned value(*x*) (Gravimetric value)	Standard uncertainty (*u*(*x*))
Nitrogen	66472.00	3.97
Carbon dioxide	29945.60	2.62
Ethane	85032.19	4.40
Propane	30428.2	2.75
iso-Butane	8186.2	2.01
n-Butane	7559.4	2.01
(any relevant impurities)		
Methane	772376	24.4

(d) calibration standard 4

Component	Assigned value(*x*) (Gravimetric value)	Standard uncertainty (*u*(*x*))
Nitrogen	81073.52	3.44
Carbon dioxide	37854.50	2.28
Ethane	112413.29	3.01
Propane	39053.8	2.52
iso-Butane	9165.9	1.74
n-Butane	14187.0	1.77
(any relevant impurities)		
Methane	706252	22.3

Preparation method:

All calibration gas standards were prepared by using an electronic mass-comparator (Mettler Toledo model KA10-3/P, capacity 15 kg , readability 1 mg) with automatic loading system of cylinders [Ref.1]. These calibration gas standards were prepared by one-step dilution.

Purity analyses :

The impurities in a nominally “pure” parent gas are determined with GC-FID, GC-TCD, GC-HID, Micro GC, and, moisture meter. The mole fraction of the major component is conventionally calculated from equation (1) in ISO6142:2001.

Tables 3-9 show the results of impurity analyses.

Table 3. Purity table for nitrogen gas used as parent gas.

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	method
N2	999999	0.43	-	-
O2	0.59	0.34	Rectangular	Micro GC
H2O	0.44	0.25	Rectangular	Capacitance type moisture meter
CO2	0.033	0.019	Rectangular	GC-FID with MTN
CH4	0.0094	0.0054	Rectangular	GC-FID
C2H6	0.017	0.010	Rectangular	GC-FID
C3H8	0.019	0.011	Rectangular	GC-FID
n-C4H10	0.11	0.064	Rectangular	GC-FID

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	method
iso-C4H10	0.11	0.064	Rectangular	GC-FID

Ref.1) N. Matsumoto, T. Watanabe, M. Maruyama, H. Horimoto, T. Maeda, K. Kato (2004) Metrologia 41 : 178-188.

Table 4. Purity table for carbon dioxide gas used as parent gas.

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	method
N2	1.64	0.95	-	GC-TCD
O2	0.59	0.34	Rectangular	GC-TCD
H2O	5.6	1.4	Normal	Capacitance type moisture meter
CO2	999991.9	1.7	Rectangular	
C2H6	0.017	0.010	Rectangular	GC-FID
C3H8	0.019	0.011	Rectangular	GC-FID
n-C4H10	0.110	0.064	Rectangular	GC-FID
iso-C4H10	0.110	0.064	Rectangular	GC-FID

Table 5. Purity table for ethane gas used as parent gas.

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	method
N2	1.6	0.95	Rectangular	Micro GC
O2	0.59	0.34	Rectangular	Micro GC
CH4	0.049	0.029	Rectangular	GC-FID
C2H6	999997.7	1.0	Rectangular	GC-FID

Table 6. Purity table for propane gas used as parent gas.

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	method
N2	3.0	1.7	Rectangular	GC-TCD
O2	2.0	1.2	Rectangular	GC-TCD
H2O	1.3	0.7	Normal	Capacitance type moisture meter
CH4	0.049	0.029	Rectangular	GC-FID
C2H6	0.15	0.087	Rectangular	GC-FID
C3H8	999993.5	1.4		

Table 7. Purity table for n-butane gas used as parent gas.

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	method
N2	1.64	0.95	Rectangular	Micro GC
O2	1.7	1.0	Rectangular	Micro GC
CH4	0.049	0.029	Rectangular	GC-FID
C2H6	0.025	0.015	Rectangular	GC-FID
n-C4H10	999996.6	1.4		

Table 8. Purity table for iso-butane gas used as parent gas.

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	method
N2	1.6	0.95	Rectangular	Micro GC
O2	5.0	0.15	Rectangular	Micro GC
CH4	0.049	0.029	Rectangular	GC-FID
C2H6	0.025	0.015	Rectangular	GC-FID
iso-C4H10	999993.2	5.3		

Table 9. Purity table for methane gas used as parent gas.

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	method
N2	0.19	0.022	Normal	GC-HID
O2	0.11	0.062	Rectangular	GC-HID
H2O	0.27	0.16	Rectangular	Capacitance type moisture meter
CO	0.025	0.014	Rectangular	GC-HID
CO2	0.38	0.22	Rectangular	GC-HID
CH4	999998.79	0.29	-	-
C2H6	0.016	0.0095	Rectangular	GC-FID
n-C4H10	0.11	0.064	Rectangular	GC-FID
iso-C4H10	0.11	0.064	Rectangular	GC-FID

Instrument Calibration:

Measurements sequence and mathematical model:

Each measurement #*k* consists of the following procedure.

1) Inject 4 calibration standards (in table 2) into the analyzer.. Record the retention times and peak areas. The following calibration data set can be obtained;
    - · analyte contents, x_1, x_2, x_3, x_4 ,
    - · standard uncertainties of the analyte contents, $u(x_1), u(x_2), u(x_3)$, $u(x_4)$,
    - · responses to the analyte contents, y_1, y_2, y_3 , y_4 ,

· standard uncertainties of the responses, $u(y_1)$, $u(y_2)$, $u(y_3)$, $u(y_4)$.

These calibration standards were exchanged manually after each measurement for one cylinder had finished.

2) Inject the sample gas with the same manner as the calibration standards. Record the retention times and the peak areas. The response y_k and its standard uncertainty $u(y_k)$ can be obtained. This sample gas was injected between the calibration standards, for example, "calibration standard 1 - calibration standard 2, sample - calibration standard 3 - calibration standard 4".
3) Parameters and its uncertainty of the analytical function $x_k = b_{0,k} + b_{1,k}y_k$ were calculated with ISO6143 implementation software "B_LEAST version 1.11". After that, the analytical content x_k and standard uncertainty $u(x_k)_{6143}$ of sample cylinder were calculated from peak area y_k and its uncertainty $u(y_k)$.

The analytical functions were validated by Goodness-of-fit. For all analytical functions of our measurements in these comparison values of Goodness-of-fit were less than 2.

Sample handling:

Stabilization

The sample cylinder was kept in air conditioning room of about 22 °C for 3 days since the sample cylinder arrived at our laboratory. After that, we started our measurements for this comparison.

Transfer of sample gas to the instrument

A pressure regulator with two gauges was attached with the sample cylinder via an adaptor (DIN-1 – JIS 22 mm left). The pressure of sample gas from the regulator to a flow controlled valve was controlled at 0.01 MPa. The flow rate of sample gas was controlled at approximately 30 mL/min. A part of the sample gas was introduced into the inlet of Micro GC. Most of the sample gas was exhausted to a draft with a scrubber.

Evaluation of measurement uncertainty

The final reported analytical concentration x, and its standard uncertainty $u(x)$ for sample cylinder was estimated by using the following equations ;

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

where J is the number of measurement #*k* and x_k is the analytical content at each measurement #*k* described in the previous section "*Instrument calibration*". For N_2, CH_4, C_3H_8, iso-C_4H_{10}, and, *n*-C_4H_{10}, The value of J was 5 (for N_2, CH_4, C_3H_8, iso-C_4H_{10}, and, n-C_4H_{10}), or, 6 (for CO_2, and, C_2H_6).

The standard uncertainty of analytical concentration $u(x)$ is evaluated from the following equations;

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

$$u^2(x)_{ISO6143} = \sum_{k=1}^{J} u^2(x_k)_{6143} \Big/ J^2 \quad , \qquad (3)$$

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

where $u(x_k)_{6143}$ is described in the previous section ”instrumental calibration”. This $u(x_k)_{6143}$ includes the following uncertainty sources ;

(a) gravimetric concentration of calibration standards ,

(b) Repeatability of measurements with the analyzer ,

(c) Appropriateness of the calibration curve ,

The uncertainty due to (a) was much less than those due to(b) and (c).

The (b) includes not only the individual measurements of peak areas for one cylinder, but also the variation due to exchanges of the cylinders and the variation between days.

The appropriateness of the (c) was evaluated by the ISO6143 method, as described in the previous section ”instrumental calibration”.

Measurement Report from NPL

Reference Method

All analyses were carried out using a Varian 3800 GC fitted with a 10-port gas sampling valve with parallel double injection, two parallel columns, FID and TCD detectors. Details of the columns and method parameters are given in the table below:

Parameter	Column A	Column B
Column	HayeSep A (120/140 mesh) packed Silcosteel tubing 4.4m x $^{1}/_{16}$” OD x 0.75mm ID	HayeSep P (100/120 mesh) packed stainless steel tubing 4.4m x $^{1}/_{16}$” OD x 0.75mm ID
Oven Temperature	160°C	160°C
Carrier Gas	Helium	Helium

Data collection and chromatogram integration are carried out automatically using a user-defined data analysis method in the Varian Star software package. The raw analytical data is transferred to an Excel spreadsheet for further analysis.

Calibration Standards:

Two Primary Reference Gas Mixtures (PRGMs) were prepared gravimetrically with the same nominal composition as Mixture II.

Composition of NG 92:

Component	Gravimetric value (x) mmol/mol	Standard uncertainty ($u(x)$)
Nitrogen	70.022	0.079
Carbon dioxide	93.949	0.121
Ethane	29.963	0.055
Propane	34.019	0.106
iso-Butane	8.0104	0.051
n-Butane	9.9818	0.042
Methane	754.05	0.011

Composition of NG 95:

Component	Gravimetric value (x) mmol/mol	Standard uncertainty ($u(x)$)
Nitrogen	69.991	0.089
Carbon dioxide	94.395	0.136
Ethane	29.990	0.061
Propane	33.912	0.120
iso-Butane	8.0336	0.051
n-Butane	9.9819	0.043
Methane	753.69	0.012

The stated amount fractions are those calculated from the gravimetric preparation process. The impurities present in the parent gases were quantified by use of using a four-channel Varian CP-2003 ‘Micro’ GC with four micro-TCD detectors.

The standard uncertainties have been calculated (according to ISO 6142) by combination of the uncertainties from three sources: gravimetry, relative molar masses and purity analysis.

Instrument Calibration:

In the first set of measurements the comparison was made against both standards, in the second against NG 95 and in third against NG 92. The measurements were carried out in parallel on two channels (TCD and FID) of the GC. The TCD channel was used to measure nitrogen, methane, carbon dioxide, ethane, propane and the butanes; the FID channel was measured propane, *iso*-butane and *n*-butane.

The unknown mixtures and PRGMs were analysed alternately. Four or five repeat analyses of each standard were carried out (equivalent to a total run time of 30-38 minutes) before changing to the next mixture.
Using the gravimetric data, Response Factors (area/mole fraction) were calculated for each peak individually. To reduce the effect of any possible drift caused by changing environmental and instrumental parameters, the results were calculated using the average of two neighbouring Response Factors.

After making 4-5 comparisons, the average amount fraction values and the standard deviations were calculated for each component.

The above process was carried out three times for each mixture - the final (reported) amount fractions for each mixture were determined using the weighted average of these three independent measurements.

Sample handling:

In order to sample the mixtures, the cylinders were equipped with a MDV (Minimised Dead Volume) connector and an Adjustable Direct Flow Restrictor (these devices have been developed in-house). A continuous, controlled, sample flow was applied and parallel sampling for the two channels made possible using a 10-port Valco membrane valve built in the GC oven.

Evaluation of measurement uncertainty

The evaluation of measurement uncertainties is based on the statistical analysis of the individual and the repeated intercomparisons. For each of the three analyses of the unknown Mixture, a standard deviation was calculated from the repeated measurements comprising each analysis. The final 'analytical' uncertainty was then calculated as the mean of these three standard deviations divided by $\sqrt{3}$.

The gravimetric uncertainty of each PRGM was determined as described in the 'Calibration Standards' section (above). As two standards were used to measure the unknown Mixture, the gravimetric uncertainty used is the mean of the uncertainties of the two standards.

To calculate the final (reported) uncertainty, the analytical and gravimetric uncertainties described above were combined as the square root of the sum of squares. Expanded uncertainties were determined by multiplication of the standard uncertainties by a suitable coverage factor (two).

Measurement Report from NIM

Reference Method:

Three different systems were used to analyse the N_2, CO_2 and hydrocarbons.

Components	N_2	CO_2	Hydrocarbons
Chromatography	GC-8A (Shimadzu)	GC-8A (Shimadzu)	6890N (Agilent)
Detector	TCD	TCD	FID
Column	13X molecular sieve packed column with 3 m × 3 mm	Porapak PN steel packed column with 2 m × 3 mm	Al_2O_3/Na_2SO_4 capillary column with 50 m × 0.53 mm ×15 μm
Oven temperature	50 ºC, constant	70 ºC, constant	100 ºC, constant
Inlet temperature	80 ºC	80 ºC	150 ºC
Carrier gas	He	He	He
Injection	Manual switch valve	Manual switch valve	Automatic switch valve
Other parameter	Bridge current: 180mA	Bridge current: 180mA	Flow rate of carrier gas: 7.0 ml/min

Calibration Standards:

Five gas mixtures were used as calibration standards to analyse the nature sample of mixture II. The calibration standards were prepared by gravimetric method, according to ISO 6142, which detail information was listed in table 1.

The impurities of complementary gas and impurities of components interested were determined with a standard normalized method by gas chromatography instrument. Experiments showed that the impurities of the material gases have no effects to the results within the measurement uncertainties. So the purity of pure gases used for preparation was taken from the certificates of producer. Their uncertainties were calculated by type B evaluation.

Table 1 Calibration standards of mixture II

Components	Assigned value (x)					Relative standard uncertainty ($u(x)$),%
Cylinder number	193630 A	193669 B	193780 C	193625 D	193633 E	
Nitrogen	6.270	6.530	6.890	8.010	6.800	0. 5
Carbon dioxide	3.100	2.650	2.950	3.000	3.020	0. 8
Ethane	9.370	11.000	9.750	8.910	9.080	0. 6
Propane	3.200	3.110	3.530	3.580	3.280	0. 5
iso-Butane	0.734	0.742	0.705	0.745	0.760	0. 5
n-Butane	0.900	0.930	0.922	0.954	0.933	0. 5
Methane	76.426	75.038	75.253	74.801	76.127	0.5

Instrument Calibration:

One point calibration method was used to determine the sample mixture. Concentrations of five standards mixture listed in table 1. The sample was measured in three different days based upon the five calibration standards. One measurement sequence was in the order of standard A - sample - standard A’ - standard B - sample - standard B’ -……- standard E - sample - standard E’. After averaging two response values of the same calibration standard, the concentration of sample mixture was calculated by direct comparison based on the following equation (1).

$$C_{sample,i} = \frac{R_{sample,i}}{\overline{R}_{st,i}} \cdot C_{st,i} \qquad (1)$$

$C_{sample,i}$ is the concentration of component *i* in sample mixture to be calculated,

$R_{sample,i}$ is the response value of component *i* in sample mixture,

$\overline{R}_{st,i}$ is the average of two response values of component *i* in the same calibration standard mixture,

$C_{st,i}$ is the concentration of component *i* in calibration standard mixture.

So five values of concentration were got from one sequence. Averaged the five values to got one final result. The sequence was repeated six times in one-day measurement.
Nitrogen, Carbon dioxide, Ethane, Propane, iso-Butane and n-Butane in the sample mixture were analysed by this way. Methane as balance gas was calculated by the equation (2).

$$C_{methane} = 1 - \sum C_{others} \qquad (2)$$

$C_{methane}$ is the concentration of methane,

C_{others} is the concentration of Nitrogen, Carbon dioxide, Ethane, Propane, iso-Butane and n-Butane, respectively.

Temperature and pressure were not corrected during the calibration procedure.

Sample handling:

Sample cylinder after arrival was stored in the room temperature. Sample and standard gas were all directly led to gas chromatography by a regulator, a flow meter and a teflon pipe. Before each sample injection, the pipe system was purged fifteen times (about one second per time) and balanced ten seconds at room pressure and temperature then.

Evaluation of measurement uncertainty

For each natural gas component (except methane) we established three types of uncertainties:

- Standard mixture uncertainty, which mainly depend upon the gravimetric method uncertainty
- stability uncertainty
- Analytical uncertainty

The Gravimetric method uncertainty contributions included:
- Balance uncertainty
- Buoyancy of cylinders
- Impurity of gases
- Absorption

The stability uncertainty is evaluated according to the past experimental results.

The analytical uncertainty was evaluated by repeatability of the measurements.
The relative standard uncertainty of component i in sample mixture was evaluated by equation (3)

$$u^2(C_{sample,i},\%) = u_{gravi}{}^2 + u_{stab}{}^2 + u^2{}_{repea} \qquad (3)$$

The relative standard uncertainty of standard mixture included the gravimetric method uncertainty, stability uncertainty and analytical uncertainty. The relative standard uncertainty of repeatability was the RSD% of the three concentration values of the component, which were determined in three different days.

The amount of each contribution to the measurement uncertainty was listed in table 2.

The absolute standard uncertainty was calculated by:

$$u(C_{sample,i}) = u(C_{sample,i},\%) \cdot C_{sample,i} \qquad (4)$$

According to equation (2), the standard uncertainty of methane was evaluated as following:

$$u^2(C_{methane}) = u^2(C_{N_2}) + u^2(C_{CO_2}) + u^2(C_{ethane}) + u^2(C_{propane}) + u^2(C_{i-bu\tan e}) + u^2(C_{n-bu\tan e})$$

Expanded uncertainty can be calculated with a confidence interval 95% and a coverage factor k= 2. The expanded uncertainty was:

$$U_i = k \cdot u(C_{sample,i},\%)$$

Table 2 Uncertainty Evaluation table

Relative standard uncertainty *u* %	**u_{gravi} Uncertainty source from standard mixture**				**U_{stab} Stability**	***u_{repea}* %**	**$U(C_{sample,\%})$**	***U_i* *K=2***
	Balance	**Buoyancy of cylinder**	**Purity of gases**	**Absorption**				
Assumed distribution	Rectangle	Rectangle	Rectangle	Rectangle	Normal	Normal		
N_2	0.12	0.06	0.15	0.03	0.11	0.07	0.25	0.5
CO_2	0.12	0.06	0.15	0.03	0.45	0.04	0.5	1.0
Ethane	0.12	0.06	0.15	0.03	0.32	0.03	0.4	0.8
Propane	0.12	0.06	0.15	0.03	0.14	0.03	0.25	0.5
i-butane	0.12	0.06	0.15	0.03	0.10	0.13	0.25	0.5
n-butane	0.12	0.06	0.15	0.03	0.10	0.06	0.25	0.5
Methane							0.25	0.5

Measurement Report from OMH

Reference Method:

HP 6890 GC-TCD/FID with two parallel columns:
8,8 m Porapak R and 4,4 m Porapak PS.
Isotherm method at 170 °C

Calibration Standards:

The Calibration Standard was prepared gravimetrically.

Composition of calibration standard:

OMH 292:

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) Rel %
Nitrogen	7,2691	0,016
Carbon dioxide	3,1860	0,024
Ethane	9,1446	0,031
Propane	3,4201	0,036
iso-Butane	0,8284	0,074
n-Butane	0,9754	0,065
Methane	75,1764	0,0014

Instrument Calibration:

Direct comparison with the Standard OMH 292.

Sample handling:

Samples were transferred continuously to the instrument on low pressure checked by differential pressure controller (10 mbar).

Evaluation of measurement uncertainty

We taking to account 2 main sources of the uncertainty of each components:

1. u_1: experimental standard deviation of the mean,

$$u_1 = \frac{s}{\sqrt{n}} .$$

2. u_2: uncertainty of the preparation of the calibration standard (OMH 292). It contains the uncertainty of the purity of the parent gases and the uncertainty of the weighing See the table of the calibration standard.

The combined uncertainty:

$$u = \sqrt{u_1^2 + u_2^2}$$

It was calculated the effective degree of freedom for each component.
Degree of freedom of the three series (in the case of three different days) is 2, degree of the freedom of the calibration standard is ∞.

The effective degree of freedom is:

$$\nu_{eff} = \frac{u^4}{\left(\frac{u_1^4}{\nu_1} + \frac{u_2^4}{\nu_2}\right)}.$$

We used coverage factor k, which for a t-distribution with effective degrees of freedom corresponds to a coverage probability of approximately 95%.
The expanded uncertainty:

U=k*u.

Measurement Report from SMU

Reference Method:

Measured on Thermoquest Trace 2000 gas chromatograph using Porabond Q column (50m-0,53mm-10µm), TCD and FID detectors, methanizer.
Carrier gas: helium @ 17mL/min
Sample loop 20µm
Oven temperature: 33°C 5min + ramp 65°C 1,8min @120°C/min + ramp 150°C 9,5min @ 180°C/min.
Method time: 17,27 min. In automated runs + about 10 min to prepare oven temperature for another injection.
Backflush from 11,86 min.
Flows of all mixtures were controlled by mass flow controller before entering the sample loop.

Calibration Standards:

All PSMs as calibration standards were made gravimetrically according ISO 6142 and 6143. Impurities in parent gases were checked on GC.

		PSM code								
component		**0011F_5**	**0013F_2**	**0014F_6**	**0029F_3**	**0695E_6**	**0715E_3**	**0717E_3**	**0718E_2**	**9304E_2**
methane	x	0.70123	0.88963	0.6848	0.8272	0.84642	0.84774	0.83717	0.90591	0.97264
	u(x); rel %	0.10%	0.10%	0.10%	0.25%	0.10%	0.10%	0.10%	0.10%	0.10%
ethane	x	0.084755	0.052934	0.092713	0.042368	0.091222	0.0923	0.035449	0.029844	0.011157
	u(x); rel %	0.10%	0.11%	0.10%	0.20%	0.10%	0.10%	0.10%	0.11%	0.13%
propane	x	0.038550	0.013844	0.033426	0.008875	0.026233	0.025754	0.007563	0.009825	0.002751
	u(x); rel %	0.13%	0.14%	0.14%	0.25%	0.13%	0.14%	0.19%	0.18%	0.18%
n-butane	x	0.006775	0.002055	0.009222	0.001398	0.002511	0.003331	0.001238	0.002006	0.000564
	u(x); rel %	0.18%	0.28%	0.16%	0.30%	0.17%	0.16%	0.16%	0.18%	0.27%
isobutane	x	0.005562	0.001827	0.007302	0.001411	0.004077	0.003992	0.001295	0.001908	0.0006
	u(x); rel %	0.18%	0.18%	0.18%	0.45%	0.16%	0.18%	0.22%	0.16%	0.30%
N_2	x	0.13320	0.024794	0.14071	0.10449	0.008509	0.009161	0.10163	0.039947	0.011481
	u(x); rel %	0.11%	0.11%	0.10%	0.15%	0.24%	0.18%	0.10%	0.10%	0.13%
CO_2	x	0.029921	0.014141	0.031827	0.012808	0.019457	0.016515	0.014484	0.009884	0.000335
	u(x); rel %	0.11%	0.11%	0.15%	0.16%	0.11%	0.12%	0.13%	0.18%	0.29%
isopentane	x	-	0.000281	-	0.000303	-	0.000507	0.00028	0.000153	0.000106
	u(x); rel %	-	0.35%	-	0.29%	-	0.28%	0.28%	0.39%	0.47%
n-pentane	x	-	0.00034	-	0.000291	0.000254	0.000471	0.000265	0.000156	9.87E-05
	u(x); rel %	-	0.32%	-	0.34%	0.55%	0.32%	0.28%	0.30%	0.51%
neopentane	x	-	0.00013	-	0.000159	0.000874	0.000217	0.000109	0.000106	5.61E-05
	u(x); rel %	-	0.76%	-	0.52%	0.33%	0.55%	0.53%	0.50%	0.95%
n-hexane	x	-	-	-	0.000722	0.00041	-	0.0005	0.000251	0.000192
	u(x); rel %	-	-	-	0.31%	0.41%	-	0.26%	0.40%	0.41%

Instrument Calibration:

All measurements were done in automated way (only in one direction) using electric selector valve. Sequence of 5 measurement cycles with 9 PSMs was used on 22.11. and 23.11.05. On 13.12. sequence of 5 measurement cycles with only 8 PSMs was used. All PSMs were used to create calibration curves.

To calculate results following calibration curves were used

- Linear (b_least): N_2 (TCD-area)

- Quadratic (b_least) calibration curve:

methane (FID-area), ethane (FID-area), n-butane (TCD-height), iso-butane (TCD-height), CO_2 (FID-area as converted to methane)

- Cubic (b_least): propane (TCD-height)

No corrections were used

2 hours before measurement all cylinders were rolled for about 10 min.

Sampling order

22.11.	**23.11.**	**13.12.**
0014F_6	9304E_2	0715E_3
0011F_5	0718E_2	0029F_3
K23b	0013F_2	0717E_3
0717E_3	0715E_3	0014F_6
0029F_3	0695E_6	**K23b**
0695E_6	0029F_3	0718E_2
0715E_3	0717E_3	0011F_5
0013F_2	**K23b**	0695E_6
0718E_2	0011F_5	9304E_2
9304E_2	0014F_6	

Sample handling:

Cylinders with natural gas were all days at SMU kept at 17 – 22 °C. Before measurement cylinders were kept at laboratory temperature for more than 4 hours.

Measurement Report from VNIIM

Reference method

The measurements were carried out by gas chromatography with flame ionization and thermal conductivity detection.

Instrument	Detectors	Columns	
Crystal-5000.1 (“Chromatec”, Russia)	TCD TCD FID	NaX Haye Sep R Haye Sep R	l= 2m, d_{int}=2mm l= 2m, d_{int}=2mm l= 3m, d_{int}=2mm

Data collection: Software support “Chromatec Analytic”(Russia).

Calibration standards

Characteristics of pure substances used for preparation of the calibration standards are shown in table 1.

Table 1 – Description of pure components

Component	Molar fraction, ppm	Standard uncertainty, ppm	Relative standard uncertainty, %	Cross-admixtures
Nitrogen	999988,5	0,812	0,00008	—
Carbon dioxide	999699	9,8	0,00098	Nitrogen – 220 ppm
Ethane	992228	111	0,01116	Nitrogen – 1770 ppm Carbon dioxide -20 ppm Methane – 115 ppm Propane - 2 ppm n-Butane – 3 ppm
Propane	998743	29,8	0,00299	Nitrogen – 42 ppm Methane – 194 ppm
iso-Butane	997580	67,5	0,00677	Nitrogen -550 ppm n-Butane -1600 ppm
n-Butane	994850	96,7	0,00972	Nitrogen – 600 ppm Methane - 100 ppm iso-Butane – 2400 ppm
Methane	999638	3,2	0,00032	Nitrogen – 334 ppm

Preparation of standard gas mixtures for Mixture II (cylinder № 2766 E) was carried out gravimetrically in 1 stage.

All mixtures were prepared in aluminium cylinders, $V=10dm^3$, type БД16-10-9,8 (“Poisk”, Russia).

There were prepared 3 standard gas mixtures by gravimetric method according to ISO 6142. The concentrations of the components in the calibration standards closely bracketed the expected concentrations in Mixture II.

Verification of molar fraction in prepared mixtures was carried out chromatographically. Discrepancy between the cylinders was not found out. Standard deviation inside measurement series was 0,2-0,5% for different components.

Composition and associated standard uncertainties (due to gravimetry) for each component of standard gas mixtures are shown in table 2

Table 2

Cylinder №	Component	Assigned value, mmol/mol	Relative standard uncertainty, %
0285	Nitrogen	73,08	0,03
	Carbon dioxide	32,12	0,05
	Ethane	102,0	0,02
	Propane	35,70	0,04
	iso-Butane	6,290	0,18
	n-Butane	11,64	0,10
	Methane	739,2	-
0272	Nitrogen	68,94	0,03
	Carbon dioxide	30,21	0,05
	Ethane	95,07	0,02
	Propane	37,25	0,04
	iso-Butane	7,512	0,15
	n-Butane	9,884	0,11
	Methane	751,1	-
0292	Nitrogen	64,06	0,04
	Carbon dioxide	26,70	0,06
	Ethane	88,92	0,02
	Propane	31,71	0,05
	iso-Butane	9,871	0,12
	n-Butane	7,899	0,14
	Methane	770,8	-

Instrument calibration

Bracketing was used as calibration method.

There were made 3 independent measurements under repeatability conditions with 3 independent calibrations (in 3 days during 7 days).

One single measurement (i.e. measurement series) consisted of 6 sub-measurements. The measurement sequence was “calibration$_1$ → measurement$_1$ →$_{......}$→ calibration$_6$ → measurement$_6$”.

Sample handling

Prior to measurements cylinders were stabilized to room temperature.

The samples were transferred to Gas-chromatograph by means of GC auto-sampler with 10-port multi-position valve, with sample loop V=1 cm^3.

Results of measurements

Measurement results of components mole fraction in gas mixture in cylinder № 2766 E are shown in the table 3**.**

Table 3 - Results of measurements of components mole fraction in cylinder № 2766 E

Measurement # 1

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	29/11/05	71,298	0,31	6
Carbon dioxide		30,060	0,30	6
Ethane		94,032	0,25	6
Propane		33,937	0,22	6
iso-Butane		7,811	0,26	6
n-Butane		9,985	0,51	6
Methane		752,88	-	-

Measurement # 2

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	01/12/05	71,165	0,27	6
Carbon dioxide		30,126	0,25	6
Ethane		93,774	0,37	6
Propane		33,872	0,38	6
iso-Butane		7,795	0,21	6
n-Butane		10,018	0,32	6
Methane		753,25	-	-

Measurement # 3

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	05/12/05	71,152	0,27	6
Carbon dioxide		30,057	0,33	6
Ethane		93,784	0,18	6
Propane		33,854	0,17	6
iso-Butane		7,768	0,27	6
n-Butane		10,023	0,46	6
Methane		753,36	-	-

Evaluation of uncertainty of measurements

Total standard uncertainty of components mole fraction in the studied MixtureII was calculated on the base of the following components:

- total standard uncertainty of components mole fraction in standard gas mixture (peak value), including the uncertainty in the weighing of the parent gases and the uncertainty in the purity of the parent gases;
- standard deviation of the components mole fraction measurement results in studied gas Mixture II

Uncertainty budget for components mole fraction in the studied gas Mixture II in cylinder № 2766 E are shown in the tables 5-10.

Table 5 Uncertainty budget for nitrogen mole fraction in the Mixture II

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,04	1	0,04
Standard deviation of the results of measurements	A	0,11	1	0,11
Total standard uncertainty				**0,117**
Expanded uncertainty (*k*=2)				**0,24**

Table 6. Uncertainty budget for carbon dioxide mole fraction in the Mixture II

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,06	1	0,06
Standard deviation of the results of measurements	A	0,13	1	0,13
Total standard uncertainty				**0,143**
Expanded uncertainty (*k*=2)				**0,29**

Table 7. Uncertainty budget for ethane mole fraction in the Mixture II

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,02	1	0,02
Standard deviation of the results of measurements	A	0,16	1	0,16
Total standard uncertainty				**0,161**
Expanded uncertainty (*k*=2)				**0,32**

Table 8. Uncertainty budget for propane mole fraction in the Mixture II

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,05	1	0,05
Standard deviation of the results of measurements	A	0,13	1	0,13
Total standard uncertainty				**0,139**
Expanded uncertainty (*k*=2)				**0,28**

Table 9. Uncertainty budget for iso-butane mole fraction in the Mixture II

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,18	1	0,18
Standard deviation of the results of measurements	A	0,28	1	0,28
Total standard uncertainty				**0,333**
Expanded uncertainty (*k*=2)				**0,67**

Table 10. Uncertainty budget for n-butane mole in the Mixture II

Source of uncertainty	Type of evaluation	Standard uncertainty, *u(x_i)*, %	Coefficient of sensitivity	Contribution *U_i(y, %)*
Preparation of standard gas mixture	B	0,14	1	0,14
Standard deviation of the results of measurements	A	0,21	1	0,21
Total standard uncertainty				**0,252**
Expanded uncertainty (*k*=2)				**0,50**

Final result of measurements

Final result of measurements of components mole fraction in studied gas mixture and expanded uncertainties are shown in the table 11.

Table 11. Assigned values of components mole fractions in studied gas Mixture II in cylinder № 2766E and expanded uncertainties

Component	Result (assigned value), mmol/mol	Expanded uncertainty, mmol/mol	Relative expanded uncertainty, %	Coverage factor
Nitrogen	71,21	0,17	0,24	2
Carbon dioxide	30,08	0,09	0,29	2
Ethane	93,86	0,30	0,32	2
Propane	33,89	0,10	0,28	2
iso-Butane	7,79	0,05	0,67	2
n-Butane	10,01	0,05	0,50	2
Methane*	753,2	0,4	0,05	2

***Note:**

Methane mole fraction $\mathbf{x}_{\mathbf{CH4}}$, mmol/mol, was calculated according to formula

$$\mathbf{x}_{\mathbf{CH4}} = \mathbf{1000} - \sum \mathbf{x}_{\mathbf{i}} \ .$$

Total standard uncertainty of methane mole fraction $\mathbf{u}_{\mathbf{CH4}}$, mmol/mol, was calculated according to formula

$$\mathbf{u}_{\mathbf{CH4}} = \sqrt{\sum \mathbf{u}_{\mathbf{Ai}}^{\mathbf{2}} + \sum \mathbf{u}_{\mathbf{Bi}}^{\mathbf{2}}}$$

$\mathbf{x}_{\mathbf{i}}$ – mole fraction of mixture components, mmol/mol.

$\mathbf{u}_{\mathbf{Ai}}$ and $\mathbf{u}_{\mathbf{Bi}}$ - standard uncertainties of type A and B of components mole fraction, mmol/mol and mmol/mol.