Final Report International Comparison CCQM K23ac – Natural gas types I and III

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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 types I and III natural gas.

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, Linfield, Australia
INMETRO	BR	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, Xerém RJ, Brasil
NRCCRM	CR	National Research Center for Certified Reference Materials, Beijing, PR China

Acronym	Country	Institute
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
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, Seoul, 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 King-dom

Measurement standards

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

Table 2: Nominal composition of the mixtures

Component	Mixture I x (10^{-2} mol mol^{-1})	Mixture III x (10^{-2} mol mol^{-1})
Nitrogen	4	13.5
Carbon dioxide	1	0.5
Ethane	3	3
Propane	1	0.5
n-Butane	0.2	0.1
iso-Butane	0.2	0.1
Methane	Balance	Balance

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 [5]. 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. The mixtures of both types I and III were prepared using a pre-mixture containing 60 mmol/mol CO_2, 60 mmol/mol C_3H_8, 12 mmol/mol n-C_4H_{10}, and 12 mmol/mol i-C_4H_{10} in methane. The other gases were introduced directly in the final mixture. The final mixture had a pressure of approximately 7 MPa.

All pre-mixtures have been made in the same matrix (methane) as that of the final mixtures. The target composition of all mixtures was identical (see table 2). After preparation, the mixtures have been verified by comparing the key comparison mixtures with PSMs from the standards maintenance programme. The mixtures have been verified using GC/TCD (nitrogen, carbon dioxide, methane, ethane,) 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 the address 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 2004	Preparation of the gas mixtures
July 2004	Shipment of distribution cylinders to participating laboratories
August 2004	Start of comparison
October 15, 2004	Close of comparison
October 15 2004	Cylinders and reports due to pilot laboratory

Measurement equation

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

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

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

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

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

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

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

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

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

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

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

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 [7,8] 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

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

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 [6]

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

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 [9] and takes advantage of the work done in the gravimetry study CCQM-P23 [10].

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

[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) [3].

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

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

Measurement methods

The measurement methods used by the participants are described in annex A of this report. 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	Report	Calibration	Traceability
NMIA	04-08-2004	03-09-2004	Bracketing	Own mixtures
IPQ	01-09-2004	08-10-2004	ISO 6143	NMi VSL+NPL
NRCCRM	29-09-2004	09-10-2004	OLS	Own mixtures
NMi VSL	11-10-2004	15-10-2004	OLS	Own mixtures
CMI	08-09-2004	18-10-2004	OLS	NMi VSL
LNE	09-09-2004	05-11-2004	Bracketing	Own mixtures
CENAM	27-10-2004	10-11-2004	ISO 6143	Own mixtures
CEM	22-09-2004	16-11-2004	ISO 6143	NMi VSL
KRISS	14-11-2004	26-11-2004	Matching	Own mixtures
VNIIM	18-11-2004	29-11-2004	Bracketing	Own mixtures
OMH	04-11-2004	30-11-2004	GDR	Own mixtures
BAM	30-08-2004	30-11-2004	ISO 6143	Own mixtures
INMETRO	01-10-2004	02-12-2004	OLS	NMi VSL
NPL	16-12-2004	24-12-2004	Matching	Own mixtures
SMU	18-11-2004	19-01-2005	ISO 6143	Own mixtures
GUM	10-02-2005	18-02-2005	ISO 6143	Own mixtures

Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as [3]

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

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

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

The standard uncertainty of D_i can be expressed as

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

assuming that the aggregated error terms are uncorrelated. As discussed, the combined standard uncertainty of the reference value comprises that from preparation and that from verification for the mixture involved. A bilateral degree of equivalence is defined as [3]

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

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

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

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

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 1-14, the degrees of equivalence for all participating laboratories are given relative to the gravimetric value. The uncertainties are, as required by the MRA [3], given as 95% confidence intervals. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor $k = 2$ was used. For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty (stated at a confidence level of 95%) from the laboratory was divided by the reported coverage factor.

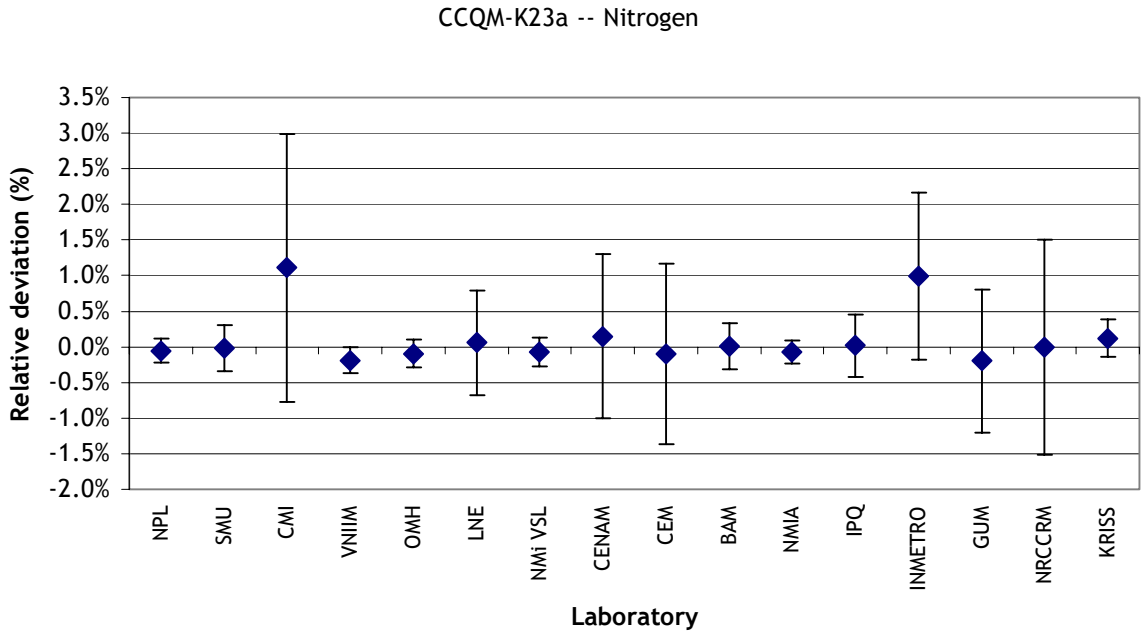

Figure 1: Degrees of equivalence for nitrogen (mixture I)

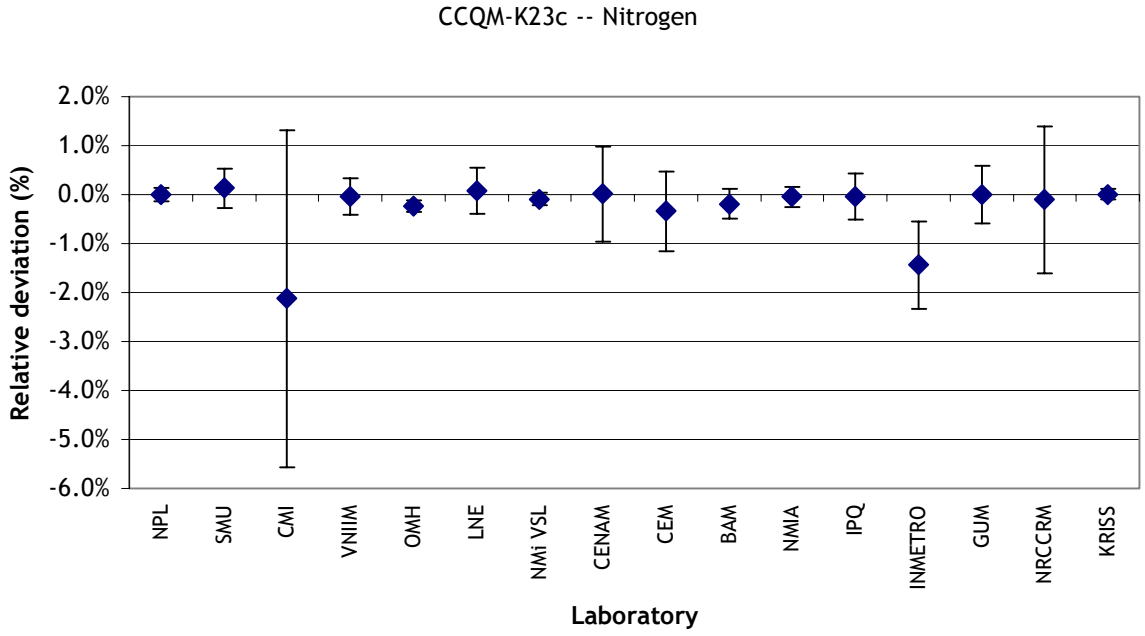

Figure 2: Degrees of equivalence for nitrogen (mixture III)

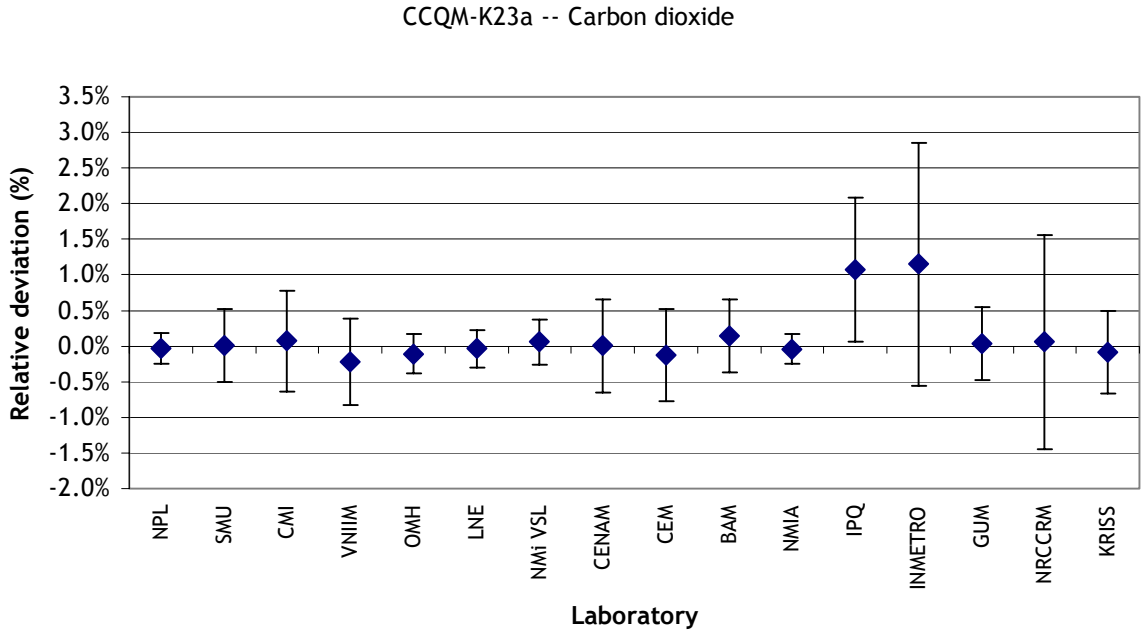

Figure 3: Degrees of equivalence for carbon dioxide (mixture I)

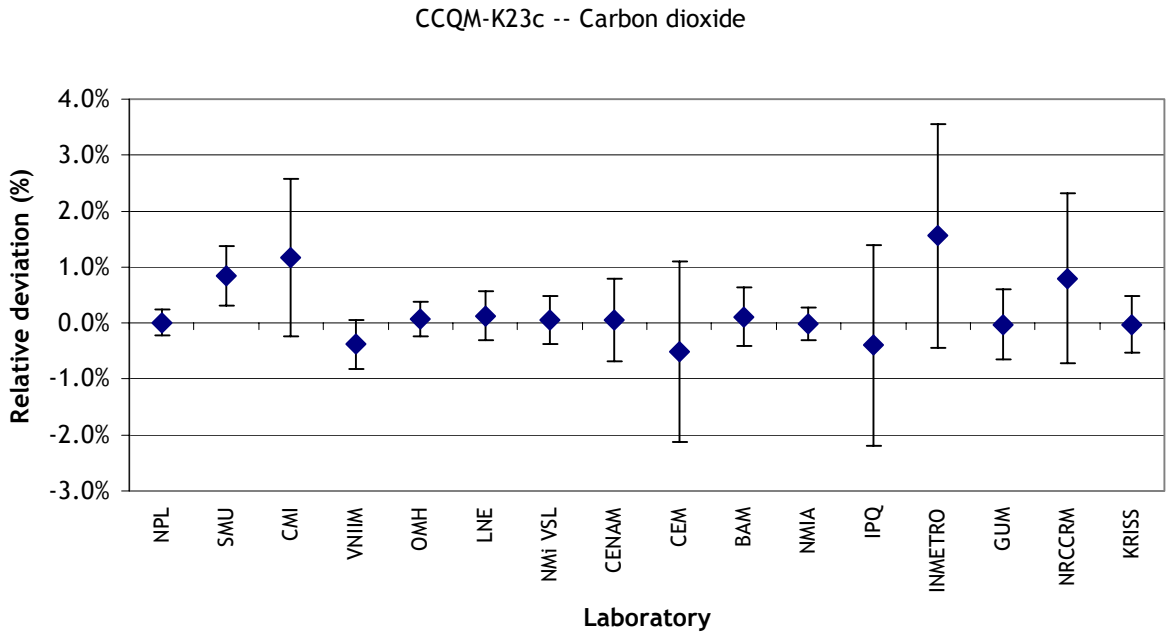

Figure 4: Degrees of equivalence for carbon dioxide (mixture III)

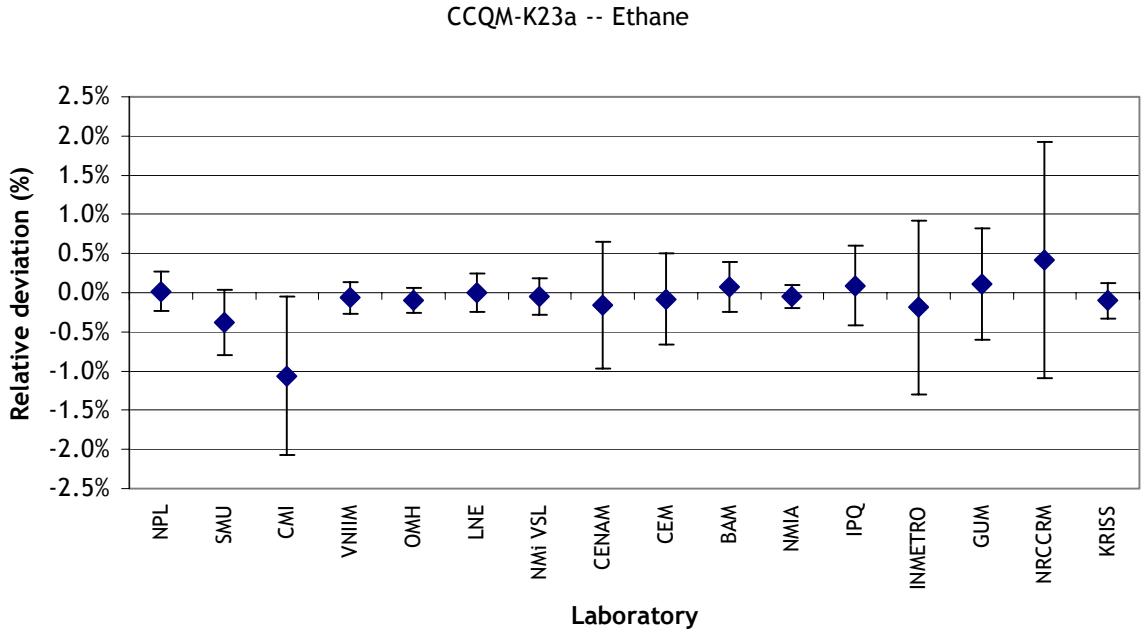

Figure 5: Degrees of equivalence for ethane (mixture I)

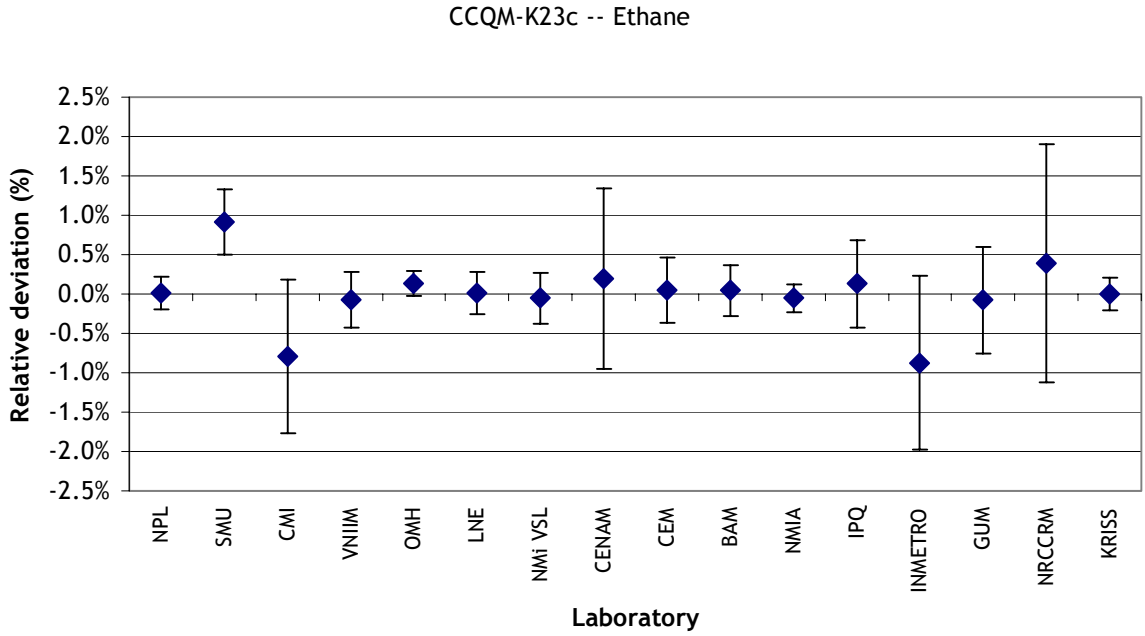

Figure 6: Degrees of equivalence for ethane (mixture III)

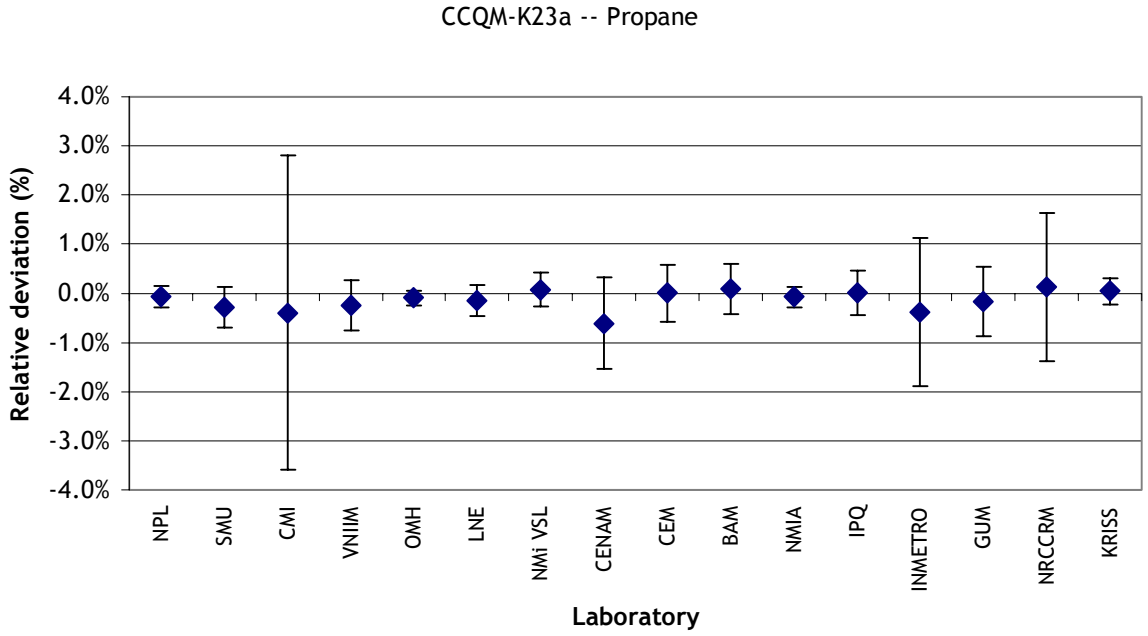

Figure 7: Degrees of equivalence for propane (mixture I)

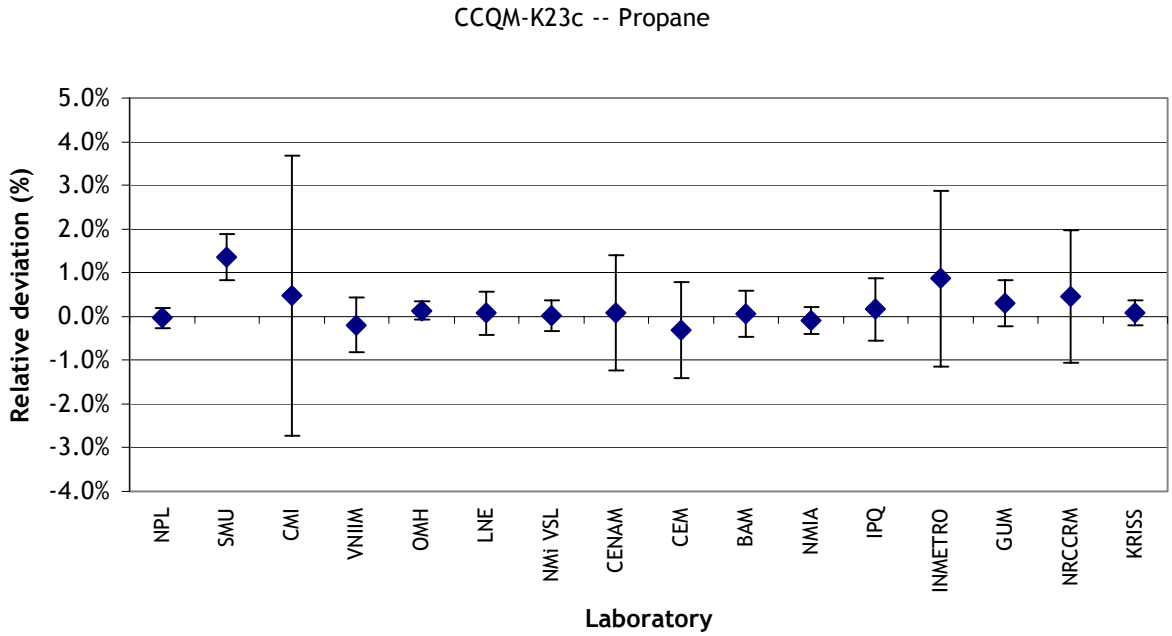

Figure 8: Degrees of equivalence for propane (mixture III)

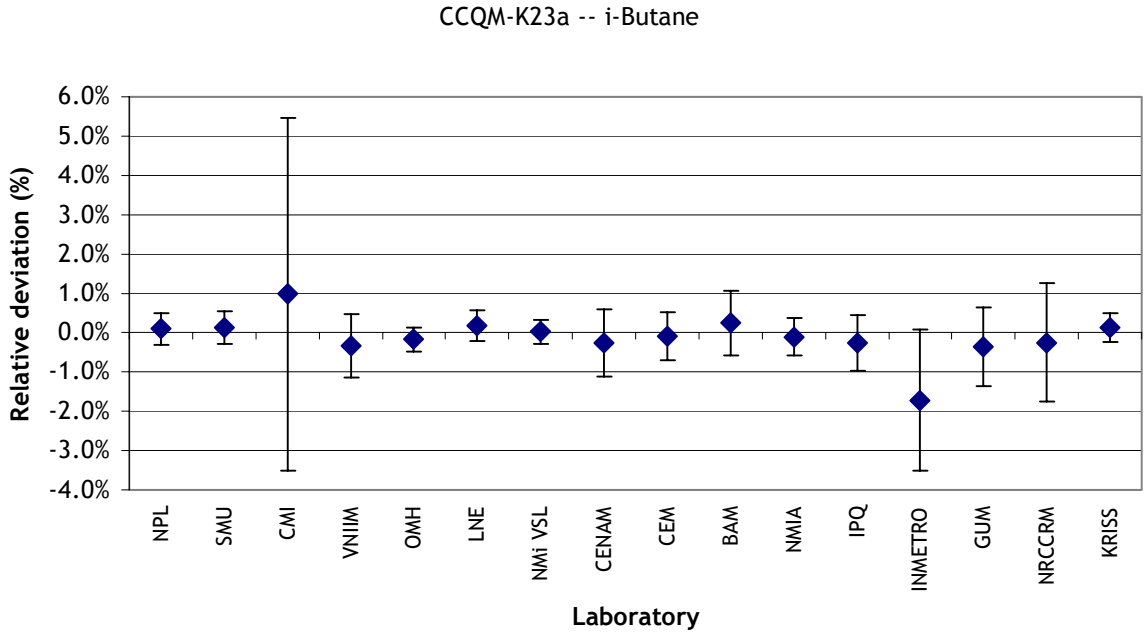

Figure 9: Degrees of equivalence for *iso*-butane (mixture I)

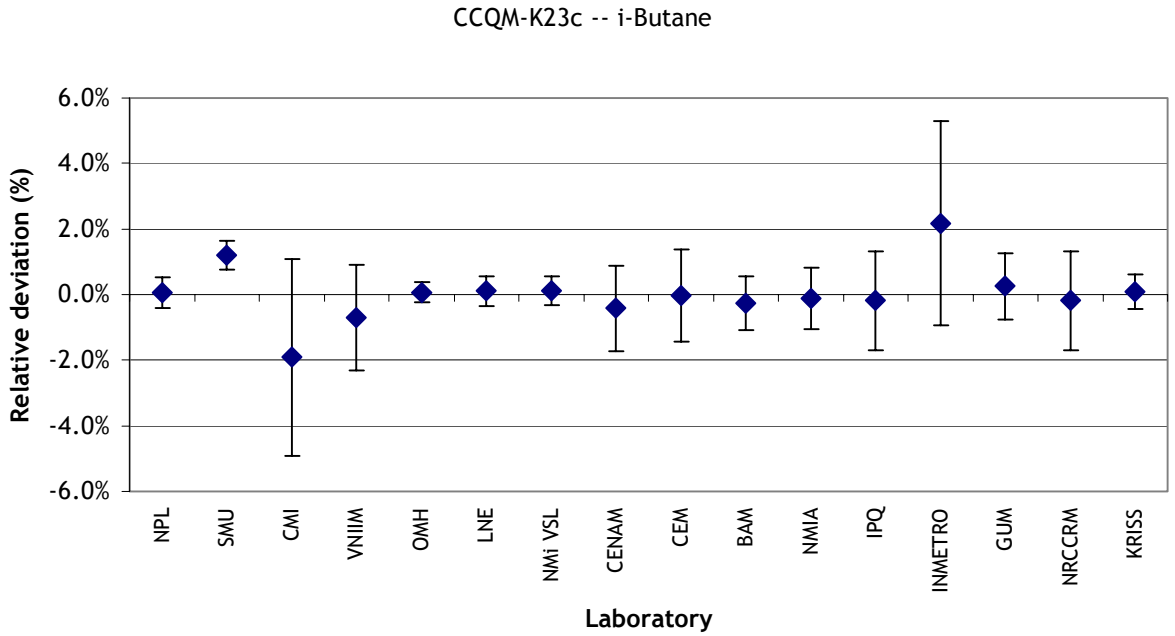

Figure 10: Degrees of equivalence for *iso*-butane (mixture III)

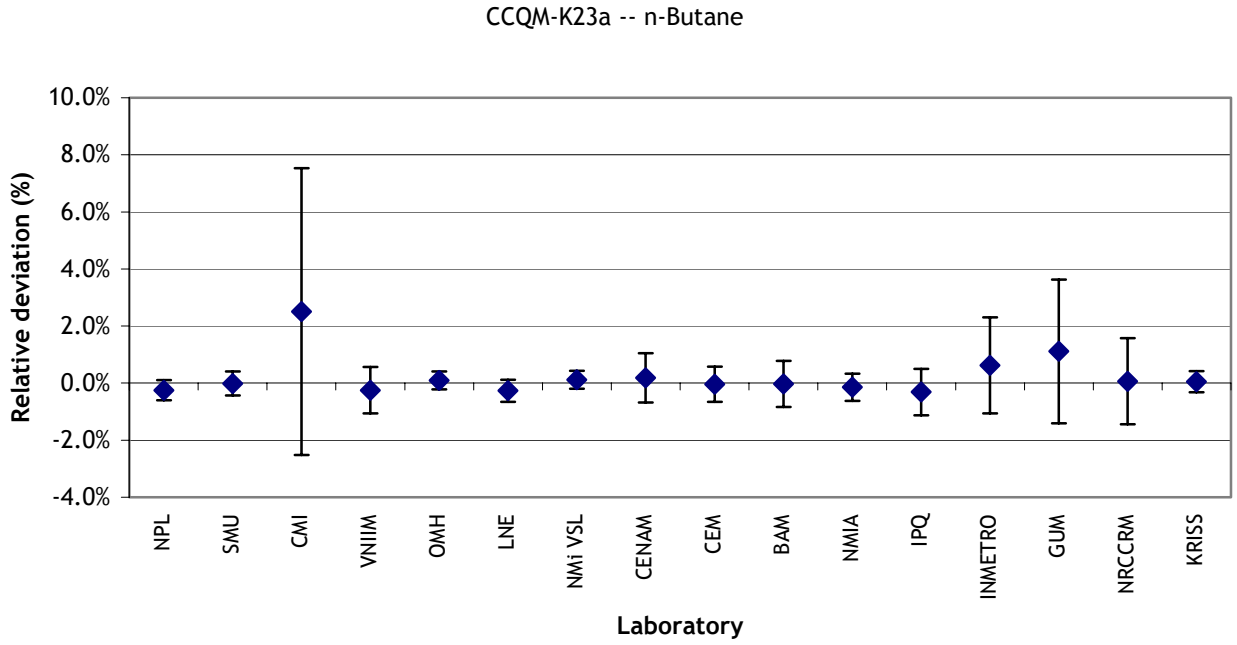

Figure 11: Degrees of equivalence for *n*-butane (mixture I)

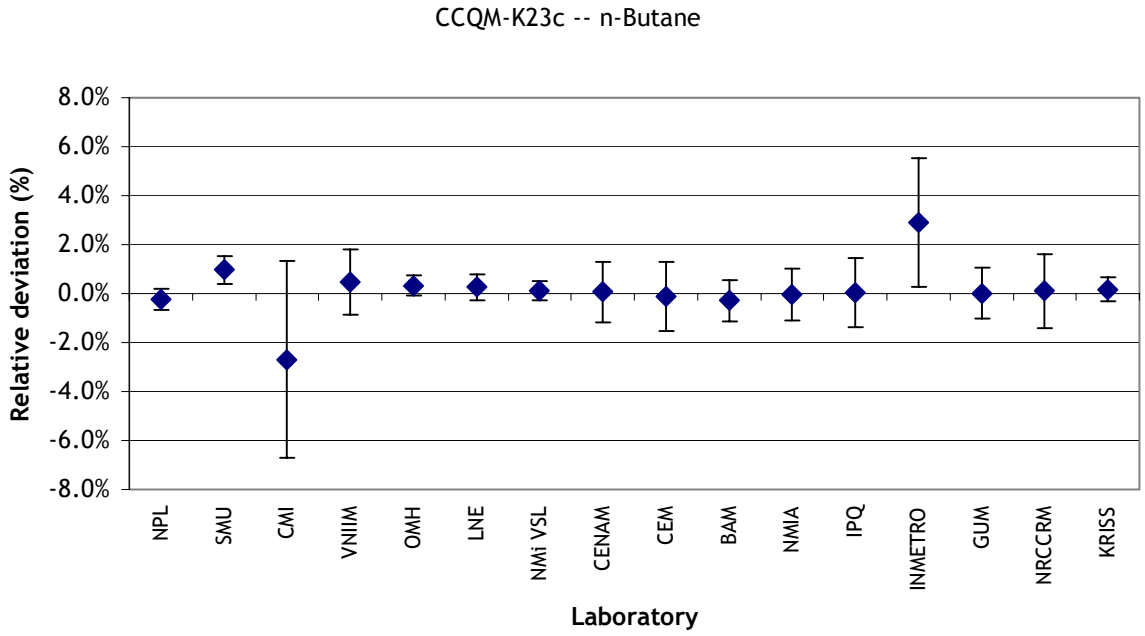

Figure 12: Degrees of equivalence for *n*-butane (mixture III)

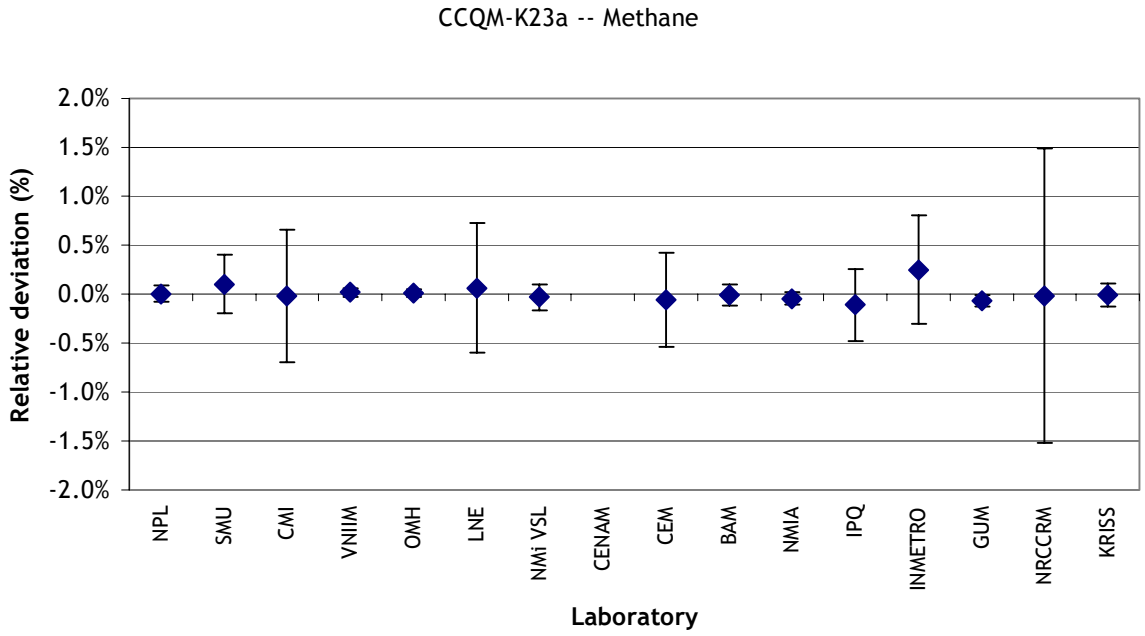

Figure 13: Degrees of equivalence for methane (mixture I)

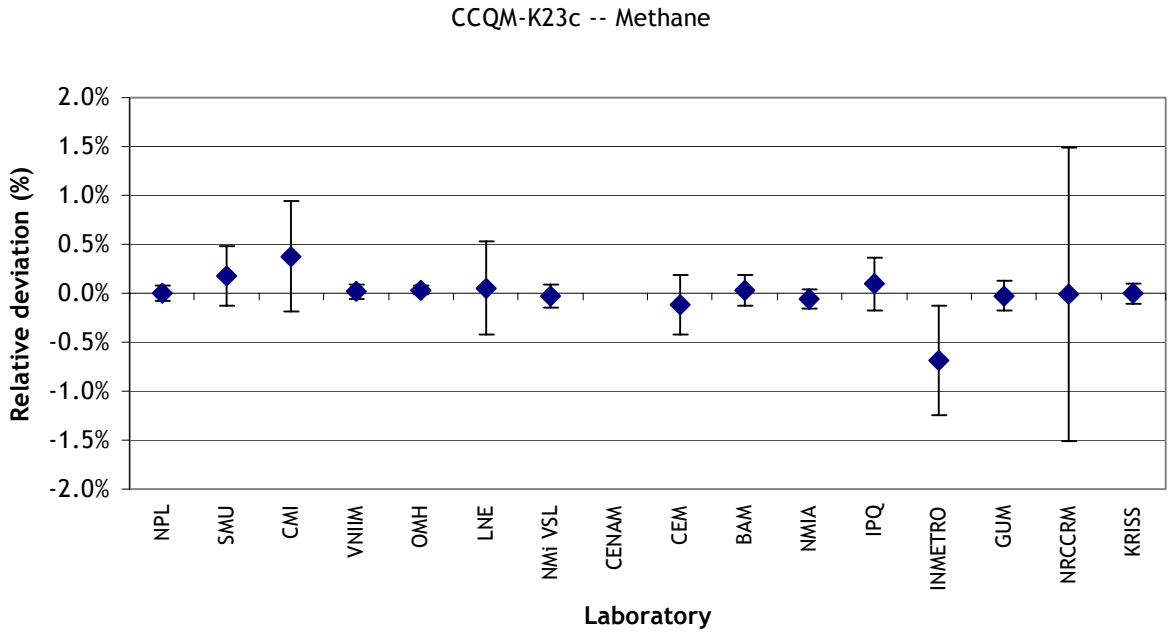

Figure 14: Degrees of equivalence for methane (mixture III)

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[3] (10^{-2} mol/mol)

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

Table 4: Results for nitrogen, mixture I

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL202748	4.01030	0.00089	0.00201	0.00219	4.008	0.005	2	-0.002	2	0.007
SMU	VSL100039	3.99779	0.00083	0.00201	0.00217	3.997	0.012	2	-0.001	2	0.013
CMI	VSL100059	3.98973	0.00083	0.00201	0.00217	4.034	0.075	2	0.044	2	0.075
VNIIM	VSL126708	4.01564	0.00081	0.00201	0.00216	4.008	0.006	2	-0.008	2	0.007
OMH	VSL100051	4.00164	0.00083	0.00201	0.00217	3.9979	0.008	2.43	-0.004	2	0.008
LNE	VSL124466	3.97075	0.00084	0.00201	0.00217	3.973	0.029	2	0.002	2	0.029
NMi VSL	VSL226686	4.05572	0.00089	0.00201	0.00219	4.053	0.007	2	-0.003	2	0.008
CENAM	VSL126717	4.02404	0.00083	0.00201	0.00217	4.03	0.046	2	0.006	2	0.046
CEM	VSL100066	4.03512	0.00082	0.00201	0.00217	4.0313	0.051	2	-0.004	2	0.051
BAM	VSL100042	4.02178	0.00083	0.00201	0.00217	4.0221	0.012	2	0.000	2	0.013
NMIA	VSL126712	4.01585	0.00084	0.00201	0.00217	4.013	0.005	2.18	-0.003	2	0.006
IPQ	VSL100038	3.99525	0.00083	0.00201	0.00217	3.996	0.017	2	0.001	2	0.018
INMETRO	VSL100041	4.02527	0.00083	0.00201	0.00217	4.065	0.047	2	0.040	2	0.047
GUM	VSL100044	3.99888	0.00083	0.00201	0.00217	3.991	0.04	2	-0.008	2	0.040
NRCCRM	VSL126730	4.02720	0.00083	0.00201	0.00217	4.027	0.060	2	0.000	2	0.061
KRISS	VSL126709	3.97473	0.00085	0.00201	0.00218	3.9796	0.0093	2	0.005	2	0.010

Table 5: Results for nitrogen, mixture III

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL206333	13.50192	0.00120	0.00675	0.00686	13.502	0.012	2	0.000	2	0.018
SMU	VSL202622	13.50495	0.00120	0.00201	0.00233	13.523	0.054	2	0.018	2	0.054
CMI	VSL205133	13.48584	0.00119	0.00201	0.00233	13.199	0.463	2	-0.287	2	0.463
VNIIM	VSL202624	13.51633	0.00121	0.00201	0.00234	13.510	0.050	2	-0.006	2	0.050
OMH	VSL206344	13.49718	0.00118	0.00201	0.00233	13.465	0.018	2.43	-0.032	2	0.016
LNE	VSL202614	13.46530	0.00120	0.00201	0.00234	13.475	0.063	2	0.010	2	0.063
NMi VSL	VSL300636	13.48812	0.00121	0.00201	0.00234	13.476	0.017	2	-0.012	2	0.018
CENAM	VSL160258	13.50852	0.00122	0.00201	0.00234	13.510	0.130	2	0.001	2	0.130
CEM	VSL202677	13.51843	0.00121	0.00201	0.00234	13.472	0.110	2	-0.046	2	0.110
BAM	VSL205189	13.50933	0.00120	0.00201	0.00234	13.484	0.040	2	-0.026	2	0.041
NMIA	VSL228583	13.50619	0.00121	0.00201	0.00234	13.500	0.030	2.18	-0.006	2	0.028
IPQ	VSL220210	13.48522	0.00120	0.00201	0.00233	13.480	0.063	2	-0.005	2	0.063
INMETRO	VSL202750	13.49382	0.00120	0.00201	0.00233	13.300	0.120	2	-0.194	2	0.120
GUM	VSL223562	13.56311	0.00119	0.00201	0.00233	13.564	0.080	2	0.001	2	0.080
NRCCRM	VSL228668	13.51400	0.00121	0.00201	0.00234	13.500	0.203	2	-0.014	2	0.203
KRISS	VSL229332	13.50019	0.00122	0.00201	0.00235	13.501	0.013	2	0.001	2	0.014

Table 6: Results for carbon dioxide, mixture I

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL202748	1.00102	0.00065	0.00050	0.00082	1.0007	0.0015	2	-0.0003	2	0.0022
SMU	VSL100039	0.99797	0.00012	0.00050	0.00051	0.9981	0.0050	2	0.0001	2	0.0051
CMI	VSL100059	1.00130	0.00012	0.00050	0.00052	1.0020	0.0070	2	0.0007	2	0.0071
VNIIM	VSL126708	1.00125	0.00012	0.00050	0.00051	0.9990	0.0060	2	-0.0023	2	0.0061
OMH	VSL100051	0.99938	0.00012	0.00050	0.00051	0.9983	0.0030	2.37	-0.0011	2	0.0027
LNE	VSL124466	0.99844	0.00012	0.00050	0.00051	0.9981	0.0024	2	-0.0003	2	0.0026
NMi VSL	VSL226686	0.99933	0.00065	0.00050	0.00082	0.9999	0.0027	2	0.0006	2	0.0032
CENAM	VSL126717	1.00095	0.00012	0.00050	0.00051	1.0010	0.0065	2	0.0000	2	0.0066
CEM	VSL100066	0.99759	0.00012	0.00050	0.00051	0.9963	0.0064	2	-0.0013	2	0.0065
BAM	VSL100042	0.99847	0.00012	0.00050	0.00051	0.9999	0.0050	2	0.0014	2	0.0051
NMIA	VSL126712	1.00043	0.00012	0.00050	0.00051	1.0000	0.0020	2.18	-0.0004	2	0.0021
IPQ	VSL100038	0.99929	0.00012	0.00050	0.00051	1.0100	0.0100	2	0.0107	2	0.0101
INMETRO	VSL100041	0.99752	0.00012	0.00050	0.00051	1.0090	0.0170	2	0.0115	2	0.0170
GUM	VSL100044	0.99924	0.00012	0.00050	0.00051	0.9996	0.0050	2	0.0004	2	0.0051
NRCCRM	VSL126730	1.00441	0.00012	0.00050	0.00052	1.0050	0.0151	2	0.0006	2	0.0151
KRISS	VSL126709	1.00506	0.00012	0.00050	0.00052	1.0042	0.0057	2	-0.0009	2	0.0058

Table 7: Results for carbon dioxide, mixture III

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL206333	0.50110	0.00034	0.00025	0.00042	0.501	0.001	2	0.0000	2	0.0012
SMU	VSL202622	0.50069	0.00034	0.00025	0.00042	0.505	0.003	2	0.0042	2	0.0026
CMI	VSL205133	0.50016	0.00034	0.00025	0.00042	0.506	0.007	2	0.0058	2	0.0070
VNIIM	VSL202624	0.50092	0.00034	0.00025	0.00042	0.499	0.002	2	-0.0019	2	0.0022
OMH	VSL206344	0.50087	0.00034	0.00025	0.00042	0.501	0.002	2.32	0.0003	2	0.0015
LNE	VSL202614	0.49885	0.00034	0.00025	0.00042	0.500	0.002	2	0.0006	2	0.0022
NMi VSL	VSL300636	0.50005	0.00034	0.00025	0.00042	0.500	0.002	2	0.0003	2	0.0022
CENAM	VSL160258	0.50151	0.00034	0.00025	0.00042	0.502	0.004	2	0.0003	2	0.0037
CEM	VSL202677	0.50027	0.00034	0.00025	0.00042	0.498	0.008	2	-0.0026	2	0.0080
BAM	VSL205189	0.50094	0.00034	0.00025	0.00042	0.502	0.003	2	0.0006	2	0.0026
NMIA	VSL228583	0.49899	0.00034	0.00025	0.00042	0.499	0.001	2.18	-0.0001	2	0.0015
IPQ	VSL220210	0.50301	0.00034	0.00025	0.00042	0.501	0.009	2	-0.0020	2	0.0090
INMETRO	VSL202750	0.50022	0.00034	0.00025	0.00042	0.508	0.010	2	0.0078	2	0.0100
GUM	VSL223562	0.50093	0.00034	0.00025	0.00042	0.501	0.003	2	-0.0001	2	0.0031
NRCCRM	VSL228668	0.50129	0.00034	0.00025	0.00042	0.505	0.008	2	0.0040	2	0.0076
KRISS	VSL229332	0.50044	0.00034	0.00025	0.00042	0.5003	0.0024	2	-0.0001	2	0.0025

Table 8: Results for ethane, mixture I

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL202748	2.99446	0.00081	0.00150	0.00170	2.9950	0.0066	2	0.0005	2	0.0074
SMU	VSL100039	2.98751	0.00077	0.00149	0.00168	2.9760	0.0120	2	-0.0115	2	0.0125
CMI	VSL100059	2.99380	0.00078	0.00150	0.00169	2.9620	0.0300	2	-0.0318	2	0.0302
VNIIM	VSL126708	2.99800	0.00076	0.00150	0.00168	2.9960	0.0050	2	-0.0020	2	0.0060
OMH	VSL100051	3.00284	0.00078	0.00150	0.00169	2.9999	0.0042	2.43	-0.0029	2	0.0048
LNE	VSL124466	3.00999	0.00078	0.00150	0.00170	3.0099	0.0065	2	-0.0001	2	0.0073
NMi VSL	VSL226686	2.98743	0.00082	0.00149	0.00170	2.9860	0.0060	2	-0.0014	2	0.0069
CENAM	VSL126717	3.00169	0.00078	0.00150	0.00169	2.9970	0.0240	2	-0.0047	2	0.0242
CEM	VSL100066	2.98971	0.00077	0.00149	0.00168	2.9873	0.0170	2	-0.0024	2	0.0173
BAM	VSL100042	2.98643	0.00078	0.00149	0.00168	2.9886	0.0090	2	0.0022	2	0.0096
NMIA	VSL126712	2.99041	0.00078	0.00150	0.00169	2.9890	0.0030	2.18	-0.0014	2	0.0044
IPQ	VSL100038	2.99427	0.00078	0.00150	0.00169	2.9970	0.0150	2	0.0027	2	0.0154
INMETRO	VSL100041	2.98755	0.00078	0.00149	0.00168	2.9820	0.0330	2	-0.0055	2	0.0332
GUM	VSL100044	2.99268	0.00078	0.00150	0.00169	2.9960	0.0210	2	0.0033	2	0.0213
NRCCRM	VSL126730	3.00055	0.00077	0.00150	0.00169	3.0130	0.0452	2	0.0125	2	0.0453
KRISS	VSL126709	3.01002	0.00080	0.00151	0.00170	3.0069	0.0060	2	-0.0031	2	0.0069

Table 9: Results for ethane, mixture III

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL206333	2.98963	0.00079	0.00149	0.00169	2.990	0.005	2	0.0004	2	0.0061
SMU	VSL202622	3.00063	0.00079	0.00150	0.00170	3.028	0.012	2	0.0274	2	0.0125
CMI	VSL205133	2.98672	0.00078	0.00149	0.00169	2.963	0.029	2	-0.0237	2	0.0292
VNIIM	VSL202624	2.99821	0.00080	0.00150	0.00170	2.996	0.010	2	-0.0022	2	0.0106
OMH	VSL206344	2.99665	0.00078	0.00150	0.00169	3.001	0.004	2.43	0.0040	2	0.0048
LNE	VSL202614	3.00924	0.00080	0.00150	0.00170	3.010	0.007	2	0.0003	2	0.0081
NMi VSL	VSL300636	2.99555	0.00080	0.00150	0.00170	2.994	0.009	2	-0.0015	2	0.0096
CENAM	VSL160258	2.97632	0.00081	0.00149	0.00169	2.982	0.034	2	0.0057	2	0.0342
CEM	VSL202677	2.99762	0.00080	0.00150	0.00170	2.999	0.012	2	0.0014	2	0.0125
BAM	VSL205189	2.99508	0.00080	0.00150	0.00170	2.996	0.009	2	0.0013	2	0.0096
NMIA	VSL228583	3.00583	0.00081	0.00150	0.00171	3.004	0.004	2.18	-0.0016	2	0.0052
IPQ	VSL220210	2.95513	0.00079	0.00148	0.00167	2.959	0.016	2	0.0039	2	0.0163
INMETRO	VSL202750	3.00221	0.00079	0.00150	0.00170	2.976	0.033	2	-0.0262	2	0.0332
GUM	VSL223562	2.99424	0.00078	0.00150	0.00169	2.992	0.020	2	-0.0022	2	0.0203
NRCCRM	VSL228668	2.97740	0.00080	0.00149	0.00169	2.989	0.045	2	0.0116	2	0.0450
KRISS	VSL229332	2.99219	0.00082	0.00150	0.00170	2.9922	0.0051	2	0.0000	2	0.0061

Table 10: Results for propane, mixture I

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL202748	0.99993	0.00065	0.00050	0.00082	0.9993	0.0013	2	-0.0007	2	0.0021
SMU	VSL100039	0.99868	0.00013	0.00050	0.00052	0.9959	0.0040	2	-0.0028	2	0.0041
CMI	VSL100059	1.00096	0.00013	0.00050	0.00052	0.9970	0.0320	2	-0.0040	2	0.0320
VNIIM	VSL126708	1.00240	0.00013	0.00050	0.00052	1.0000	0.0050	2	-0.0024	2	0.0051
OMH	VSL100051	0.99904	0.00013	0.00050	0.00052	0.9981	0.0012	2.37	-0.0009	2	0.0014
LNE	VSL124466	0.99958	0.00013	0.00050	0.00052	0.9981	0.0030	2	-0.0015	2	0.0032
NMi VSL	VSL226686	0.99825	0.00065	0.00050	0.00082	0.9990	0.0030	2	0.0008	2	0.0034
CENAM	VSL126717	1.00210	0.00013	0.00050	0.00052	0.9960	0.0092	2	-0.0061	2	0.0093
CEM	VSL100066	0.99830	0.00013	0.00050	0.00052	0.9983	0.0057	2	0.0000	2	0.0058
BAM	VSL100042	0.99778	0.00013	0.00050	0.00052	0.9986	0.0050	2	0.0008	2	0.0051
NMIA	VSL126712	1.00276	0.00012	0.00050	0.00052	1.0020	0.0020	2.18	-0.0008	2	0.0021
IPQ	VSL100038	0.99999	0.00013	0.00050	0.00052	1.0001	0.0043	2	0.0001	2	0.0044
INMETRO	VSL100041	0.99683	0.00013	0.00050	0.00051	0.9930	0.0150	2	-0.0038	2	0.0150
GUM	VSL100044	0.99890	0.00013	0.00050	0.00052	0.9972	0.0070	2	-0.0017	2	0.0071
NRCCRM	VSL126730	1.00675	0.00012	0.00050	0.00052	1.0080	0.0151	2	0.0013	2	0.0152
KRISS	VSL126709	1.00740	0.00012	0.00050	0.00052	1.0078	0.0024	2	0.0004	2	0.0026

Table 11: Results for propane, mixture III

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL206333	0.50016	0.00034	0.00025	0.00042	0.5000	0.0007	2	-0.0002	2	0.0011
SMU	VSL202622	0.50016	0.00034	0.00025	0.00042	0.5069	0.0025	2	0.0067	2	0.0026
CMI	VSL205133	0.49963	0.00034	0.00025	0.00042	0.5020	0.0160	2	0.0024	2	0.0160
VNIIM	VSL202624	0.49998	0.00034	0.00025	0.00042	0.4990	0.0030	2	-0.0010	2	0.0031
OMH	VSL206344	0.49993	0.00033	0.00025	0.00042	0.5006	0.0007	2.25	0.0007	2	0.0010
LNE	VSL202614	0.49792	0.00033	0.00025	0.00042	0.4983	0.0023	2	0.0004	2	0.0024
NMi VSL	VSL300636	0.49952	0.00034	0.00025	0.00042	0.4996	0.0015	2	0.0001	2	0.0017
CENAM	VSL160258	0.50057	0.00034	0.00025	0.00042	0.5010	0.0065	2	0.0004	2	0.0066
CEM	VSL202677	0.49974	0.00034	0.00025	0.00042	0.4982	0.0054	2	-0.0015	2	0.0055
BAM	VSL205189	0.50001	0.00034	0.00025	0.00042	0.5003	0.0025	2	0.0003	2	0.0026
NMIA	VSL228583	0.49806	0.00033	0.00025	0.00042	0.4976	0.0014	2.18	-0.0005	2	0.0015
IPQ	VSL220210	0.50248	0.00034	0.00025	0.00042	0.5033	0.0035	2	0.0008	2	0.0036
INMETRO	VSL202750	0.49969	0.00034	0.00025	0.00042	0.5040	0.0100	2	0.0043	2	0.0100
GUM	VSL223562	0.49999	0.00033	0.00025	0.00042	0.5015	0.0025	2	0.0015	2	0.0026
NRCCRM	VSL228668	0.50035	0.00034	0.00025	0.00042	0.5026	0.0075	2	0.0022	2	0.0076
KRISS	VSL229332	0.49950	0.00034	0.00025	0.00042	0.4999	0.0012	2	0.0004	2	0.0015

Table 12: Results for *iso*-butane, mixture I

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL202748	0.200292	0.000152	0.000100	0.000182	0.20050	0.00072	2	0.0002	2	0.0008
SMU	VSL100039	0.200339	0.000068	0.000100	0.000121	0.20061	0.00080	2	0.0003	2	0.0008
CMI	VSL100059	0.201033	0.000069	0.000101	0.000122	0.20300	0.00900	2	0.0020	2	0.0090
VNIIM	VSL126708	0.200557	0.000067	0.000100	0.000121	0.19990	0.00160	2	-0.0007	2	0.0016
OMH	VSL100051	0.200648	0.000068	0.000100	0.000121	0.20030	0.00070	2.43	-0.0003	2	0.0006
LNE	VSL124466	0.199993	0.000067	0.000100	0.000121	0.20037	0.00074	2	0.0004	2	0.0008
NMi VSL	VSL226686	0.199955	0.000152	0.000100	0.000182	0.20000	0.00050	2	0.0000	2	0.0006
CENAM	VSL126717	0.200497	0.000068	0.000100	0.000121	0.20000	0.00170	2	-0.0005	2	0.0017
CEM	VSL100066	0.200262	0.000068	0.000100	0.000121	0.20010	0.00120	2	-0.0002	2	0.0012
BAM	VSL100042	0.199815	0.000067	0.000100	0.000121	0.20030	0.00160	2	0.0005	2	0.0016
NMIA	VSL126712	0.200704	0.000068	0.000100	0.000121	0.20050	0.00100	2.18	-0.0002	2	0.0009
IPQ	VSL100038	0.200602	0.000068	0.000100	0.000121	0.20010	0.00140	2	-0.0005	2	0.0014
INMETRO	VSL100041	0.199624	0.000067	0.000100	0.000120	0.19620	0.00360	2	-0.0034	2	0.0036
GUM	VSL100044	0.200620	0.000068	0.000100	0.000121	0.19990	0.00200	2	-0.0007	2	0.0020
NRCCRM	VSL126730	0.201502	0.000068	0.000101	0.000121	0.20100	0.00302	2	-0.0005	2	0.0030
KRISS	VSL126709	0.201631	0.000068	0.000101	0.000122	0.20190	0.00070	2	0.0003	2	0.0007

Table 13: Results for *iso*-butane, mixture III

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL206333	0.100281	0.000078	0.000050	0.000093	0.10034	0.00043	2	0.0001	2	0.0005
SMU	VSL202622	0.100018	0.000078	0.000050	0.000093	0.10121	0.00040	2	0.0012	2	0.0004
CMI	VSL205133	0.099912	0.000078	0.000050	0.000093	0.09800	0.00300	2	-0.0019	2	0.0030
VNIIM	VSL202624	0.100305	0.000078	0.000050	0.000093	0.09960	0.00160	2	-0.0007	2	0.0016
OMH	VSL206344	0.100236	0.000078	0.000050	0.000093	0.10030	0.00030	2.43	0.0001	2	0.0003
LNE	VSL202614	0.099891	0.000078	0.000050	0.000093	0.10000	0.00042	2	0.0001	2	0.0005
NMi VSL	VSL300636	0.099889	0.000078	0.000050	0.000093	0.10000	0.00040	2	0.0001	2	0.0004
CENAM	VSL160258	0.100424	0.000079	0.000050	0.000093	0.10000	0.00130	2	-0.0004	2	0.0013
CEM	VSL202677	0.099934	0.000078	0.000050	0.000093	0.09990	0.00140	2	0.0000	2	0.0014
BAM	VSL205189	0.100250	0.000078	0.000050	0.000093	0.10000	0.00080	2	-0.0002	2	0.0008
NMIA	VSL228583	0.099919	0.000078	0.000050	0.000093	0.09980	0.00100	2.18	-0.0001	2	0.0009
IPQ	VSL220210	0.100481	0.000079	0.000050	0.000093	0.10030	0.00150	2	-0.0002	2	0.0015
INMETRO	VSL202750	0.099923	0.000078	0.000050	0.000093	0.10210	0.00310	2	0.0022	2	0.0031
GUM	VSL223562	0.100247	0.000078	0.000050	0.000093	0.10050	0.00100	2	0.0003	2	0.0010
NRCCRM	VSL228668	0.100379	0.000079	0.000050	0.000093	0.10020	0.00150	2	-0.0002	2	0.0015
KRISS	VSL229332	0.100209	0.000078	0.000050	0.000093	0.10030	0.00050	2	0.0001	2	0.0005

Table 14: Results for *n*-butane, mixture I

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL202748	0.199406	0.000152	0.000100	0.000181	0.19891	0.00060	2	-0.0005	2	0.0007
SMU	VSL100039	0.198861	0.000068	0.000099	0.000121	0.19883	0.00080	2	0.0000	2	0.0008
CMI	VSL100059	0.199004	0.000069	0.000100	0.000121	0.20400	0.01000	2	0.0050	2	0.0100
VNIIM	VSL126708	0.198692	0.000067	0.000099	0.000120	0.19820	0.00160	2	-0.0005	2	0.0016
OMH	VSL100051	0.198622	0.000068	0.000099	0.000121	0.19880	0.00070	2.43	0.0002	2	0.0006
LNE	VSL124466	0.198133	0.000067	0.000099	0.000120	0.19760	0.00073	2	-0.0005	2	0.0008
NMi VSL	VSL226686	0.199070	0.000151	0.000100	0.000181	0.19930	0.00050	2	0.0002	2	0.0006
CENAM	VSL126717	0.198632	0.000068	0.000099	0.000120	0.19900	0.00170	2	0.0004	2	0.0017
CEM	VSL100066	0.198785	0.000068	0.000099	0.000121	0.19870	0.00120	2	-0.0001	2	0.0012
BAM	VSL100042	0.196758	0.000067	0.000098	0.000119	0.19670	0.00157	2	-0.0001	2	0.0016
NMIA	VSL126712	0.198084	0.000068	0.000099	0.000120	0.19780	0.00100	2.18	-0.0003	2	0.0009
IPQ	VSL100038	0.199122	0.000068	0.000100	0.000121	0.19850	0.00160	2	-0.0006	2	0.0016
INMETRO	VSL100041	0.196570	0.000067	0.000098	0.000119	0.19780	0.00330	2	0.0012	2	0.0033
GUM	VSL100044	0.198595	0.000068	0.000099	0.000121	0.20080	0.00500	2	0.0022	2	0.0050
NRCCRM	VSL126730	0.198872	0.000068	0.000099	0.000120	0.19900	0.00299	2	0.0001	2	0.0030
KRISS	VSL126709	0.199000	0.000068	0.000099	0.000120	0.19910	0.00070	2	0.0001	2	0.0007

Table 15: Results for *n*-butane, mixture III

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL206333	0.099917	0.000078	0.000100	0.000127	0.09969	0.00036	2	-0.0002	2	0.0004
SMU	VSL202622	0.099800	0.000078	0.000100	0.000127	0.10077	0.00050	2	0.0010	2	0.0006
CMI	VSL205133	0.099695	0.000078	0.000100	0.000127	0.09700	0.00400	2	-0.0027	2	0.0040
VNIIM	VSL202624	0.099523	0.000078	0.000100	0.000126	0.10000	0.00130	2	0.0005	2	0.0013
OMH	VSL206344	0.099872	0.000078	0.000100	0.000127	0.10020	0.00040	2.43	0.0003	2	0.0004
LNE	VSL202614	0.099112	0.000078	0.000099	0.000126	0.09937	0.00046	2	0.0003	2	0.0005
NMi VSL	VSL300636	0.099672	0.000078	0.000100	0.000127	0.09980	0.00030	2	0.0001	2	0.0004
CENAM	VSL160258	0.099641	0.000078	0.000100	0.000127	0.09970	0.00120	2	0.0001	2	0.0012
CEM	VSL202677	0.099716	0.000078	0.000100	0.000127	0.09960	0.00140	2	-0.0001	2	0.0014
BAM	VSL205189	0.099886	0.000078	0.000100	0.000127	0.09960	0.00080	2	-0.0003	2	0.0008
NMIA	VSL228583	0.099140	0.000078	0.000099	0.000126	0.09910	0.00110	2.18	0.0000	2	0.0010
IPQ	VSL220210	0.100262	0.000078	0.000100	0.000127	0.10030	0.00140	2	0.0000	2	0.0014
INMETRO	VSL202750	0.099706	0.000078	0.000100	0.000127	0.10260	0.00260	2	0.0029	2	0.0026
GUM	VSL223562	0.099883	0.000078	0.000100	0.000127	0.09990	0.00100	2	0.0000	2	0.0010
NRCCRM	VSL228668	0.099597	0.000078	0.000100	0.000127	0.09970	0.00150	2	0.0001	2	0.0015
KRISS	VSL229332	0.099428	0.000078	0.000099	0.000126	0.09960	0.00040	2	0.0002	2	0.0005

Table 16: Results for methane, mixture I

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL202748	90.5943	0.0090	0.0181	0.0202	90.5980	0.0634	2	0.004	2	0.075
SMU	VSL100039	90.6185	0.0012	0.0181	0.0182	90.7100	0.2700	2	0.092	2	0.272
CMI	VSL100059	90.6138	0.0012	0.0181	0.0182	90.5970	0.6150	2	-0.017	2	0.616
VNIIM	VSL126708	90.5831	0.0012	0.0181	0.0182	90.5990	0.0120	2	0.016	2	0.038
OMH	VSL100051	90.5975	0.0012	0.0181	0.0182	90.6067	0.0102	2.43	0.009	2	0.037
LNE	VSL124466	90.6227	0.0012	0.0181	0.0182	90.6800	0.6000	2	0.057	2	0.601
NMi VSL	VSL226686	90.5599	0.0090	0.0181	0.0202	90.5300	0.1100	2	-0.030	2	0.117
CENAM	VSL126717	90.5717	0.0012	0.0181	0.0182			2			
CEM	VSL100066	90.5799	0.0012	0.0181	0.0182	90.5280	0.4310	2	-0.052	2	0.433
BAM	VSL100042	90.5986	0.0012	0.0181	0.0182	90.5938	0.0906	2	-0.005	2	0.098
NMIA	VSL126712	90.5914	0.0012	0.0181	0.0182	90.5500	0.0500	2.18	-0.041	2	0.059
IPQ	VSL100038	90.6111	0.0012	0.0181	0.0182	90.5100	0.3300	2	-0.101	2	0.332
INMETRO	VSL100041	90.5963	0.0012	0.0181	0.0182	90.8200	0.5000	2	0.224	2	0.501
GUM	VSL100044	90.6107	0.0012	0.0181	0.0182	90.5500	0.0400	2	-0.061	2	0.054
NRCCRM	VSL126730	90.5604	0.0012	0.0181	0.0182	90.5470	1.3582	2	-0.013	2	1.359
KRISS	VSL126709	90.6018	0.0012	0.0181	0.0182	90.5970	0.1000	2	-0.005	2	0.106

Table 17: Results for methane, mixture III

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NPL	VSL206333	82.3067	0.0044	0.0165	0.0170	82.307	0.058	2	0.000	2	0.067
SMU	VSL202622	82.2935	0.0044	0.0165	0.0170	82.440	0.250	2	0.147	2	0.252
CMI	VSL205133	82.3277	0.0044	0.0165	0.0170	82.635	0.463	2	0.307	2	0.464
VNIIM	VSL202624	82.2844	0.0044	0.0165	0.0170	82.297	0.051	2	0.013	2	0.061
OMH	VSL206344	82.3050	0.0044	0.0165	0.0170	82.332	0.018	2.43	0.027	2	0.037
LNE	VSL202614	82.3294	0.0044	0.0165	0.0170	82.370	0.390	2	0.041	2	0.391
NMi VSL	VSL300636	82.3169	0.0044	0.0165	0.0170	82.290	0.090	2	-0.027	2	0.096
CENAM	VSL160258	82.3127	0.0044	0.0165	0.0170			2			
CEM	VSL202677	82.2840	0.0044	0.0165	0.0170	82.188	0.245	2	-0.096	2	0.247
BAM	VSL205189	82.2942	0.0044	0.0165	0.0170	82.319	0.125	2	0.024	2	0.130
NMIA	VSL228583	82.2916	0.0044	0.0165	0.0170	82.240	0.080	2.18	-0.052	2	0.081
IPQ	VSL220210	82.3531	0.0044	0.0165	0.0171	82.430	0.220	2	0.077	2	0.223
INMETRO	VSL202750	82.3041	0.0044	0.0165	0.0170	81.740	0.460	2	-0.564	2	0.461
GUM	VSL223562	82.2413	0.0044	0.0164	0.0170	82.220	0.120	2	-0.021	2	0.125
NRCCRM	VSL228668	82.3067	0.0044	0.0165	0.0170	82.300	1.235	2	-0.007	2	1.235
KRISS	VSL229332	82.3077	0.0044	0.0165	0.0170	82.304	0.074	2	-0.004	2	0.081

Discussion of results

With the exception of CMI and INMETRO, all results for nitrogen (figures 1 and 2) agree within 0.5% relative of the key comparison reference value (KCRV). All results are consistent with the KCRV within their respective uncertainties.

For mixture I, all results for carbon dioxide agree within 0.5% of the KCRV, with the exception of IPQ and INMETRO. For mixture III, there is an agreement within 1% of the KCRV, with the exceptions of CMI and INMETRO. The results of IPQ for mixture I (figure 3) and SMU for mixture III (figure 4) are not consistent with the KCRV within the respective uncertainties.

For ethane, all results are consistent with the KCRV, except for CMI for mixture I (figure 5), and SMU for mixture III (figure 6). The results agree within 0.5% of the KCRV, apart from CMI for mixture I, and SMU, CMI, and INMETRO for mixture III.

For propane, all results agree with the KCRV within 1%, apart from that of SMU for mixture III (figure 7). Most results agree within 0.5% or better (figures 7, 8). The result of SMU for mixture III is neither consistent with the KCRV within the associated uncertainty.

With the exception of INMETRO, CMI (only mixture III), and SMU (only mixture III), all results for *iso*-butane agree within 1% with the KCRV (figures 9, 10). The result of SMU for mixture III is neither consistent with the KCRV within the associated uncertainty.

The results for *n*-butane of GUM and CMI for mixture I deviate by more than 1% relative from the KCRV (figure 11). Both results are nevertheless consistent with the KCRV. The results of CMI and INMETRO for mixture III deviate by more than 1% relative from the KCRV (figure 12). The result of INMETRO is neither consistent with the KCRV.

CENAM did not report methane (figures 13, 14). The results for mixture I agree generally within 0.1% relative with the KCRV, with the exceptions IPQ and INMETRO. For mixture III, there are more exceptions: SMU, CMI, CEM, and INMETRO. Apart from the result of INMETRO for mixture III, all results are consistent with the KCRV within the respective uncertainty.

"How far does the light shine?"

Results from key comparisons can be used to review CMCs (calibration and measurement capabilities). This section of the report is intended for this purpose only and provides some guidance to reviewers of CMC-claims. Unlike the rest of this report, the contents of this section are an "expert opinion" and are based on the best available knowledge in the field at present. Table 18 gives the ranges and components for which the results of this key comparison give direct support on the basis of

- interpolation
- some mild extrapolation

From broad experience in the field of natural gas analysis, it is known that when the detector response is known for the ranges as indicated in table 18, measuring two mixtures in these ranges allows predicting the measurement uncertainty for other amount-of-substance fraction levels. An essential requirement is that all components in a gas mixture are in the gas phase down to a temperature of 0°C (no condensation should take place in the mixture at 0°C).

Table 18: Components and ranges

Component	**Range** x **(10^{-2} mol mol^{-1})**
Nitrogen	1 – 20
Carbon dioxide	0.1 – 5
Ethane	1 – 20

Component	Range x (10^{-2} mol mol^{-1})
Propane	0.1 – 5
n-Butane	0.05 – 1.5
iso-Butane	0.05 – 1.5
Methane	70 – 98

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.

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.

Conclusions

The agreement of the results in this key comparison is very good. For all parameters, with a few exceptions, the results agree within 1% (or better) with the key comparison reference value. For ethane, nitrogen, and carbon dioxide, the agreement is within 0.5% (or better), and for methane 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.

References

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

[2] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML, “Guide to the expression of uncertainty in measurement”, first edition, ISO Geneva, 1995

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

[4] BIPM, Annex B to the MRA, http://kcdb.bipm.fr/BIPM-KCDB//AppendixB/

[5] Alink A., Van der Veen A.M.H., “Uncertainty calculations for the preparation of primary gas mixtures. 1. Gravimetry”, Metrologia **37** (2000), pp 641-650

[6] International Organization for Standardization, ISO 6142:2001 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods, 2nd edition

[7] Van der Veen A.M.H., Pauwels J., "Uncertainty calculations in the certification of reference materials. 1. Principles of analysis of variance", Accreditation and Quality Assurance **5** (2000), pp. 464-469

[8] Van der Veen A.M.H., Linsinger T.P.J., Lamberty A., Pauwels J., "Uncertainty calculations in the certification of reference materials. 3. Stability study", Accreditation and Quality Assurance **6** (2001), pp. 257-263

[9] Van der Veen A.M.H, De Leer E.W.B., Perrochet J.-F., Wang Lin Zhen, Heine H.-J., Knopf D., Richter W., Barbe J., Marschal A., Vargha G., Deák E., Takahashi C., Kim J.S., Kim Y.D., Kim B.M., Kustikov Y.A., Khatskevitch E.A., Pankratov V.V., Popova T.A., Konopelko L., Musil S., Holland P., Milton M.J.T., Miller W.R., Guenther F.R., International Comparison CCQM-K3, Final Report, 2000

[10] Van der Veen A.M.H., Van Wijk J.I.T., "CCQM P23 – Gravimetry", Protocol, NMi VSL, Delft (NL), October 2000

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Annex A: Measurement Reports

Measurement Report from BAM

Reference Method:

For the analysis a GC were used, with specifically applications.

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 standard.

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

BAM 5039-040812

Component	Assigned value(x) mmol /mol	Standard uncertainty ($u(x)$) % relativ (k=2)
Nitrogen	38,746	0,03
Carbon dioxide	9,6706	0,10
Ethane	29,122	0,06

Component	Assigned value(*x*) mmol /mol	Standard uncertainty ($u(x)$) % relativ (k=2)
Propane	9,6871	0,10
iso-Butane	1,9127	0,12
n-Butane	1,9269	0,12
Methane	908,9342	0,02

BAM 5081-040812

Component	Assigned value(*x*) mmol /mol	Standard uncertainty ($u(x)$) % relativ (k=2)
Nitrogen	41,5600	0,03
Carbon dioxide	10,0373	0,10
Ethane	31,2383	0,06
Propane	10,4013	0,10
iso-Butane	2,0864	0,12
n-Butane	2,0836	0,12
Methane	902,2578	0,02

C49255-040728

Component	Assigned value(*x*) mmol /mol	Standard uncertainty ($u(x)$) % relativ (k=2)
Nitrogen	129,7812	0,03
Carbon dioxide	4,8346	0,10
Ethane	28,7070	0,06
Propane	4,7522	0,10
iso-Butane	0,9591	0,13
n-Butane	0,9583	0,13
Methane	830,0076	0,02

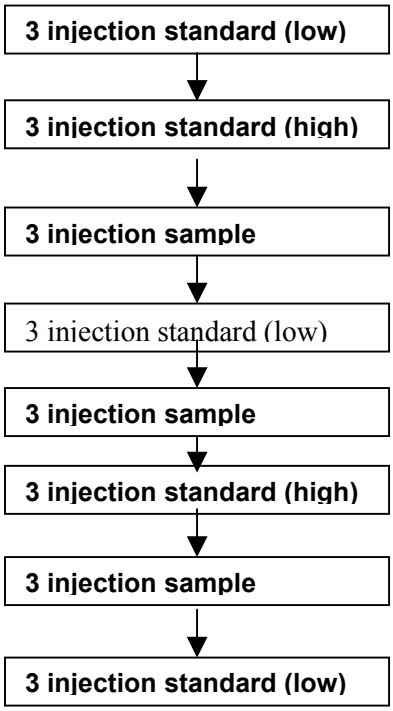
C49358-040722

Component	Assigned value(*x*) mmol /mol	Standard uncertainty ($u(x)$) % relativ (k=2)
Nitrogen	141,6153	0,03
Carbon dioxide	5,2755	0,10
Ethane	31,3246	0,06
Propane	5,1855	0,10
iso-Butane	1,0526	0,13
n-Butane	1,0517	0,13
Methane	814,4947	0,02

Instrument Calibration:

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



temperature correction: no
pressure correction : if the atmospheric pressure differs more than 0,5 mbar yes.

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 $U_{(pure\ gas)}$
- Residual-uncertainty of non-recovery errors related to the gas cylinder and to the component gas $U_{(imp./pure\ gas)}$

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

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

Measurement Report from CEM

Reference Method:

The measurements were carried out using a GC Agilent 6890 N, with the following configuration:
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

Composition of calibrants may be reported in the following format:

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/sample/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

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

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 four times each by triplicate.

Calibration Standards:

The calibration standards for the measurements were primary standards (primary standard mixtures, PSMs), this mean prepared by weigh, the cylinders were weighted after each compound addition and thermal equilibrium with the room. 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 I Standards

Cylinder Number	Component	Assigned Value (10^{-2} mol/mol)	Standard uncertainty (10^{-2} mol/mol)
FF31094	Nitrogen	3,5997	2,3E-04
	Carbon dioxide	0,90715	4,2E-04
	Ethane	3,2348	1,1E-04
	Propane	1,1085	1,5 E-04
	Iso-Butane	0,18130	1,0E-04
	n-Butane	0,22040	2,0E-04
FF31141	Nitrogen	4,0232	2,1E-04
	Carbon dioxide	1,0066	4,4E-04

Cylinder Number	Component	Assigned Value (10^{-2} mol/mol)	Standard uncertainty (10^{-2} mol/mol)
	Ethane	2,9679	1,0E-04
	Propane	1,0162	1,3E-04
	Iso-Butane	0,20101	1,0E-04
	n-Butane	0,19908	1,8E-04
FF31123	Nitrogen	4,4191	2,1E-04
	Carbon dioxide	1,1280	4,2E-04
	Ethane	2,6517	1,0E-04
	Propane	0,88974	1,2E-04
	Iso-Butane	0,22160	1,0E-04
	n-Butane	0,18089	1,6E-04

Mixture III Standards

Cylinder Number	Component	Assigned value (10^{-2} mol/mol)	Standard uncertainty (10^{-2} mol/mol)
FF31071	Nitrogen	12,170	2,8E-04
	Carbon dioxide	0,45815	1,5E-04
	Ethane	3,2894	1,0E-04
	Propane	0,54971	1,0E-04
	Iso-Butane	0,090375	1,0E-04
	n-Butane	0,11012	1,0E-04
FF31144	Nitrogen	13,544	27E-04
	Carbon dioxide	0,50779	1,5E-04
	Ethane	3,0240	1,0E-04
	Propane	0,49447	1,0E-04
	Iso-Butane	0,099410	1,0E-04
	n-Butane	0,10032	1,0E-04
FF31145	Nitrogen	14,770	2,5E-04
	Carbon dioxide	0,55107	1,5E-04
	Ethane	2,6501	1,0E-04
	Propane	0,44953	1,0E-04
	Iso-Butane	0,11006	1,0E-04

Cylinder Number	Component	Assigned value (10^{-2} mol/mol)	Standard uncertainty (10^{-2} mol/mol)
	n-Butane	0,089927	1,0E-04

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: $Std_2SmStd_1SmStd_3$…

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)

This contribution corresponds to the effect of the trend observed in the instrument performance during the measurement.

In the case of the sample ML 6717, it was carried out a set of additional measurements, and as a consequence of these measurements the results of the fifth day (there was a replicate of the N_2 with not expected behaviour) were substituted by the seventh day results to obtain a better estimated of the composition for all the components of the sample.

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:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

Primary reference material – NMi, NL
Certified reference materials – Linde Praha, CZ, prepared by ISO 6142

Composition of calibrants may be reported in the following format:

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:

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 is provide as one-point calibration 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 standard (PRM, CRM)

- uncertainty of calibration

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:

I 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
II Unicam 610 gas chromatograph with two independent channels, software 4880
Channel A with packed column with Molsieve protected by Porapack Backflush column, TCD
Channel B with Porapack analysis and backflush columns, FID
Helium and nitrogen was used as the carrier gas.

Calibration Standards:

GUM standards were prepared by gravimetric method according to ISO 6142. All the standards were prepared from separate premixtures. 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.

Composition of calibrants may be reported in the following format:
The cylinder number 0274_2

Component	Assigned value(x)	Standard uncertainty ($u(x)$)
Nitrogen	0,13328	0,00067
Carbon dioxide	0,00504	0,00005
Ethane	0,02980	0,00005
Propane	0,00501	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	0,0860	0,00008
Carbon dioxide	0,00846	0,00008
Ethane	0,02679	0,00005
Propane	0,00823	0,00001
iso-Butane	0,001481	0,000005
n-Butane	0,001540	0,000006
(any relevant impurities)		
Methane	0,8669	0,0007

The cylinder number 6721_2

Component	Assigned value(x)	Standard uncertainty ($u(x)$)
Nitrogen	0,0405	0,0004
Carbon dioxide	0,01028	0,00008
Ethane	0,03022	0,00005
Propane	0,0100	0,0001
iso-Butane	0,002003	0,000007
n-Butane	0,002005	0,000007
(any relevant impurities)		
Methane	0,9050	0,0007

Instrument Calibration:

The measurement depending on the component was done as point in point or bracketing procedure. The sample and standard were measured in both procedures one by one, repeated 5 or 10 times 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:

The analysis was carried out using Gas Chromatography (Shimadzu CG 2010). For N_2, CO_2 and methane Thermal Conductivity Detector (TCD) was used and for the other measurements Flame Ionization Detector (FID) was used. Two columns were used in the analysis of the samples: Plot Fused Silica 50mx0.32mm Coating Al_2O_3/KCl and Plot Fused Silica 25x0.32mm Coating Poraplot Q. For all measurements the split mode was used and Helium as gas carrier. The data were collected using LabSolution/GC Solution Software (from Shimadzu).

Calibration Standards:

In the analysis four standards were used in the GC calibration. They were prepared in accordance with International Standard ISO 6142: 2001 (Gas analysis - Preparation of calibration gas mixtures - Gravimetric method). The standards gas mixtures are contained in a passivated aluminium cylinder (11 MPa). The stability of the gas mixture is regularly checked and no evidence of significant change in composition has been observed over a period of three years.

OBS.: These standards were ordered from NMi-VSL. We do not have the facilities to produce Calibration standards.

Instrument Calibration:

The number and concentrations of standards used in the calibration were described in topic above. All experiments were made at controlled temperature and humidity conditions. The sequence of analysis was N_2, CO_2 and Methane (TCD) and after the other components (FID). Each standard composition was analysed eighteen times and a calibration curve was prepared.

Sample handling:

After arrival in the lab the cylinder was checked and stabilised at the temperature and humidity of 21º C and 55%, respectively. The standards and sample were transferred directly to the GC automatically using a system composed of pressure regulator, filter, flowmeter, loop (0,5 ml) and one 6-vial valve.

Evaluation of measurement uncertainty

In this study the uncertainty of the unknown samples were calculated according to GUM. Three sources of uncertainty were considered:

-Uncertainty of the standards (from certificate - type B)

-Standard deviation (analysis - type A)

-Calibration curve (type A)

Measurement Report from IPQ

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, 10 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

Calibration Standards:

Six primary standard mixtures were used for natural gas analysis. Two of them are from NPL and the other four come 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 determine the best model for data handling. All components of mixture have a goodness of fit less than 2 using a linear function except for ethane where we should use a 2nd polynomial function.
For n-C_4H_{10} and i-C_4H_{10} were used a set of four PSM (from NMi) and to the others components were used a set of six PSM (from NMi and NPL). At least six repeat analyses were performed and sometimes the first of these was rejected.

Sample handling:

After arrival the two cylinders were storage at ambient temperature in a storage room.
The samples were transferred to the instrument through an auto-sampler.

Evaluation of measurement uncertainty

The uncertainty measurement were done according ISO 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 Primary Standard mixtures;
- Standard deviation of the mean (GC-Analysis)

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

Measurement Report from KRISS

1. Reference Method:

Instruments:

- Gas-Chromatograph(GC, HP 6890) with a FID detector for the determination of hydrocarbons.
- Gas-Chromatograph(GC, HP 5890) with a TCD detector 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 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.

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:

- 8 reference cylinders for each concentration level 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 produced for the reference gases.

Purity analyses:

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

Ethane gas		Propane gas		iso-Butane gas		n-Butane gas	
Impurity	Concentra-tion, µmol/mol	Impurity	Concentra-tion, µmol/mol	Impurity	Concentra-tion, µmol/mol	Impurity	Concentra-tion, µmol/mol
CH_4	0.02	CH_4	0.81	CH_4	<0.5	CH_4	<0.5
H_2	<0.5	H_2	<0.5	H_2	<0.5	H_2	<0.5
O_2	2.5	O_2	1.3	O_2	24.5	O_2	45
CO	0.07	CO	0.06	CO	2.4	CO	1.3
CO_2	0.25	CO_2	9.5	CO_2	19.2	CO_2	4.8
N_2	10.9	N_2	31.3	N_2	123	N_2	254
C_2H_2	<0.025	C_2H_2	0.03	C_2H_2	0.28	C_2H_2	<0.025
C_2H_4	0.9	C_2H_6	143	C_2H_6	42.9	C_2H_6	0.45
C_3H_8	1.1	C_2H_4	<0.025	C_2H_4	0.28	C_2H_4	0.28
C_3H_6	298	Cyclo-C_3H_6	4.2	C_3H_8	132.3	C_3H_8	89.7
iso-C_4H_{10}	<0.013	C_3H_6	298	C_3H_6	0.21	C_3H_6	0.87
n-C_4H_{10}	0.57	iso-C_4H_{10}	9.4	n-C_4H_{10}	104.7	i-C_4H_{10}	842
unknown C_5	0.7	n-C_4H_{10}	0.3	unknown C_5	4.7	i- C_5H_{12}	0.28
<C_6	<0.1	unknown C_5	0.28	<C_6	<0.1	n-C_5H_{12}	15.4
H_2O	27	<C_6	<0.1	H_2O	43	<C_6	<0.1
		H_2O	43			H2O	25.9

Purity of Methane, Carbon dioxide and Nitrogen gases;

Methane gas		Carbon dioxide gas		Nitrogen gas	
Impurity	Concentration, µmol/mol	Impurity	Concentration, µmol/mol	Impurity	Concentration, µmol/mol
H_2	<0.5	H_2	<0.05	H_2	<0.05
O_2	1.4	CO	<0.1	CO	<0.1
CO	<0.05	CH_4	0.99	CH_4	0.0013
CO_2	0.11	CO_2	-	CO_2	<0.01
N_2	13.1	Ar	<1	Ar	<0.35
C_2H_2	<0.025	O_2	2.43	O_2	0.35
C_2H_6	0.51	N_2	4.11	N_2	-
C_2H_4	<0.025	NMHC	45.1	NMHC	<0.1
C_3H_8	0.18	H_2O	5	H_2O	1.2
C_3H_6	<0.013				
iso-C_4H_{10}	0.6				
n-C_4H_{10}	0.006				
n-C_5H_{12}	0.11				
<C_6	<0.1				
H2O	11.2				

Certified value and Uncertainty of a calibration standard:

- As an example, cylinder No., MK0735 for mixture I;

Component	Assigned value(x) %mol/mol	Standard uncertainty ($u(x)$), %mol/mol
Nitrogen	3.9537	0.0046
Carbon dioxide	1.0287	0.0028
Ethane	3.0894	0.0029
Propane	0.9716	0.0012
iso-Butane	0.1990	0.00037
n-Butane	0.1895	0.00036
Methane	90.566	0.062

- As an example, cylinder No., MK0698 for mixture III;

Component	Assigned value(x) %mol/mol	Standard uncertainty ($u(x)$), %mol/mol
Nitrogen	13.382	0.0057
Carbon dioxide	0.5094	0.0012
Ethane	2.9623	0.0025
Propane	0.5157	0.00058
iso-Butane	0.1004	0.00025
n-Butane	0.09418	0.00019
Methane	82.434	0.033

3. 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.

4. Sample handling:

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

5. Evaluation of measurement uncertainty

- As an example, an evaluation procedure for ethane in mixture I is described below;

(1) Model equation:

$C_x = C_x^0 \times f_{std}$

where, C_x is concentration of ethane in sample gas(mixture I) as a measurand,

C_x^0 is concentration of ethane in sample gas(mixture I) with a variation due to repeatability,

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 methane in Mixture I and repeatability of the determination were obtained from the following data;

No.	Results %mol/mol
1	3.0080
2	3.0052
3	3.0087
4	3.0075
5	3.0076
6	3.0068
7	3.0071
8	3.0076
9	3.0039
Average	3.0062
standard Deviation	0.0015
standard uncertainty, $u(C_x^0)$	0.0005

- $u(C_x^0)$ is 0.0005 %mol/mol obtained by the evaluation of type A.

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

- f_{std} =1.

- The concentration of ethane in standard gas used was 3.0894 %mol/mol and standard uncertainty was 0.0029 %mol/mol obtained from the certificate.

- Therefore, $u(f_{std})$ was 0.0029/3.0894=0.00094 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	3.0894 %mol/mol	$u(C_x^0)$	0.0005 %mol/mol	1	*t*	A
f_{std}	1	$u(f_{std})$	0.00094	3.0894 %mol/mol	Normal	B

-$u^2(C_x) = (1 \times 0.0005)^2 + (3.0894 \times 0.00094)^2$

-$u(C_x) = 0.0030$ %mol/mol

(4) Expanded uncertainty, *U*

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

- $U = 2 \times 0.00295 = 0.0060$ %mol/mol

(5) Results

- Measurand is the concentration of ethane(C_x);

$C_x = 3.0062 \pm 0.0060$ %mol/mol (level of confidence, 95 %)

Measurement Report from LNE

Reference Method:

The analysis is done by using a Varian CP-2003 "Micro" Gas Chromatograph with 3 modules. Each module is composed of an injector, a column and a detector.

	n-C_4H_{10} and i-C_4H_{10}	N_2 and CH_4	CO_2, C_2H_6 and C_3H_8
Column	CP SIL 5	HaySep A	HaySep A
Detector	TCD	TCD	TCD
Carrier gas	Helium	Helium	Helium
Column temp (°C)	30	30	100
Injection time (ms)	50	5	30
Column pressure (kPa)	60	200	200
Run time (s)	255	255	255

Calibration Standards:

The calibration standards are prepared by the gravimetric method in LNE.

Composition of calibrants are the following for each calibration standard :

Component	Assigned value(x)	Expanded uncertainty $U(x)$ (k=2)
Nitrogen	13.1728	0.0516
Carbon dioxide	0.5508	0.0020
Ethane	3.4135	0.0072
Propane	0.4764	0.0020
iso-Butane	0.1102	0.0004
n-Butane	0.0951	0.0004
(any relevant impurities)		
Methane	82.1812	0.3206

Calibration standard number 1

Component	Assigned value(x)	Expanded uncertainty U(x) (k=2)
Nitrogen	4.4072	0.0246
Carbon dioxide	1.0757	0.0022
Ethane	2.8494	0.0057
Propane	0.9096	0.0026
iso-Butane	0.2067	0.0007
n-Butane	0.2211	0.0007
(any relevant impurities)		
Methane	90.3304	0.4870

Calibration standard number 2

Instrument Calibration:

Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.)[4]:

The calibration procedure is the following :

- Injection of the calibration standard (C_{ref}) in the gas chromatograph and determination of the chromatographic surface (S_a)
- Injection of the unknown gas mixture (C_s) in the gas chromatograph and determination of the chromatographic surface (S_s)
- Injection of the calibration standard (C_{ref}) in the gas chromatograph and determination of the chromatographic surface (S_b)

Then, the mean of the 2 chromatographic surfaces obtained for the calibration standard is calculated with:

$$S_{refmean} = \frac{S_a + S_b}{2}$$

And the concentration of the unknown gas mixture is calculated with the following equation:

$$C_s = \frac{C_{ref} \times S_s}{S_{ref\ \mathrm{mean}}}$$

Sample handling:

The cylinders are used in an air-conditioned laboratory.

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

Evaluation of measurement uncertainty

Each concentration of the unknown gas mixture is calculated with the following equation :

$$C_s = \frac{C_{ref} \times S_s}{S_{ref\ \mathrm{mean}}}$$

So, the variance on the concentration of the unknown gas mixture is given by :

$$u^2(C_s) = \left(\frac{C_{ref}}{S_{ref\ \mathrm{mean}}}\right)^2 \times u^2(S_s) + \left(\frac{S_s}{S_{ref\ \mathrm{mean}}}\right)^2 \times u^2(C_{ref}) + \left(\frac{C_{ref} \times S_s}{S_{ref\ \mathrm{mean}}^{\ 2}}\right)^2 \times u^2(S_{ref\ \mathrm{mean}})$$

But, as 3 concentrations are measured for each component at 3 different days, the mean concentration is obtained with the following equation :

$$\overline{C_s} = \frac{C_{s1} + C_{s2} + C_{S3}}{3}$$

And, the variance on this mean concentration is :

$$u^2(\overline{C_s}) = \frac{u^2(C_{s1}) + u^2(C_{s2}) + u^2(C_{s3})}{9} + \frac{2}{3}u^2(C_{ref}) + u^2(\text{Dispersion on the 3 measurements})$$

The expanded uncertainty is given by :

$U(\overline{C_s}) = 2 \times \sqrt{u^2(\overline{C_s})}$ for the mean concentration $\overline{C_s}$ (for each component)

Measurement Report from NMi VSL

Reference Method:

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

GC:	HP6890 N (ISO 6974 configuration)
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:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

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 in appendix 1.

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 P_0 is the standard pressure.

The models used for the different curves are second order polynomials (see table 1) and unweighted regression is used.

Table 1: Order of regression model

Component	Order of model
Nitrogen	2
Carbon dioxide	2
Ethane	2
Propane	2
iso-Butane	2
n-Butane	2
Methane	2

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[5]. 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 component. Because it is difficult or impossible to discern between these different uncertainty contributions, the standard deviation of the results of the stability measurements for a cylinder having a similar mole fraction was chosen to cover these uncertainties.

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

Appropriateness of the calibration curve (model and its residuals) and repeatability
Uncertainty evaluation of inverse regression for a second order linear polynomial is problematic. Therefore, the uncertainty of the analyses was evaluated using the variance equation for inverse regression of a straight-line case even when a second order calibration curve was used. This approach can be used because the second order regression functions show only minor curvature.

For the equation:

$$\hat{Y} = b_0 + b_1 X$$

The variance can be expressed as:

$$V\left(\hat{X}\right) = \frac{k^2 s^2}{b_1^2 (1-g)} \left\{ 1 + \frac{1}{n} + \frac{1}{q} + \frac{\left(\hat{X} - \overline{X}\right)^2}{S_{XX}} \right\}$$

Where g is:

$$g = \frac{k^2 s^2}{b_1^2 S_{XX}}$$

Where k is the coverage factor (k = 1 results in the standard uncertainty), n is the number of cylinders, q is the number of measurements used to calculate the average response, Sxx is the squared sum of the x's. Because the deviation between the second order curve and a straight line are relatively small, this will only result in minor deviations. When using this equation for a second order polynomial the slope of the line at the estimated mole fraction of the sample was used instead of b_1. The s^2 is the estimate for the variance of a single response and is estimated by:

$$s^2 = \frac{SS_{res}}{n - p}$$

Where n is the number of points used and p is the number of parameters (coefficients in the regression model).

This estimation of the uncertainty not only incorporates the appropriateness of the curve, but it also incorporates the repeatability of the measurements.

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 each CCQM K23 cylinder. The concentrations of the components in the calibration standards closely bracketed the expected concentrations of the components in the CCQM K23 cylinders. In total four calibration standards were used to determine the concentrations of the two study cylinders. The natural gas calibration standards were prepared in our laboratory from very high purity commercial gases with the concentrations of the natural gas components determined gravimetrically.

Prior to calibration standard preparation, the purity and composition of the high purity 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.

CCQM Comparison, Mixture 1A – Cylinder MD8846

Component	Assigned value(x) (mmol/mol)	Standard uncertainty ($u(x)$) (mmol/mol)
Nitrogen	38.182	0.009
Carbon dioxide	9.496	0.006
Methane	910.382	0.021
Ethane	28.595	0.008
Propane	9.505	0.006
iso-Butane	1.918	0.004
n-Butane	1.912	0.004
(any relevant impurities)		
Total impurities	0.01056	

CCQM Comparison, Mixture 1B – Cylinder MD8847

Component	Assigned value(x) (mmol/mol)	Standard uncertainty ($u(x)$) (mmol/mol)
Nitrogen	42.512	0.009
Carbon dioxide	10.645	0.006
Methane	900.803	0.021
Ethane	31.237	0.009
Propane	10.549	0.006
iso-Butane	2.127	0.004
n-Butane	2.115	0.004
(any relevant impurities)		
Total impurities	0.01130	

CCQM Comparison, Mixture 3A – Cylinder MD8848

Component	Assigned value(x) (mmol/mol)	Standard uncertainty ($u(x)$) (mmol/mol)
Nitrogen	130.135	0.009
Carbon dioxide	4.788	0.006
Methane	830.644	0.0196
Ethane	27.808	0.009
Propane	4.780	0.006
iso-Butane	0.928	0.004
n-Butane	0.895	0.004
(any relevant impurities)		
Total impurities	0.02089	

CCQM Comparison, Mixture 3B – Cylinder MD8849

Component	Assigned value(x) (mmol/mol)	Standard uncertainty ($u(x)$) (mmol/mol)
Nitrogen	139.496	0.009
Carbon dioxide	5.227	0.006
Methane	816.246	0.019
Ethane	31.592	0.009
Propane	5.219	0.006
iso-Butane	1.095	0.004
n-Butane	1.103	0.004
(any relevant impurities)		
Total impurities	0.02216	

Instrument Calibration:

Each CCQM cylinder was run individually with two calibration reference cylinders containing components at concentrations that closely bracketed the expected concentrations in the CCQM cylinders. The CCQM cylinder ML6712 was run with the calibration cylinders MD8846 and MD8847. The CCQM cylinder 8583E was run with the calibration cylinders MD8848 and MD8849.

A sequence of runs $AB_1AB_2CB_3C$ was used to determine the concentration of components in each sample cylinder:

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

Each stage of the measurement sequence represents 27 repeat analyses of a cylinder. Fourteen runs were required to equilibrate the gas lines with each new gas sample, after which time the gas chromatograph response was found to be highly repeatable. 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 (eg Mixture 1, Measurement 1).
For each CCQM cylinder 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 8583E. Two tables of measurement results are presented for the cylinder ML6712.

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:

The calibration reference standards were rolled at approximately 20 rpm for a period of three hours to homogenise the gas mixtures after manufacture. After delivery, the CCQM sample cylinders were left to equilibrate in the measurement laboratory for a period of 24 hours. After this time high-purity stainless steel regulators with a maximum outlet pressure of 4 Bar were fitted to the CCQM cylinders and the reference standards. The regulators were purged with gas, adjusted to an outlet pressure of 3 Bar, and left to equilibrate over a period of 24 hours.

The two CCQM K23 cylinders and four calibration reference standards were connected to a sampling rig with quick-connect fittings. The sampling rig automatically changed the cylinder for analysis, and used vacuum to evacuate the rig between each new cylinder. The rig was equipped with a low pressure regulator to control the pressure of the gas delivered to the sample loop on the GC and an electronic pressure controller after the sample loop. This maintained a constant pressure-gradient through

the sample loop, and therefore a constant amount of gas in the sample loop. The regulator on the sampling rig was adjusted to deliver a flow of 10 ml/min of gas through the sample loop.

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.

Attached below are a series of tables showing the distribution of measurement uncertainty for the components of the CCQM test cylinders. The tables show the amount of combined uncertainty in mmol/mol, and the relative percentages attributed to each source of measurement uncertainty.

Evaluation of measurement uncertainty Mixture 1

Mixture 1, Measurement 1 – Cylinder ML6712

	Contribution of Xi to total uncertainty (%)						
Quantity Xi	Nitrogen	CO2	Ethane	Propane	*iso*-Butane	*n*-Butane	Methane
Standard 1	15.4	55.0	31.1	73.1	97.1	97.4	0.7
Standard 2	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Response 1	42.7	39.6	16.6	18.5	1.9	1.8	7.4
Response 2	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Sample response	41.9	5.4	52.3	8.4	1.0	0.8	91.8
	Combined uncertainty (mmol/mol)						
	0.022	0.008	0.015	0.007	0.005	0.005	0.245

Mixture 1, Measurement 2 – Cylinder ML6712

	Contribution of Xi to total uncertainty (%)						
Quantity Xi	Nitrogen	CO2	Ethane	Propane	*iso*-Butane	*n*-Butane	Methane
Standard 1	17.1	71.4	51.6	88.1	98.9	98.8	1.5
Standard 2	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Response 1	37.5	26.9	25.7	7.0	0.7	0.7	60.6
Response 2	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Sample response	45.3	1.7	22.7	4.9	0.4	0.5	37.9
	Combined uncertainty (mmol/mol)						
	0.021	0.007	0.011	0.007	0.004	0.005	0.172

Evaluation of measurement uncertainty **Mixture 3**

Mixture 3, Measurement 1 – Cylinder 8583E

	Contribution of Xi to total uncertainty (%)						
Quantity Xi	Nitrogen	CO2	Ethane	Propane	*iso*-Butane	*n*-Butane	Methane
Standard 1	1.5	79.2	49.8	72.8	87.0	84.7	0.8
Standard 2	< 0.05	< 0.05	< 0.05	12.1	11.8	14.1	< 0.05
Response 1	45.6	9.9	1.6	3.6	0.3	0.2	25.2
Response 2	< 0.05	< 0.05	1.4	0.7	< 0.05	< 0.05	< 0.05
Sample response	52.8	11	47.3	10.8	0.9	0.9	74.0
	Combined uncertainty (mmol/mol)						
	0.074	0.006	0.013	0.006	0.005	0.005	0.217

Mixture 3, Measurement 2 – Cylinder 8583E

	Contribution of Xi to total uncertainty (%)						
Quantity Xi	Nitrogen	CO2	Ethane	Propane	*iso*-Butane	*n*-Butane	Methane
Standard 1	0.6	88	16.8	81.3	88.8	86.3	0.3
Standard 2	< 0.05	< 0.05	< 0.05	10.8	10.5	12.9	< 0.05
Response 1	86.2	8.0	69.6	3.9	0.4	0.4	90.7
Response 2	< 0.05	< 0.05	< 0.05	1.0	0.1	0.1	< 0.05
Sample response	13.2	4.0	13.6	3.1	0.2	0.3	9.0
	Combined uncertainty (mmol/mol)						
	0.114	0.006	0.020	0.006	0.005	0.005	0.380

Mixture 3, Measurement 3 – Cylinder 8583E

	Contribution of Xi to total uncertainty (%)						
Quantity Xi	Nitrogen	CO2	Ethane	Propane	*iso*-Butane	*n*-Butane	Methane
Standard 1	2.1	85.7	68.5	83.2	88.2	85.7	2
Standard 2	< 0.05	< 0.05	< 0.05	12.2	11.4	13.9	< 0.05
Response 1	45.6	8.2	11.3	1.7	0.2	0.2	39.5
Response 2	< 0.05	< 0.05	< 0.05	0.4	< 0.05	< 0.05	< 0.05
Sample response	52.3	6.1	20.2	2.5	0.2	0.3	58.5
	Combined uncertainty (mmol/mol)						
	0.067	0.06	0.011	0.006	0.005	0.005	0.137

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:

Four Primary Reference Gas Mixtures (PRGMs) were prepared gravimetrically. Two of the PRGMs were prepared with the same nominal composition as Mixture I, and two with the same composition as Mixture III.

Composition of NG 60:

Component	Gravimetric value (x) mmol/mol	Standard uncertainty ($u(x)$)
Nitrogen	40.147	0.020
Carbon dioxide	9.9573	0.0054
Ethane	30.118	0.036
Propane	2.0361	0.0054
iso-Butane	1.9652	0.0023
n-Butane	9.9850	0.0023
Methane	905.78	0.05

Composition of NG 71:

Component	Gravimetric value (x) mmol/mol	Standard uncertainty ($u(x)$)
Nitrogen	40.187	0.013
Carbon dioxide	9.9672	0.0039
Ethane	29.915	0.023
Propane	2.0381	0.0039
iso-Butane	1.9672	0.0022
n-Butane	9.9950	0.0022
Methane	905.92	0.03

Composition of NG 58:

Component	Gravimetric value (x)	Standard uncertainty ($u(x)$)

	mmol/mol	
Nitrogen	135.15	0.03
Carbon dioxide	4.9788	0.0031
Ethane	29.872	0.021
Propane	1.0181	0.0031
iso-Butane	0.9826	0.0012
n-Butane	4.9926	0.0012
Methane	823.00	0.03

Composition of NG 69:

Component	Gravimetric value (x) mmol/mol	Standard uncertainty ($u(x)$)
Nitrogen	134.04	0.03
Carbon dioxide	5.0161	0.0041
Ethane	30.029	0.025
Propane	1.0003	0.0010
iso-Butane	0.9981	0.00131
n-Butane	4.9893	0.00131
Methane	823.92	0.04

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:

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. A double injection procedure was employed, with the result that each analytical run yielded two peaks for nitrogen, methane, carbon dioxide and ethane; three for *n*-butane and four for propane and *iso*-butane - a total of 19 peaks per run. (Propane and *n*-butane and *iso*-butane are measured on both detectors. In order to keep the experimental run time to a minimum, one of the n-Butane peaks on the TCD is not measured: hence only three peaks.)

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 5-9 comparisons, the average amount fraction values and the standard deviations were calculated for each component. These were determined using the weighted average of the data obtained from all the chromatographic peaks of each component (e.g. two four ethane, four for propane).

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 (250 to 600 data points per component). For each of the three analyses of each unknown Mixture, a standard deviation was calculated from the repeated measurements (5-9 in total) comprising each analysis. The final 'analytical' uncertainty was then calculated as the mean of these three standard deviations divided by √3.

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

No changes have been made to the uncertainties as a result of the normalisation process. For all six analysis of the two cylinders, the sum of amount fractions was found to be very close to unity (the totals being 0.99982, 1.00015 and 1.00005 for Mixture I and 1.00046, 1.00011 and 0.99976 for Mixture III. It can therefore be assumed that any deviation form unity is due to random errors (rather than systematic errors). The data can then be treated as if it was entirely non-correlated, i.e. the uncertainties are not reduced as a result of the normalisation process. All uncertainties reported are in fact already below NPL's current CMCs.

Measurement Report from NRCCRM

Reference Method:

A GC-FID instrument was used to analyze the natural gas components in the gas mixtures, the type of the GC is Agilent 6890 with FID and TCD detectors and six-way gas sample valve, which is controlled by a EPC. The sample cylinder was directly connected to the six-way valve, and sample volume is 1~5 milliliters. A Al_2O_3/Na_2SO_4 capillary column with 50 m × 0.53 mm×15 μm was used to separate the organic components interested and detected with FID. A Porapak PN steel packed column with 2 m× 3 mm and a 13X molecular sieve packed column with 3m×3 mm were used to separate the inorganic components interested and detected with a TCD. The data was collected and calculated by Agilent 6890 GC ChemStation.

Calibration Standards:

A series of natural gas mixtures were used as calibration standards, which were prepared by gravimetric method. The information of calibration standards of mixtures I and III were listed in table 1 and table 2. 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. The expanded uncertainty of the gravimetric method is about1% with confidence interval 95% and coverage factor k is 2.

Table 1 Calibration standards of mixture I

Components	Assigned value(x_i)			Standard uncertainty ($u(x)$)
Nitrogen	4.089	3.860	3.792	0.5
Carbon dioxide	0.971	0.990	0.953	0.5
Ethane	3.002	2.774	2.972	0.5
Propane	0.986	0.933	0.972	0.5
iso-Butane	0.203	0.194	0.196	0.5
n-Butane	0.209	0.197	0.198	0.5
(any relevant impurities)				

Table 2 Calibration standards of mixture III

Components	Assigned value(x_i) mmol/mol			Standard uncertainty ($u(x)$)
Nitrogen	13.080	13.300	13.287	0.5
Carbon dioxide	0.511	0.529	0.534	0.5
Ethane	2.972	3.026	3.002	0.5
Propane	0.491	0.495	0.492	0.5
iso-Butane	0.0975	0.0997	0.0979	0.5
n-Butane	0.0970	0.0974	0.0990	0.5
(any relevant impurities)				

Instrument Calibration:

One point calibration method was used to determine the sample and the standards concentration listed in table 1 and table 2. The sample was measured based upon the different calibration standards in different days. Measurement sequence was in the order standard-sample-standard-sample-standard. 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 GC-FID/TCD by a reduce valve and a flow meter and a Teflon pipe. Before each sample injection, the reduce valve was opened and shut off for fifteen times (about one second per time) to purge the pipe system, then balance ten seconds at room pressure and temperature. After that, by pushing the "Start" button on the GC panel to introduce the sample into the instrument.

Evaluation of measurement uncertainty

The potential sources that influence the uncertainty of the final measurement result are figured out in the follow tree chart. However, most of them can be neglected. The main sources that influence the uncertainty were listed in the uncertainty evaluation table 3.

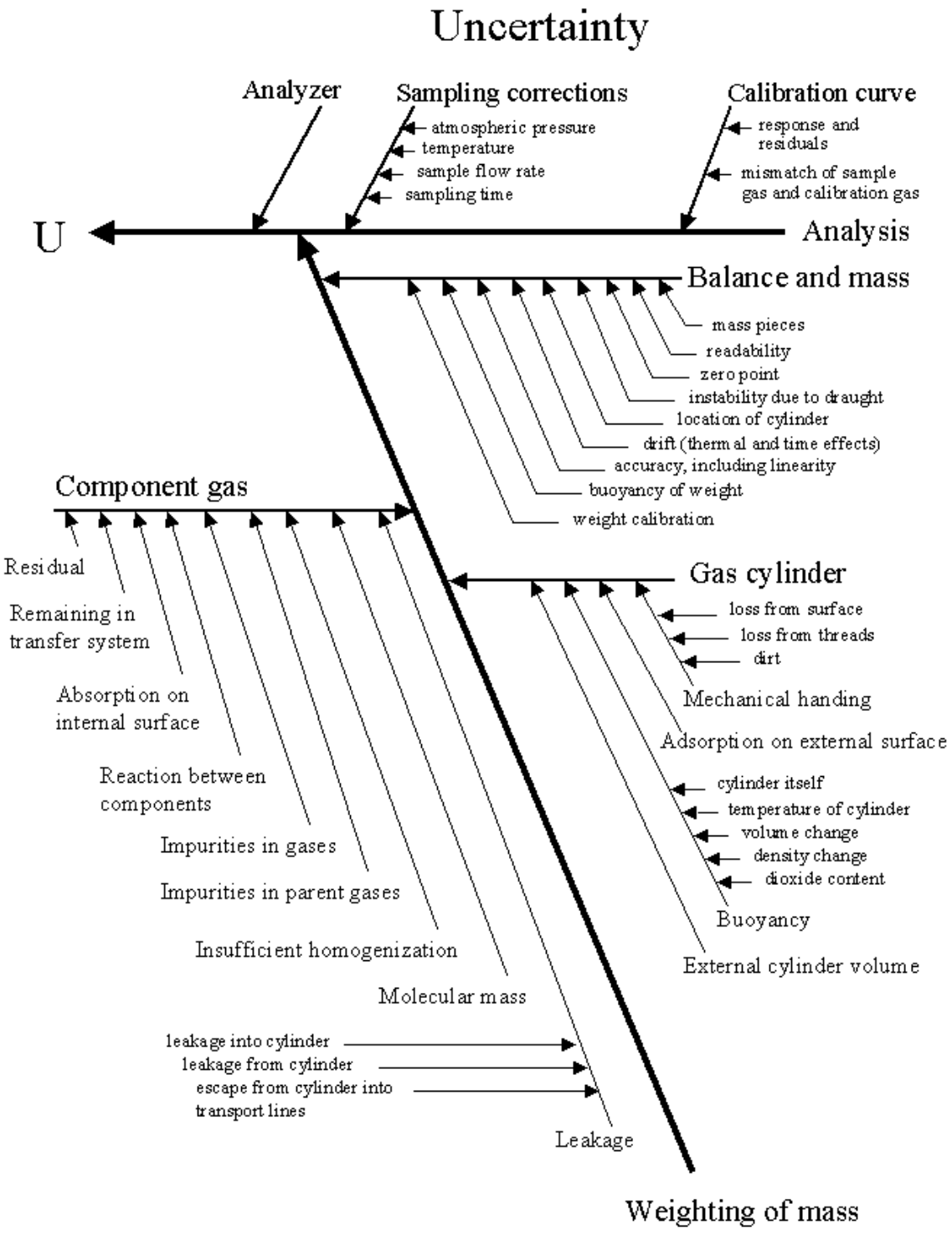

Uncertainty
Analyzer
Sampling corrections
atmospheric pressure
temperature
sample flow rate
sampling time
Calibration curve
response and residuals
mismatch of sample gas and calibration gas
U
Analysis
Balance and mass
mass pieces
readability
zero point
instability due to draught
location of cylinder
drift (thermal and time effects)
accuracy, including linearity
buoyancy of weight
weight calibration
Component gas
Residual
Remaining in transfer system
Absorption on internal surface
Reaction between components
Impurities in gases
Impurities in parent gases
Insufficient homogenization
Molecular mass
leakage into cylinder
leakage from cylinder
escape from cylinder into transport lines
Leakage
Gas cylinder
loss from surface
loss from threads
dirt
Mechanical handing
Adsorption on external surface
cylinder itself
temperature of cylinder
volume change
density change
dioxide content
Buoyancy
External cylinder volume
Weighting of mass

Table 3 Uncertainty Evaluation table

Uncertainty source X_I	Estimate x_I	Assumed distribution	Relative standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Analysis	0.5%	normal	0.20%	1	0.20%
Analyzer	0.5%	rectangle	0.29%	1	0.29%
Sampling corrections	0.5%	Rectangle	0.29%	1	0.29%
Balance and mass	0.05%	rectangle	0.029%	1	0.029%
Gas cylinder	0.5%	rectangle	0.29%	1	0.29%
Leakage	0.02%	rectangle	0.01%	1	0.01%
Purity of complementary gas and components interested	0.1%	rectangle	0.06%	1	0.06%
Absorption	0.5%	rectangle	0.29%	1	0.29%

Coverage factor or degree of freedom: 2

Expanded uncertainty: 1.5%

The combined uncertainty can be expressed with follow equation:

$$u_c = \sqrt{(\frac{S_i}{\sqrt{n}})^2 + \sum (u_j)^2}$$

And the total uncertainty can be calculated with a confidence interval 95% and a coverage factor k= 2:

$$U = ku_c \approx 1.5\%$$

By taking a series of measurements, we can eliminate or reduce most parts of uncertainties (including those related to the balance and poises, gas cylinder, components interest, etc.) to the level that can be neglected. In this work, for the final measurement results, we mainly take two parts of uncertainties into account. One of them is the main uncertainties of the calibration gas mixtures prepared by gravimetric method. The other is the main uncertainties of the calibration procedure we used.

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 180 °C

Calibration Standards:
The Calibration Standards were prepared gravimetrically.

Composition of calibration standards:

OMH 287

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %(n/n)
Nitrogen	3,3217	0,007
Carbon dioxide	1,4604	0,003
Ethane	1,4907	0,003
Propane	0,5027	0,002
iso-Butane	0,1259	0,0004
n-Butane	0,1241	0,0004
Methane	92,9745	0,028

OMH 300

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %(n/n)
Nitrogen	0,7505	0,002
Carbon dioxide	0,0355	0,001
Ethane	0,3360	0,001
Propane	0,1132	0,001
iso-Butane	0,0284	0,0001
n-Butane	0,0278	0,0001
Methane	98,7086	0,030

OMH 281

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %(n/n)
Nitrogen	5,7809	0,012
Carbon dioxide	2,7319	0,005
Ethane	2,5950	0,005
Propane	0,8752	0,003
iso-Butane	0,2192	0,0007
n-Butane	0,2161	0,0006
Methane	87,5816	0,026

OMH 282

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %(n/n)
Nitrogen	19,3759	0,039
Carbon dioxide	8,2171	0,016
Ethane	8,6995	0,017
Propane	2,9337	0,009
iso-Butane	0,7350	0,0022
n-Butane	0,7239	0,0022
Methane	59,3148	0,018

OMH 297

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %(n/n)
Nitrogen	14,0920	0,028
Carbon dioxide	11,6876	0,023
Ethane	6,3286	0,013
Propane	2,1363	0,006
iso-Butane	0,5342	0,0016
n-Butane	0,5307	0,0016
Methane	64,6907	0,018

OMH 283

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %(n/n)
Nitrogen	8,7009	0,017
Carbon dioxide	6,3974	0,013
Ethane	3,9052	0,008
Propane	1,3157	0,004
iso-Butane	0,3302	0,0010
n-Butane	0,3226	0,0010
Methane	79,0280	0,018

OMH 213

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %(n/n)
Nitrogen	13,7044	0,027
Carbon dioxide	2,1966	0,004
Ethane	5,0986	0,010
Propane	2,1948	0,007
iso-Butane	0,9346	0,0028

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %(n/n)
n-Butane	0,9506	0,0029
Methane	74,9204	0,022

OMH 289

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %
Nitrogen	7,1078	0,035
Carbon dioxide	2,7904	0,025
Ethane	9,4841	0,03
Propane	2,6937	0,03
iso-Butane	0,9619	0,06
n-Butane	1,0181	0,06
Methane	75,9439	0,01

OMH 286

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %
Nitrogen	3,9794	0,07
Carbon dioxide	1,0128	0,06
Ethane	3,1066	0,09
Propane	0,9776	0,07
iso-Butane	0,1987	0,1
n-Butane	0,2104	0,1
Methane	90,5145	0,01

OMH 291

Component	Assigned value, x %(n/n)	Expanded uncertainty, U (k=2) %
Nitrogen	13,5056	0,01
Carbon dioxide	0,4950	0,05
Ethane	3,0423	0,05
Propane	0,4778	0,06
iso-Butane	0,1044	0,1
n-Butane	0,1105	0,1
Methane	82,2645	0,005

Methane 5.5 was also used in the case of calibration of methane.

Instrument Calibration:
Each calibration standard was measured three times, the whole calibration process was done within a day. We used air-pressure correction.
To the 10 calibration points (in the case of methane we had 11 points) were fitted quadratic polynomials.

Sample handling:

Samples were transferred continuously to the instrument on low pressure checked by mass-flow controller.

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 calibration which contains the uncertainty of the calibration curve and the uncertainty of the normalisation to 100%.

   The uncertainties of preparation of calibration standards were included in u_2.

   (See: E. Gáti: Fitting of a parabola fulfilling predetermined metrological requirements, Mérésügyi Közlemények, 2004/1., p.87-92.)

$$u_2 = \sqrt{\left((1-x_i)^2 u_{c,i}^2 + x_1^2 u_{c,1}^2 + \ldots + x_{i-1}^2 u_{c,i-1}^2 + x_{i+1}^2 u_{c,i+1}^2 + \ldots + x_m^2 u_{c,m}^2\right)} ,$$

where

x_i mole fraction of component i,

$u_{c,i}$ uncertainty of calibration curve of component i at the mole fraction x_i,

m number of components.

The combined uncertainty:

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

We calculated the effective degree of freedom for each component.
Degree of freedom of a calibration curve is 7, because we used 10 calibration standards.

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

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 Gas Chromatograph Varian 3 800 using two DC 200/500 and one molsieve 13X packed columns, 2 sample loops (0,1mL and 0,05mL) , TCD and FID detectors, 90 °C oven temperature (no ramps), 16 min method. Full backflush started with C5+.

All measurements were done in automatic way.

Calibration Standards:

All calibration standards were made gravimetrically according ISO 6142 and 6143. Purity table and uncertainties include impurities of parent gases checked on GC or estimated.

6 SMU calibration standards (with n-pentane, iso-pentane, neopentane, n-hexane) were used.

Component	Assigned value(x)	Standard uncertainty (u(x))
Methane	0,84 – 0,98	0,1 – 0,12
Nitrogen	0,005 – 0,11	0,1 – 0,3
Carbon dioxide	0,001 – 0,02	0,1 – 0,35
Ethane	0,005	0,053
Propane	0,001 – 0,013	0,18 – 0,35
iso-Butane	0,00035 – 0,0021	0,16 – 0,5
n-Butane	0,00035 – 0,002	0,17 – 0,32
neopentane	0,00005 – 0,00015	
n-pentane	0,000055 - 0,001	
iso-pentane	0,00007 – 0,00028	
n-hexane	0,000078 – 0,001	

Instrument Calibration:

Sequence of 6 measurement cycles with 10 cylinders in each was used. 6 of them were calibration standards (with n-pentane, iso-pentane, neopentane, n-hexane).

Quadratic (b_least) calibration curve: methane, CO_2, N_2

Linear (b_least): ethane, propane, n-butane, iso-butane

no correction

Sample handling:

Cylinders with natural gas were at SMU kept at 17 – 22 °C. Before measurement cylinders were kept at laboratory temperature for more than 4 hours. All measurements were done in automatic way (in both directions) using selector valve. To have the same sample loop flushing time mass flow controller was used.

Evaluation of measurement uncertainty

Uncertainty of device response consisted from immediate repeatability and from signal drift estimated. Calibration curves were made from each cycle using b_least program (weighted least square regression taking into account both standard uncertainties of mole fractions and standard uncertainties of responses).

From each calibration curve using b_least unknown sample molar fraction with its standard uncertainty was determined. For each i^{-th} day the average x_i was calculated *(1)*. Standard uncertainty assigned *to* each i^{-th} day *result* is maximum *(4)* either from standard deviation of the average *(2)* or average from all b_least uncertainties that day *(3)*.

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

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

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

$$u(\bar{x}_i) = \max\left[u_1(\bar{x}_i); u_2(x_i)\right] \qquad (4)$$

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

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

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

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

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

Final result is average from 3 day results

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

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

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

Expanded uncertainty (k=2) of final result

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

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

Measurement Report from VNIIM

Reference method

Molar fraction of the components was determined by gas chromatography with flame ionization and thermal conductivity detection. Two Gas-chromatographs were used for measurements “Crystal-5000M” and “Crystal-2000M” (“Chromatec”, Russia).

Instrument	Detectors	Columns	
Crystal-5000M	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
Crystal-2000M	TCD FID	Haye Sep R Haye Sep R	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, %	Presence of cross-admixtures
Nitrogen	999988,5	0,812	0,0000812	—
Carbon dioxide	999680	18	0,0018	Nitrogen – 220 ppm
Ethane	996137	602	0,0604	Methane – 170 ppm Nitrogen – 340 ppm
Propane	999410	28	0,0028	n-Butane – 170 ppm Nitrogen – 220 ppm
iso-Butane	999070	84	0,0084	Methane -50 ppm Nitrogen -550 ppm
n-Butane	995125	243	0,0244	Methane - 647 ppm Propane – 2 ppm iso-Butane– 773 ppm Nitrogen – 1224 ppm
Methane	999720	19	0,0019	Nitrogen – 130 ppm

All mixtures were prepared in aluminum cylinders, V=10dm^3, type БД16-10-9,8 (“Poisk”, Russia). Preparation of standard gas mixtures for Mixture I (cylinder № ML 6708) was carried out in 1 stage. There were prepared 3 standard gas mixtures with composition identical to investigated Mixture I (bracketing). Verification of molar fraction in prepared mixtures was carried out chromatographically. Discrepancy between the cylinders was not found out. Standard deviation for measurement series was 0,1-0,5 % for different components.

Preparation of standard gas mixtures for investigated Mixture III (cylinder № ML 2624E) was carried out in 2 stages.

a) Pre- mixtures of n-Butane and iso-Butane in Nitrogen with molar fractions of both components about 5 % were prepared first. There were prepared 3 pre- mixtures in sum. Verification of molar fraction in pre-mixtures was carried out chromatographically. Discrepancy between the cylinders was not found out. Standard deviation for measurement series was 0,2-0,3 %.

b) At the second stage there were prepared 3 standard gas mixtures with composition identical to Mixture III (bracketing).

Verification of molar fraction in prepared mixtures was carried out chromatographically. Discrepancy between the cylinders was not found out. Standard deviation for measurement series was 0,1-0,5 % for different components.

Standard uncertainty of molar fraction (peak value) for each component in standard gas mixtures are shown in table 2

Table 2

	Component	**Relative standard uncertainty, % (peak value)**
Standard gas mixtures with composition identical to investigated Mixture I	Nitrogen	**0,010**
	Carbon dioxide	**0,022**
	Ethane	**0,013**
	Propane	**0,022**
	iso-Butane	**0,083**
	n-Butane	**0,083**
	Methane	**-**
Standard gas mixtures with composition identical to investigated Mixture III	Nitrogen	**0,003**
	Carbon dioxide	**0,042**
	Ethane	**0,012**
	Propane	**0,042**
	iso-Butane	**0,025**
	n-Butane	**0,028**
	Methane	**-**

Instrument calibration

Bracketing was used as calibration method.

There were made 4 independent measurements for each studied Mixture under repeatability conditions with 4 independent calibrations (in 4 days during 10 days).

One single measurement consisted of 6 sub-measurements. The measurement sequence was “calibration→measurement”.

Sample handling

Prior to measurements cylinders were stabilized to room temperature.

Influence of temperature and pressure changes in comparison method is negligible and it was not taken into account.

The samples were transferred to Gas-chromatograph through the valve, with sample loop V=1 cm3.

Results of measurements

Measurement results of components’ molar fraction in gas mixture in cylinder № ML6708 are shown in the table 3 (Mixture I).

Table 3 - Results of measurements of components' molar fraction in cylinder № ML6708

Mixture I, measurement # 1

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	11/11/04	40,067	0,08	6
Carbon dioxide		10,014	0,51	6
Ethane		29,986	0,25	6
Propane		10,014	0,25	6
iso-Butane		1,996	0,22	6
n-Butane		1,977	0,24	6
Methane		905,946	-	-

Mixture I, measurement # 2

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	13/11/04	40,045	0,11	6
Carbon dioxide		10,019	0,19	6
Ethane		29,955	0,26	6
Propane		10,026	0,21	6
iso-Butane		1,993	0,17	6
n-Butane		1,991	0,23	6
Methane		905,971	-	-

Mixture I, measurement # 3

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	15/11/04	40,135	0,18	6
Carbon dioxide		9,989	0,27	6
Ethane		29,963	0,10	6
Propane		9,958	0,40	6
iso-Butane		1,995	0,25	6
n-Butane		1,972	0,28	6
Methane		905,988	-	-

Mixture I, measurement # 4

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	17/11/04	40,082	0,12	6
Carbon dioxide		9,953	0,39	6
Ethane		29,920	0,41	6
Propane		10,007	0,31	6
iso-Butane		2,012	0,38	6
n-Butane		1,989	0,39	6
Methane		906,037	-	-

Measurement results of components' molar fraction in gas mixture in cylinder № 2624E are shown in the table 4 (Mixture III).

Table 4 - Results of measurements of components' molar fraction in cylinder № 2624E

Mixture III, measurement # 1

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	10/11/04	134,71	0,11	6
Carbon dioxide		4,988	0,36	6
Ethane		29,887	0,14	6
Propane		4,976	0,13	6
iso-Butane		0,999	0,20	6
n-Butane		0,991	0,20	6
Methane		823,449	-	-

Mixture III, measurement # 2

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	12/11/04	135,16	0,17	6
Carbon dioxide		4,990	0,25	6
Ethane		29,987	0,12	6
Propane		4,990	0,22	6
iso-Butane		1,005	0,17	6
n-Butane		0,994	0,16	6
Methane		822,874	-	-

Mixture III, measurement # 3

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	16/11/04	135,07	0,11	6
Carbon dioxide		4,978	0,47	6
Ethane		29,951	0,21	6
Propane		4,986	0,20	6
iso-Butane		1,007	0,12	6
n-Butane		1,009	0,20	6
Methane		822,999	-	-

Mixture III, measurement # 4

Component	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	18/11/04	135,42	0,12	6
Carbon dioxide		5,006	0,52	6
Ethane		30,023	0,24	6
Propane		5,012	0,15	6
iso-Butane		0,990	0,16	6
n-Butane		0,988	0,15	6
Methane		822,561	-	-

Evaluation of uncertainty of measurements

Total standard uncertainty of components' molar fraction in investigated Mixtures was calculated on the base of the following components:

- total standard uncertainty of components' molar fraction in standard gas mixture (gravimetry);
- standard deviation of the components' molar fraction measurement results in studied gas Mixture.

Uncertainty budget for components' molar fraction in investigated gas Mixture I in cylinder

№ ML6708 are shown in the tables 5-10.

Table 5. Uncertainty budget for nitrogen molar fraction in investigated gas Mixture I in cylinder № ML6708

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,010	1	0,010
Standard deviation of the results of measurements	A	0,08	1	0,08
Total standard uncertainty				**0,08**
Expanded uncertainty (*k*=2)				**0,16**

Table 6. Uncertainty budget for carbon dioxide molar fraction in investigated gas Mixture I in cylinder № ML6708

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,022	1	0,022
Standard deviation of the results of measurements	A	0,30	1	0,30
Total standard uncertainty				**0,30**
Expanded uncertainty (*k*=2)				**0,60**

Table 7. Uncertainty budget for ethane molar fraction in investigated gas Mixture I in cylinder № ML6708

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,013	1	0,013
Standard deviation of the results of measurements	A	0,09	1	0,09
Total standard uncertainty				**0,09**
Expanded uncertainty (*k*=2)				**0,18**

Table 8. Uncertainty budget for propane molar fraction in investigated gas Mixture I in cylinder № ML6708

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,022	1	0,022
Standard deviation of the results of measurements	A	0,26	1	0,26
Total standard uncertainty				**0,26**
Expanded uncertainty (*k*=2)				**0,52**

Table 9. Uncertainty budget for iso-butane molar fraction in investigated gas Mixture I in cylinder № ML6708

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,083	1	0,083
Standard deviation of the results of measurements	A	0,38	1	0,38
Total standard uncertainty				**0,39**
Expanded uncertainty (*k*=2)				**0,78**

Table 10. Uncertainty budget for n-butane molar fraction in investigated gas Mixture I in cylinder № ML6708

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,083	1	0,083
Standard deviation of the results of measurements	A	0,40	1	0,40
Total standard uncertainty				**0,41**
Expanded uncertainty (*k*=2)				**0,82**

Uncertainty budget for components' molar fraction in investigated gas Mixture III in cylinder № 2624E are shown in the tables 11-16.

Table 11. Uncertainty budget for nitrogen molar fraction in investigated gas Mixture III in cylinder № 2624E

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,003	1	0,003
Standard deviation of the results of measurements	A	0,19	1	0,19
Total standard uncertainty				**0,19**
Expanded uncertainty (*k*=2)				**0,38**

Table 12. Uncertainty budget for carbon dioxide molar fraction in investigated gas Mixture III in cylinder № 2624E

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,042	1	0,042
Standard deviation of the results of measurements	A	0,20	1	0,20
Total standard uncertainty				**0,20**
Expanded uncertainty (*k*=2)				**0,40**

Table 13. Uncertainty budget for ethane molar fraction in investigated gas Mixture III in cylinder № 2624E

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,012	1	0,012
Standard deviation of the results of measurements	A	0,17	1	0,17
Total standard uncertainty				**0,17**
Expanded uncertainty (*k*=2)				**0,34**

Table 14. Uncertainty budget for propane molar fraction in investigated gas Mixture III in cylinder № 2624E

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,042	1	0,042
Standard deviation of the results of measurements	A	0,30	1	0,30
Total standard uncertainty				**0,30**
Expanded uncertainty (*k*=2)				**0,60**

Table 15. Uncertainty budget for iso-butane molar fraction in investigated gas Mixture III in cylinder № 2624E

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,025	1	0,025
Standard deviation of the results of measurements	A	0,66	1	0,66
Total standard uncertainty				**0,66**
Expanded uncertainty (*k*=2)				**1,3**

Table 16. Uncertainty budget for n-butane molar fraction in investigated gas Mixture III in cylinder № 2624E

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture	B	0,028	1	0,028
Standard deviation of the results of measurements	A	0,81	1	0,81
Total standard uncertainty				**0,81**
Expanded uncertainty (*k*=2)				**1,6**