International Supplementary comparison

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Supplementary comparison of analytical capabilities for synthetic natural gas

Final report

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Project number: Euramet 1212

Field

Metrology in Chemistry: Gas analysis

Subject

Supplementary comparison in the field of natural gas analysis

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Introduction

This supplementary comparison involves standard gas mixtures of synthetic natural gas. It is similar to the key comparison CCQM-K16 (2001-2002). Analysed were gas mixtures of synthetic natural gas containing nitrogen, carbon dioxide and the alkanes up to hexane with a total of 10 components.
Four laboratories participated in this supplementary comparison. All of the participants, except CMI, have established facilities for natural gas analysis, and have existing claims for their Calibration and Measurement Capabilities (CMCs) for natural gas mixtures.

Participants

Table 1 lists the participants in this comparison.

Table 1

Acronym	Country	Institute
SMU	SK	Slovak Institute of Metrology, Bratislava, Slovak Republic
CMI	CZ	Czech Metrology Institute, Brno, Czech Republic
INMETRO	BR	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, Xerém RJ, Brasil
VSL	NL	Van Swinden Laboratorium B.V., Delft, the Netherlands

Measurement standards

The mixtures for this supplementary comparison were prepared gravimetrically according to ISO 6142 [1] at the Centre of Chemistry of SMU.

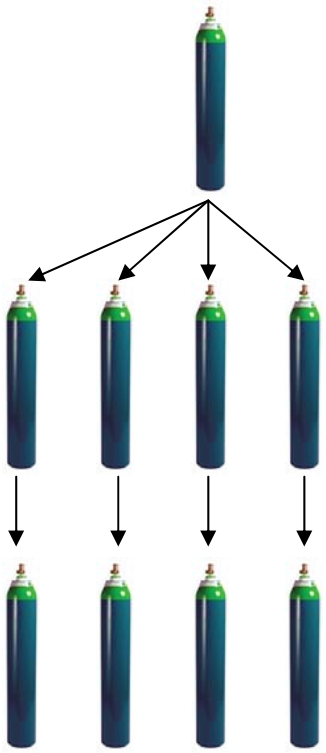
Nominal compositions of the natural gas mixtures read as follows:

Nitrogen	10 mmol/mol
Carbon dioxide	10 mmol/mol
Ethane	10 mmol/mol
Propane	5 mmol/mol
iso-Butane	1 mmol/mol
n-Butane	1 mmol/mol
iso-Pentane	0.5 mmol/mol
n-Pentane	0.5 mmol/mol
n-Hexane	0.2 mmol/mol
Methane	961.8 mmol/mol

The pressure in the cylinders was approximately 45 bar; cylinders of 5 dm^3 nominal were used. Final mixtures were prepared in three steps (see Figure 1):

1. premixture: 0.035 mol/mol *n*-butane, 0.035 mol/mol *iso*-butane and 0.175 mol/mol propane in methane;
2. premixture: 10 mmol/mol ethane, 5 mmol/mol propane, 10 mmol/mol nitrogen, 10 mmol/mol carbon dioxide, 1 mmol/mol *iso*-butane and 1 mmol/mol *n*-butane;
3. final mixture: similar topremixture 2 with added liquid components of *n*-hexane 0.2 mmol/mol, *n*-pentane 0.5 mmol/mol and *iso*-pentane 0.5 mmol/mol by syringe injection.

Figure 1 Scheme of the preparation



1. Step: C_3, *n*-C_4, *iso*-C_4, C_1

2. Step: 1+ C_2, N_2, CO_2, C_1

3. Step: 2 + *iso*-C_5, *n*-C_5, *n*-C_6

The mixtures were validated against a set of SMU PSMs in accordance with ISO 6143 [2] using a Varian GC system. The method of validation is described in Annex C Measurement report from SMU. In Table 2 the values of the standard uncertainties from verification are listed.

Table 2

Component	**u_{ver} (% relative)**
Nitrogen	0.17
Carbon dioxide	0.18
Methane	0.06
Ethane	0.10
Propane	0.13
iso-Butane	0.20
n-Butane	0.20
iso-Pentane	0.25
n-Pentane	0.25
n-Hexane	0.25

The amount-of-substance fractions as obtained from gravimetry and purity verification of the parent gases were used as reference values in this comparison.
The stability measurement in SMU was accomplished after the return of the cylinders from participants to SMU in 01/2013 using the same method for analysis as for verification. All

results from the stability measurements were comparable with the stated uncertainties from the gravimetric preparation.

Measurement protocol

The measurement protocol requested each laboratory to perform at least 3 measurements obtained under repeatability conditions including at least three separate calibrations. The protocol informed the participants about the nominal concentration of the comparison sample. The laboratories were also requested to submit a summary of the uncertainty evaluation for the presented results.

Schedule

The schedule of this supplementary comparison is listed in Table 3.

Table 3

Contents	Date
Start of comparison	January 2012
Shipment of cylinders with gas mixtures to participants	February - March 2012
Analysis of samples by participants	March– September 2012
Submission of measurement reports to SMU	October 2012
Dispatch of the cylinders with gas mixtures to pilot	October 2012
SMU's re-analysis of gas mixtures in the cylinders	January 2013
Draft A	February 2013
Draft B	October 2013

Measurement equation

The amount-of-substance fractions as obtained from gravimetry and purity analysis of the parent substances were used as reference values.
The amount of substance fraction $x_{i,prep}$ of a particular component in mixture i, as it appears during use of the cylinder, can be expressed as [3] :

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

Furthermore, long-term stability study data has shown that:

$$\Delta x_{i,stab} = 0 \quad (2)$$

Summarising, the model reduces to:

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} \quad (3)$$

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

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2 \quad (4)$$

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

$$\left| x_{i,prep} - x_{i,ver} \right| \leq 2\sqrt{u_{i,prep}^2 + u_{i,ver}^2} \quad (5)$$

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 reference value of mixture *i* in the supplementary comparison can be defined as:

$$x_{i,ref} = \left\langle x_{i,ref} \right\rangle + \delta x_{i,ref} \quad (6)$$

where:

$$x_{i,ref} = x_{i,prep} + \Delta x_{i,ver} \quad (7)$$

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, (7) can be expressed as:

$$x_{i,ref} = \left\langle x_{i,prep} \right\rangle + \delta x_{i,prep} + \delta \Delta x_{i,ver} \quad (8)$$

This expression forms the basis for the evaluation of the degrees of equivalence in this supplementary comparison. For all mixtures, it is a requirement that:

$$\Delta x_{i,ver} = 0 \quad (9)$$

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 supplementary comparison mixtures agreed with older measurement standards.

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

$$u_{i,ref}^2 = u_{i,prep}^2 + u_{i,ver}^2 . \quad (10)$$

The values for $u_{i,ver}$ are given in Table 2.

Measurement methods

All of the laboratories use the same measurement technique - gas chromatography equipped with TCD and FID detectors. A summary of the measurement technique, calibration methods and metrological traceability is given in Table 4.

Table 4

Laboratory	Measurement technique	Calibration	Traceability
SMU	GC-TCD, GC-FID	Quadratic analytical function, ISO-6143	Own standards
CMI	GC-TCD, GC-FID	Linear analytical function, 3 points, ISO 6143	Own standards
INMETRO	GC-TCD, GC-FID	Quadratic, linear analytical function, ISO 6143	VSL, NPL
VSL	GC-TCD, GC-FID	Quadratic analytical function, ISO 6143	Own standards

Supported CMC claims

Components and ranges supported by this supplementary comparison are presented in Table 5.

Table 5

Component	**Supported amount-of-substance fraction range Δx (mmol/mol)**
Nitrogen	5 – 100
Carbon dioxide	5 – 50
Methane	700 – 980
Ethane	5 – 100
Propane	1 – 20
iso-Butane	0.5 – 10
n-Butane	0.5 – 10
iso-Pentane	0.2 – 2
n-Pentane	0.2 – 2
n-Hexane	0.1 – 1

Degrees of equivalence

A unilateral degree of equivalence in comparisons is defined:

$$\Delta x_i = D_i = x_i - x_{\mathrm{KCRV}} \tag{11}$$

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

$$\Delta x_i = D_i = x_i - x_{i,ref}\,. \tag{12}$$

The standard uncertainty of D_i can be expressed as:

$$u(D_i) = \sqrt{u_{i,lab}^2 + u_{i,grav}^2 + u_{i,ver}^2} \tag{13}$$

Expanded uncertainty could be expressed as

$$U(D_i) = 2 * u(D_i) \qquad (14)$$

In Figures 1-10, the degrees of equivalence in relative form for all participating laboratories are given. The uncertainties are, as required by the MRA, 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 2.

Figure 1 Degrees of equivalence for Nitrogen

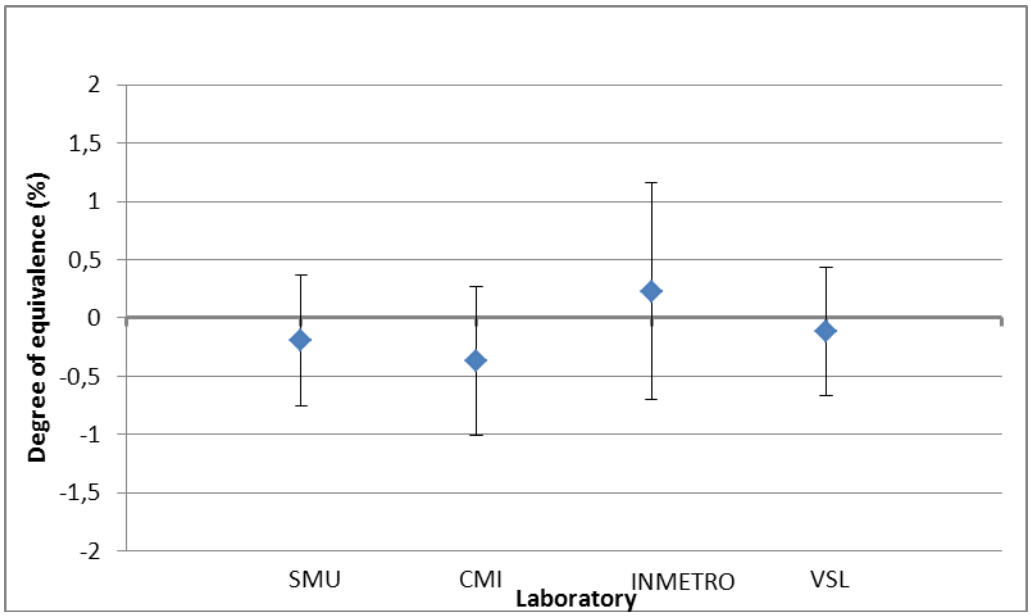


Figure 2 Degrees of equivalence for CO_2

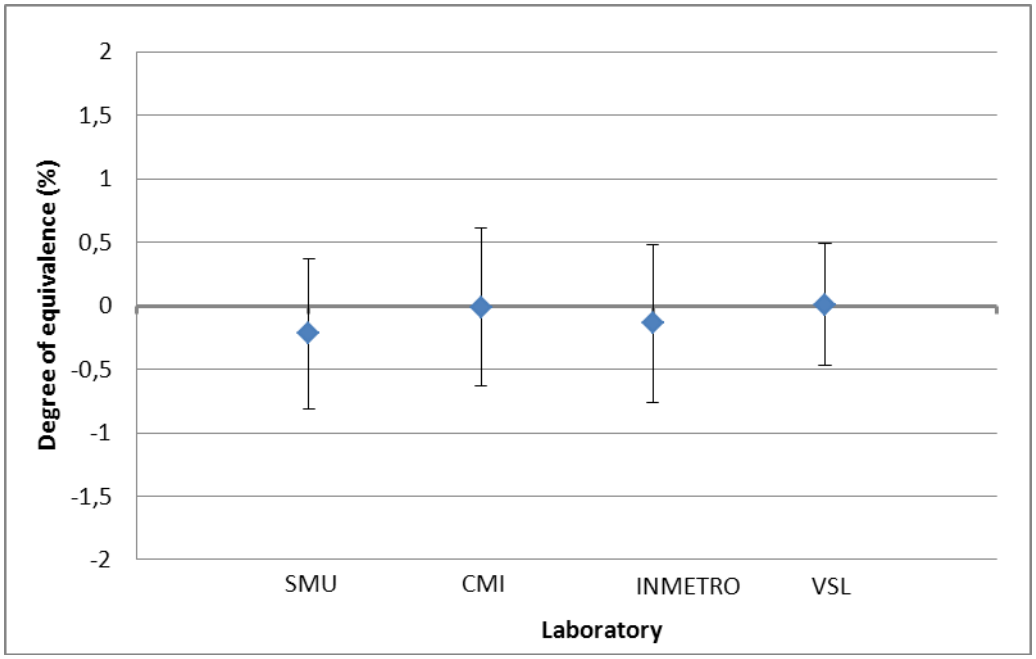


Figure 3 Degrees of equivalence for Ethane

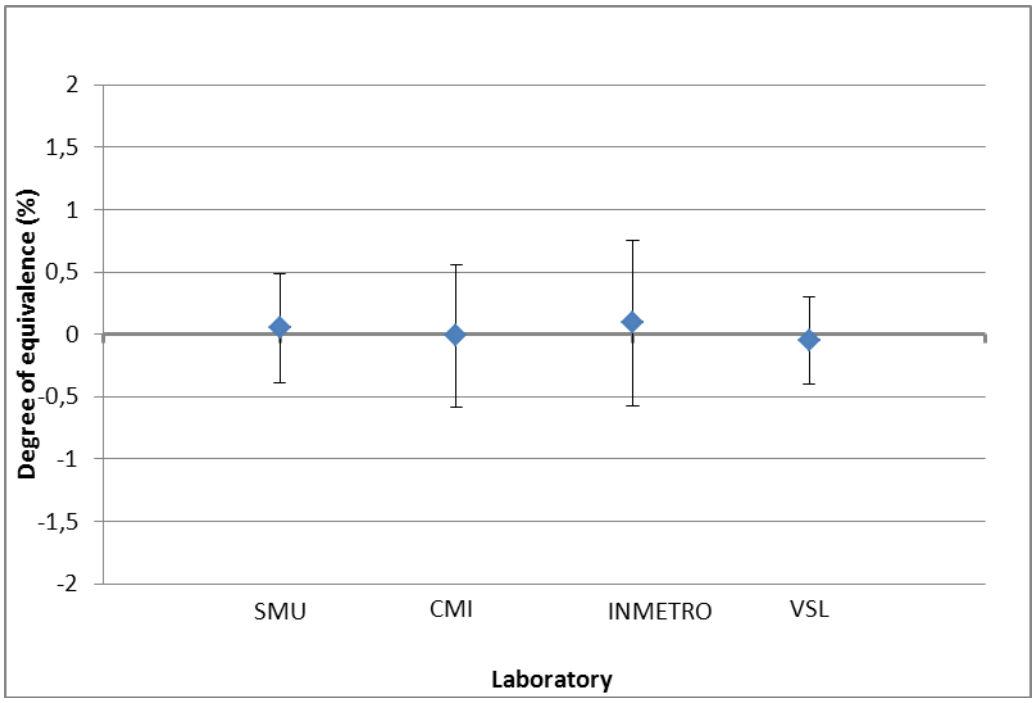


Figure 4 Degrees of equivalence for Propane

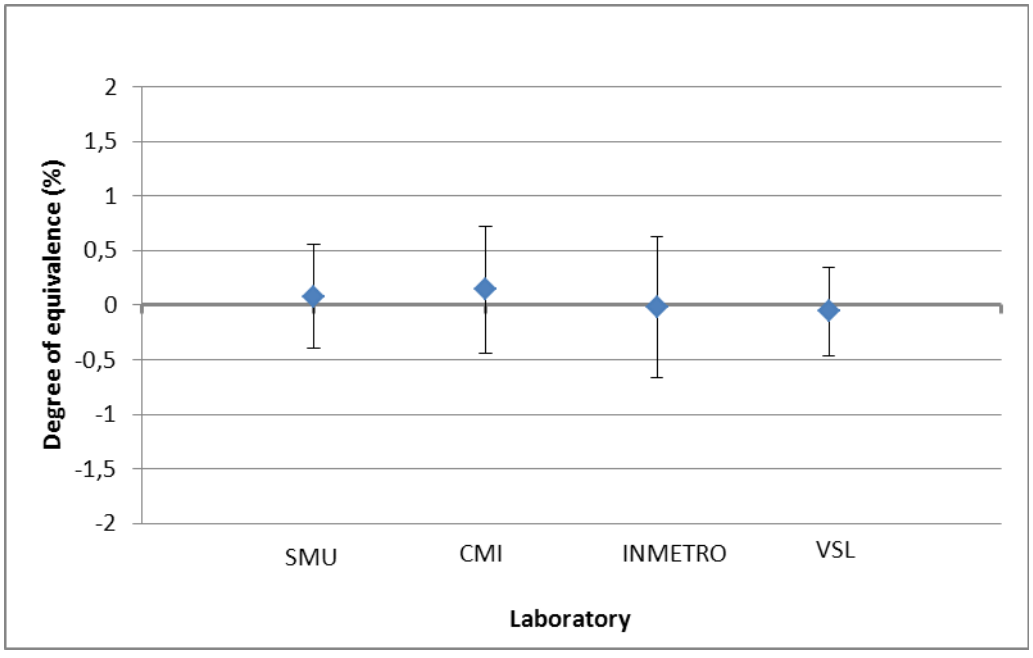


Figure 5 Degrees of equivalence for *iso*-Butane

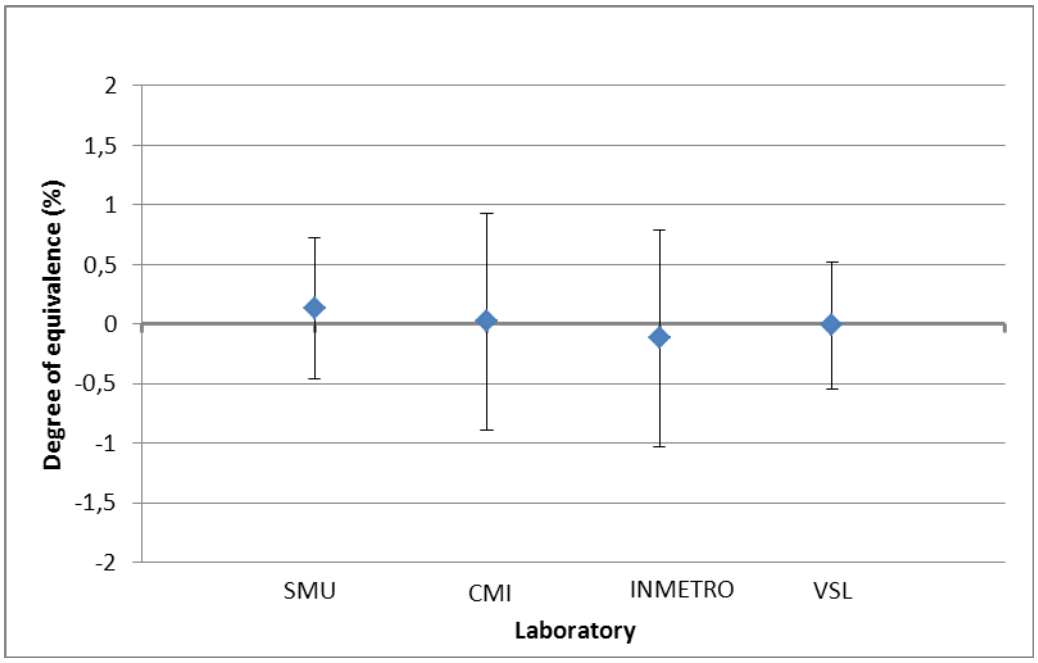


Figure 6 Degrees of equivalence for *n*-Butane

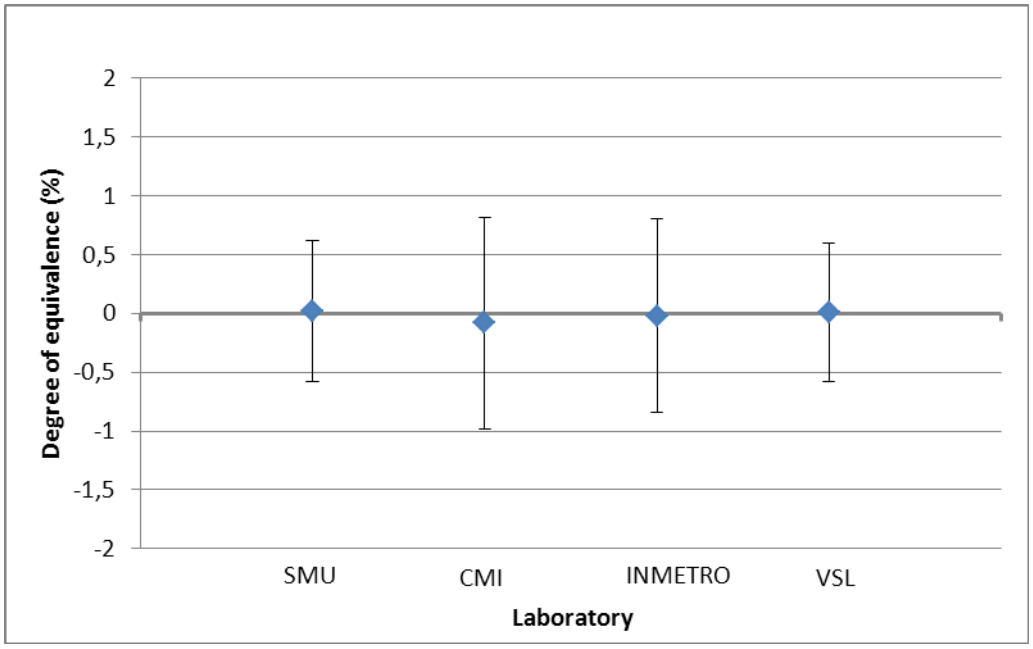


Figure 7 Degrees of equivalence for *iso*-Pentane

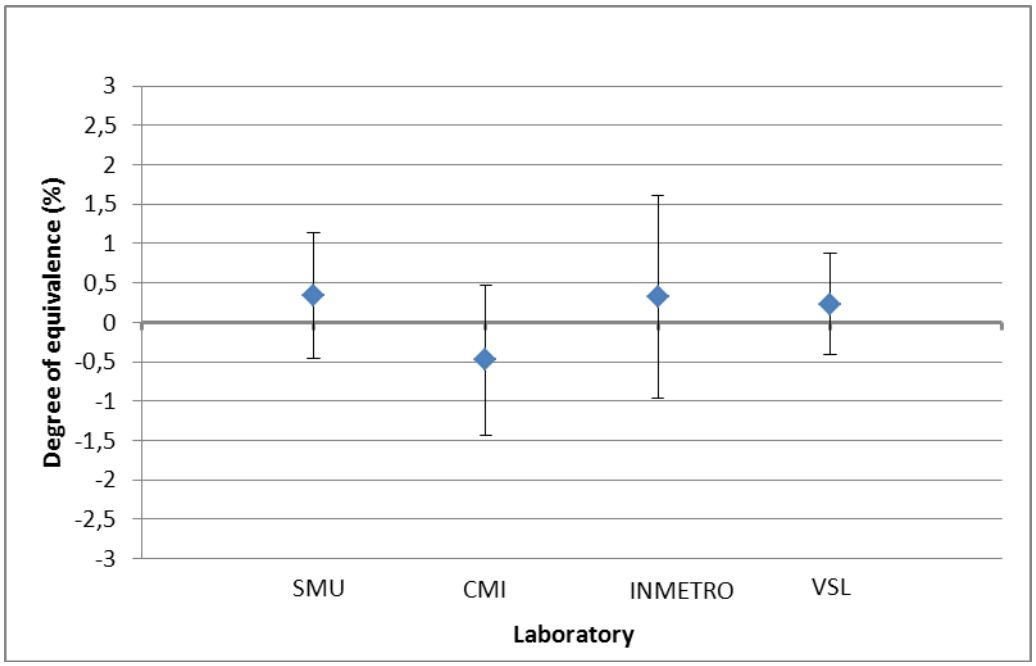


Figure 8 Degrees of equivalence for *n*-Pentane

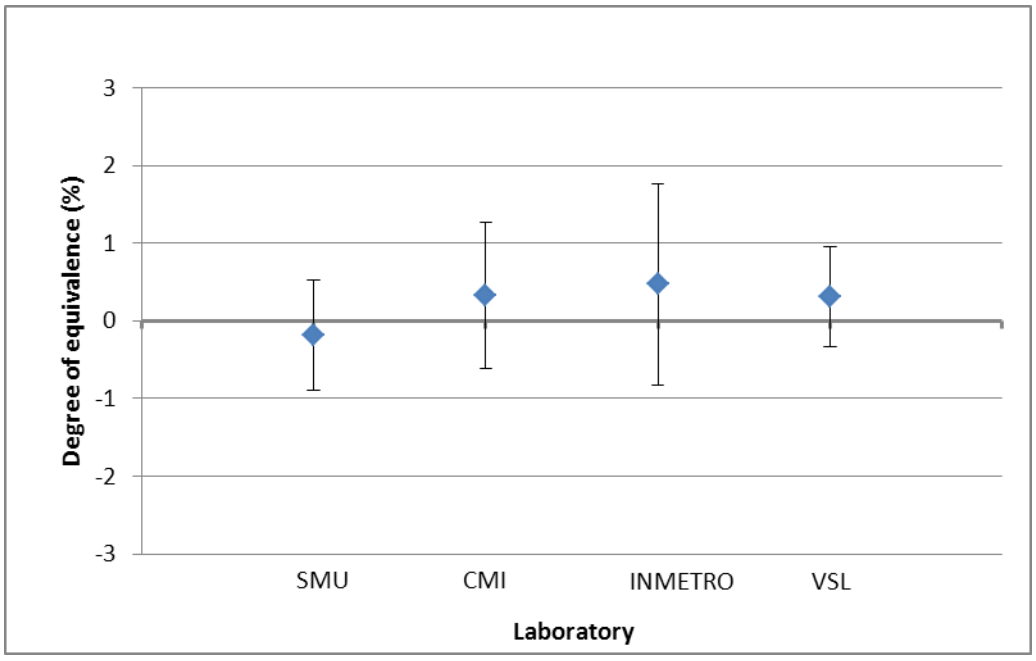


Figure 9 Degrees of equivalence for *n*-Hexane

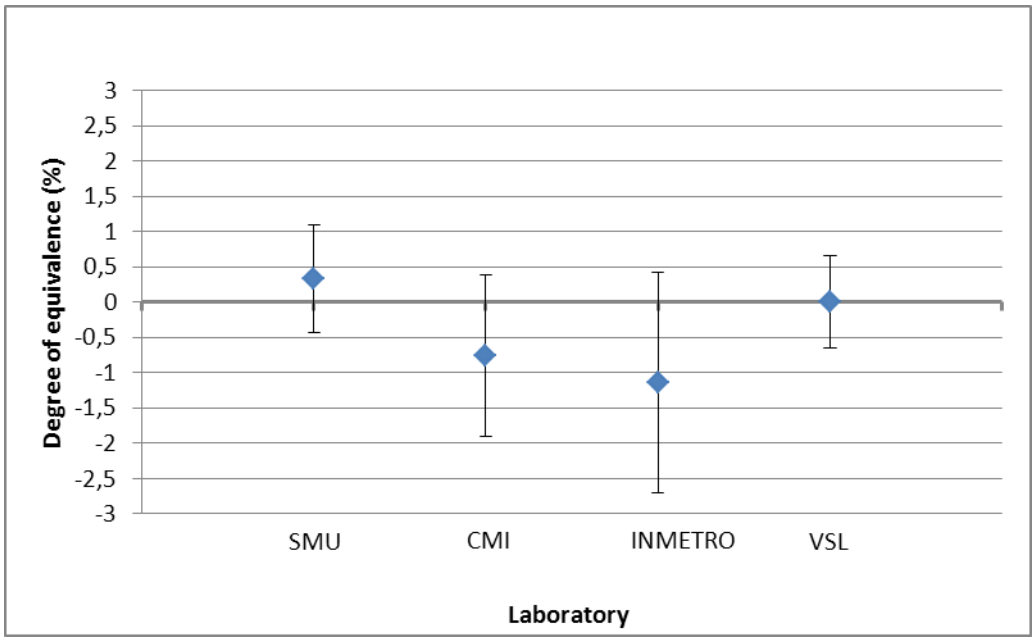
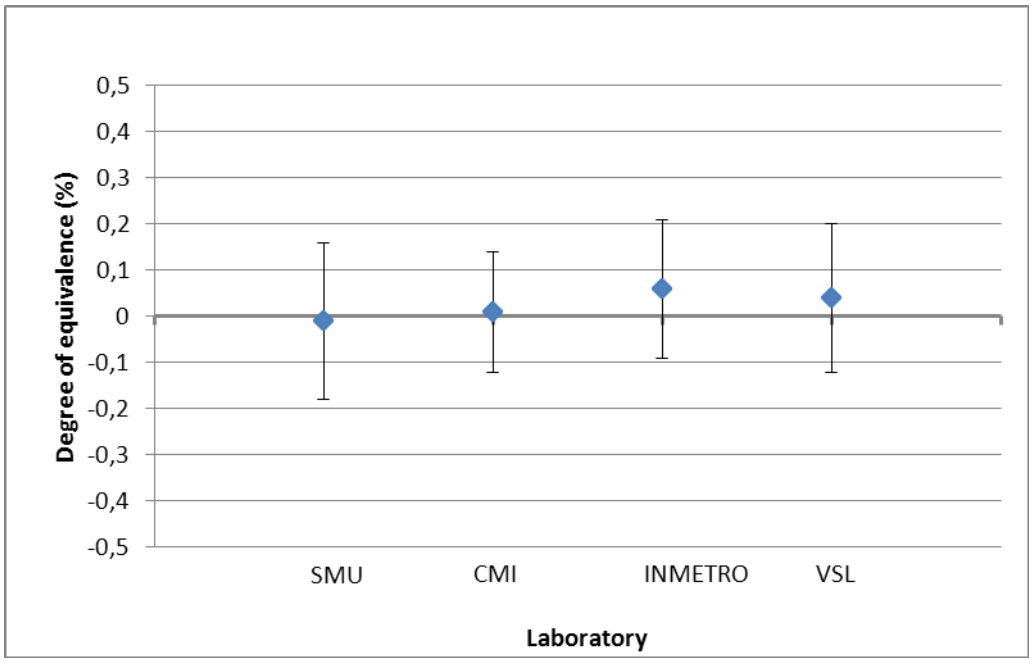


Figure 10 Degrees of equivalence for Methane



Results

In this section, the results of this supplementary comparison are summarised. In following tables, the stated data are 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)
$U_{lab,rel}$	relative form for expanded uncertainty of laboratory U_{lab}
k_{lab}	stated coverage factor
D_i	degree of equivalence - difference Δx between laboratory result and reference value (10^{-2} mol/mol)
k	assigned coverage factor for degree of equivalence
$U(D_i)$	expanded uncertainty of difference x, at 95% level of confidence (mol/mol)
Di,rel	relative form for degree of equivalence
$U(D_i)_{rel}$	relative form for expanded uncertainty of D_i

Table 6 Results for Nitrogen

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u^*_{ref}	x_{lab}	U_{lab}	k_{lab}	$U_{lab,rel}$	D_i	k	$U(D_i)$	$D_{i,rel}$	$U(D_i)_{rel}$
SMU	0040F_4	1.0046	0.0011	0.0016	0.0020	1.0027	0.0039	2	0.40%	-0.0019	2	0.0056	-0.19%	0.56%
CMI	0039F_4	1.0047	0.0011	0.0017	0.0020	1.0010	0.0050	2	0.50%	-0.0037	2	0.0064	-0.37%	0.64%
INMETRO	0043F_4	1.0607	0.0010	0.0018	0.0021	1.0630	0.0090	2	0.85%	0.0023	2	0.0099	0.22%	0.93%
VSL	0044F_4	1.0252	0.0009	0.0017	0.0020	1.0240	0.0040	2	0.39%	-0.0012	2	0.0056	-0.12%	0.55%

Table 7 Results for CO_2

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u^* ref	x_{lab}	U_{lab}	k_{lab}	$U_{lab,rel}$	D_i	k	$U(D_i)$	$D_{i,rel}$	$U(D_i)_{rel}$
SMU	0040F_4	1.0343	0.0006	0.0018	0.0019	1.0320	0.0047	2	0.46%	-0.0023	2	0.0061	-0.22%	0.59%
CMI	0039F_4	1.0343	0.0006	0.0017	0.0019	1.0342	0.0052	2	0.50%	-0.0001	2	0.0065	-0.01%	0.62%
INMETRO	0043F_4	1.0054	0.0006	0.0018	0.0005	1.0040	0.0050	2	0.50%	-0.0014	2	0.0062	-0,14%	0.62%
VSL	0044F_4	0.9919	0.0006	0.0017	0.0005	0.9920	0.0030	2	0.30%	0.0001	2	0.0047	0.01%	0.48%

Table 8 Results for Ethane

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u^* ref	x_{lab}	U_{lab}	k_{lab}	$U_{lab,rel}$	D_i	k	$U(D_i)$	$D_{i,rel}$	$U(D_i)_{rel}$
SMU	0040F_4	0.9878	0.0009	0.0010	0.0014	0.9883	0.0033	2	0.33%	0.0005	2	0.0043	0.05%	0.44%
CMI	0039F_4	0.9878	0.0009	0.0010	0.0013	0.9877	0.0049	2	0.50%	-0.0001	2	0.0056	-0.01%	0.57%
INMETRO	0043F_4	0.9931	0.0009	0.0010	0.0013	0.9940	0.0060	2	0.60%	0.0009	2	0.0066	0.09%	0.66%
VSL	0044F_4	1.1062	0.0008	0.0011	0.0014	1.1056	0.0027	2	0.24%	-0.0006	2	0.0038	-0.05%	0.35%

Table 9 Results for Propane

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u^* ref	x_{lab}	U_{lab}	k_{lab}	$U_{lab,rel}$	D_i	k	$U(D_i)$	$D_{i,rel}$	$U(D_i)_{rel}$
SMU	0040F_4	0.5073	0.0002	0.0006	0.0007	0.5077	0.0020	2	0.39%	0.0004	2	0.0024	0.08%	0.48%
CMI	0039F_4	0.5074	0.0002	0.0006	0.0007	0.5081	0.0026	2	0.51%	0.0007	2	0.0029	0.14%	0.58%
INMETRO	0043F_4	0.5081	0.0002	0.0006	0.0007	0.5080	0.0030	2	0.59%	-0.0001	2	0.0033	-0.02%	0.65%
VSL	0044F_4	0.5004	0.0002	0.0006	0.0007	0.5001	0.0015	2	0.30%	-0.0003	2	0.0020	-0.06%	0.40%

Table 10 Results for *iso*-Butane

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u^* ref	x_{lab}	U_{lab}	k_{lab}	$U_{lab,rel}$	D_i	k	$U(D_i)$	$D_{i,rel}$	$U(D_i)_{rel}$
SMU	0040F_4	0.1001	0.0001	0.0002	0.0002	0.1002	0.0004	2	0.40%	0.0001	2	0.0006	0.13%	0.59%
CMI	0039F_4	0.1001	0.0001	0.0002	0.0002	0.1001	0.0008	2	0.80%	0.0000	2	0.0009	0.02%	0.91%
INMETRO	0043F_4	0.1002	0.0001	0.0002	0.0002	0.1001	0.0008	2	0.80%	-0.0001	2	0.0009	-0.12%	0.91%
VSL	0044F_4	0.0987	0.0001	0.0002	0.0002	0.0987	0.0003	2	0.30%	0.0000	2	0.0005	-0.01%	0.53%

Table 11 Results for *n*-Butane

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u^* ref	x_{lab}	U_{lab}	k_{lab}	$U_{lab,rel}$	D_i	k	$U(D_i)$	$D_{i,rel}$	$U(D_i)_{rel}$
SMU	0040F_4	0.1010	0.0001	0.0002	0.0002	0.1010	0.0004	2	0.40%	0.0000	2	0.0006	0.02%	0.60%
CMI	0039F_4	0.1010	0.0001	0.0002	0.0002	0.1009	0.0008	2	0.79%	-0.0001	2	0.0009	-0.08%	0.91%
INMETRO	0043F_4	0.1009	0.0001	0.0002	0.0002	0.1009	0.0007	2	0.69%	0.0000	2	0.0008	-0.02%	0.82%
VSL	0044F_4	0.0994	0.0001	0.0002	0.0002	0.0994	0.0004	2	0.40%	0.0000	2	0.0006	0.01%	0.59%

Table 12 Results for *iso*-Pentane

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u^* ref	x_{lab}	U_{lab}	k_{lab}	$U_{lab,rel}$	D_i	k	$U(D_i)$	$D_{i,rel}$	$U(D_i)_{rel}$
SMU	0040F_4	0.05040	0.00003	0.00013	0.00013	0.05057	0.00031	2	0.61%	0.00017	2	0.00040	0.34%	0.80%
CMI	0039F_4	0.04974	0.00002	0.00013	0.00013	0.04950	0.00040	2	0.81%	-0.00024	2	0.00047	-0.48%	0.95%
INMETRO	0043F_4	0.05034	0.00001	0.00013	0.00013	0.05050	0.00060	2	1.19%	0.00016	2	0.00065	0.32%	1.29%
VSL	0044F_4	0.05080	0.00001	0.00013	0.00013	0.05092	0.00020	2	0.39%	0.00012	2	0.00032	0.23%	0.64%

Table 13 Results for *n*-Pentane

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u^* ref	x_{lab}	U_{lab}	k_{lab}	$U_{lab,rel}$	D_i	k	$U(D_i)$	$D_{i,rel}$	$U(D_i)_{rel}$
SMU	0040F_4	0.05324	0.00003	0.00013	0.00014	0.05314	0.00026	2	0.49%	-0.00010	2	0.00038	-0.19%	0.71%
CMI	0039F_4	0.05044	0.00002	0.00013	0.00013	0.05060	0.00040	2	0.79%	0.00016	2	0.00047	0.32%	0.94%
INMETRO	0043F_4	0.05056	0.00001	0.00013	0.00013	0.05080	0.00060	2	1.18%	0.00024	2	0.00065	0.47%	1.29%
VSL	0044F_4	0.05118	0.00001	0.00013	0.00013	0.05134	0.00021	2	0.41%	0.00016	2	0.00033	0.31%	0.65%

Table 14 Results for *n*-Hexane

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u^* ref	x_{lab}	U_{lab}	k_{lab}	$U_{lab,rel}$	D_i	k	$U(D_i)$	$D_{i,rel}$	$U(D_i)_{rel}$
SMU	0040F_4	0.02028	0.00002	0.00006	0.00007	0.02436	0.00013	2	0.53%	0.00008	2	0.00018	0.33%	0.76%
CMI	0039F_4	0.01975	0.00001	0.00005	0.00002	0.01960	0.00020	2	1.02%	-0.00015	2	0.00022	-0.76%	1.14%
INMETRO	0043F_4	0.02023	0.00001	0.00005	0.00002	0.02000	0.00030	2	1.50%	-0.00023	2	0.00032	-1.14%	1.57%
VSL	0044F_4	0.02021	0.00001	0.00005	0.00002	0.02021	0.00008	2	0.40%	0.00000	2	0.00013	0.00%	0.65%

Table 15 Results for Methane

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u^* ref	x_{lab}	U_{lab}	k_{lab}	$U_{lab,rel}$	D_i	k	$U(D_i)$	$D_{i,rel}$	$U(D_i)_{rel}$
SMU	0040F_4	96.136	0.004	0.058	0.058	96.130	0.111	2	0.12%	-0.006	2	0.160	-0.01%	0.17%
CMI	0039F_4	96.143	0.004	0.058	0.058	96.148	0.048	2	0.05%	0.005	2	0.125	0.01%	0.13%
INMETRO	0043F_4	96.110	0.002	0.058	0.058	96.170	0.090	2	0.09%	0.060	2	0.146	0.06%	0.15%
VSL	0044F_4	96.055	0.001	0.025	0.058	96.090	0.100	2	0.10%	0.035	2	0.153	0.04%	0.16%

Conclusion

The reported results for nitrogen (figure 1) agree with the reference value within 0.40 % relative. For carbon dioxide (figure 2) results agree with the reference value within 0.25% relative.

For ethane (figure 3) results agree with the reference value within 0.10 % relative. In the case of propane and iso-butane (figure 4, 5) results agree with the reference value within 0.15 % relative. For n-butane (figure 6) results agree with the reference value within 0.10 % relative. For iso-pentane and n-pentane (figure 7, 8) results agree with the reference value within 0.50% relative. For n-hexane (figure 9) most results agree with the reference value within 1 % relative (except INMETRO). For methane (figure 10) results agree with the reference value within 0.06 % relative.

The agreement of the results in this supplementary comparison is very good. All the results with their reported uncertainties are in agreement with the reference values for all the participants. SMU and VSL participated in the key comparison CCQM-K16. VSL obtained very good results in both the supplementary comparison and the CCQM-K16 comparison. SMU obtained better results in the supplementary comparison than in CCQM-K16.

References

[1] ISO 6142: Gas Analysis – Preparation of calibration gas mixtures – Gravimetric method, 2nd ed., Switzerland, 2001;

[2] ISO 6143: Gas Analysis – Determination of the composition of calibration gas mixtures, Comparison Methods, 2nd ed., Switzerland, 2001;

[3] Veen van der, A.M.H. - Heine, H.J. - Brinkmann, F. et al: International Comparison CCQM-K16 : Composition of natural gas types IV and V, Final report - Paris : BIPM, 2005;

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

Annex A Measurement report from CMI

Supplementary comparison EURAMET.QM-S9

MEASUREMENT REPORT

Laboratory: CMI (Czech metrology institute)

Cylinder number:

Measurement № 1	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	30.7.2012	1,0012	0,02	10
Carbon dioxide	30.7.2012	1,0341	0,03	10
Ethane	30.7.2012	0,9878	0,03	10
Propane	30.7.2012	0,5083	0,05	10
iso-Butane	30.7.2012	0,1000	0,06	10
n-Butane	30.7.2012	0,1007	0,06	10
iso-Pentane	30.7.2012	0,0494	0,08	10
n-Pentane	30.7.2012	0,0504	0,10	10
n-Hexane	30.7.2012	0,0197	0,29	10
Methane	30.7.2012	96,1484	0,01	10

Measurement № 2	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurement n
Nitrogen	31.7.2012	1,0009	0,02	10
Carbon dioxide	31.7.2012	1,0351	0,06	10
Ethane	31.7.2012	0,9875	0,02	10
Propane	31.7.2012	0,5073	0,04	10
iso-Butane	31.7.2012	0,1001	0,08	10
n-Butane	31.7.2012	0,1009	0,14	10
iso-Pentane	31.7.2012	0,0495	0,03	10
n-Pentane	31.7.2012	0,0506	0,04	10

n-Hexane	31.7.2012	0,0196	0,19	10
Methane	31.7.2012	96,1485	0,01	10

Measurement № 3	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	1.8.2012	1,0009	0,02	10
Carbon dioxide	1.8.2012	1,0333	0,08	10
Ethane	1.8.2012	0,9877	0,02	10
Propane	1.8.2012	0,5086	0,06	10
iso-Butane	1.8.2012	0,1003	0,05	10
n-Butane	1.8.2012	0,1010	0,07	10
iso-Pentane	1.8.2012	0,0497	0,04	10
n-Pentane	1.8.2012	0,0508	0,04	10
n-Hexane	1.8.2012	0,0196	0,18	10
Methane	1.8.2012	96,1481	0,01	10

Note: Please copy this table as many times as needed for reporting additional measurements

Results:

Gas mixture	Result mol/mol	Coverage factor	Expanded uncertainty mol/mol
Nitrogen	1,0010	2	0,0050
Carbon dioxide	1,0342	2	0,0052
Ethane	0,9877	2	0,0049
Propane	0,5081	2	0,0026
iso-Butane	0,1001	2	0,0008
n-Butane	0,1009	2	0,0008
iso-Pentane	0,0495	2	0,0004
n-Pentane	0,0506	2	0,0004

n-Hexane	0,0196	2	0,0002
Methane	96,1483	2	0,0481

Reference method:

Measured on Gas Chromatograph Agilent, with using columns (19095P – CO_2 carbonplot, 19095P-MS0, 19095P-S25), TCD and FID detectors, oven temperature 40 - 120 °C, carrier gas Helium. All measurements were done in automatic way.

Calibration Standards (CS):

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

CS 1		
methane	96,4190	0,0135
ethane	0,9489	0,0013
propane	0,4495	0,0006
n-butane	0,0896	0,0002
i-butane	0,0902	0,0002
n-pentane	0,0398	0,0001
i-pentane	0,0410	0,0001
n-hexane	0,0152	0,0001
carbon dioxide	0,9536	0,0013
nitrogen	0,9532	0,0013

CS 2		
methane	96,1280	0,0144
ethane	1,0509	0,0017
propane	0,4997	0,0007
n-butane	0,0994	0,0002

i-butane	0,0998	0,0002
n-pentane	0,0498	0,0001
i-pentane	0,0509	0,0001
n-hexane	0,0198	0,0001
carbon dioxide	1,0020	0,0014
nitrogen	0,9997	0,0014

CS 3		
methane	95,9450	0,0134
ethane	0,9976	0,0013
propane	0,5509	0,0007
n-butane	0,1108	0,0003
i-butane	0,1097	0,0003
n-pentane	0,0547	0,0001
i-pentane	0,0556	0,0001
n-hexane	0,0245	0,0001
carbon dioxide	1,0511	0,0016
nitrogen	1,1001	0,0017

Instrument Calibration:

Three independent measurements were carried out under repeatability conditions. Each measurement included ten sub-measurements.

Calibration and measurement methods	
Measurement method	Type of calibration curve
GC/TCD-FID	3 points, line

Sample Handling:

Cylinders with natural gas were kept at 20 – 24 °C at CMI.

Evaluation of measurement uncertainty:

Uncertainty estimation is given bellow:

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

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

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

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

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

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

Annex B Measurement report from INMETRO

Supplementary comparison EURAMET.QM-S9

MEASUREMENT REPORT

Laboratory: INMETRO

Participants: Cristiane Rodrigues Augusto, Claudia Cipriano Ribeiro, Denise Cristine Gonçalves Sobrinho Teixeira, Rutger Jacob Oudwater.

Cylinder number: 0043F

Measurement № 1	Date dd/mm/yy	Result (10^{-2} mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	01/08/2012	1,0637	0,19	12
Carbon dioxide	01/08/2012	1,0063	0,02	12
Ethane	01/08/2012	0,9954	0,09	12
Propane	01/08/2012	0,5086	0,09	12
iso-Butane	01/08/2012	0,10024	0,10	12
n-Butane	01/08/2012	0,10093	0,11	12
iso-Pentane	01/08/2012	0,05062	0,11	12
n-Pentane	01/08/2012	0,05080	0,14	12
n-Hexane	01/08/2012	0,02000	0,32	12
Methane	01/08/2012	96,16	0,01	12

Measurement № 2	Date dd/mm/yy	Result (10^{-2} mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	14/08/2012	1,0584	0,04	10
Carbon dioxide	14/08/2012	0,9909	0,02	10
Ethane	14/08/2012	0,9924	0,12	10
Propane	14/08/2012	0,5078	0,11	10
iso-Butane	14/08/2012	0,10025	0,08	10
n-Butane	14/08/2012	0,10101	0,12	10
iso-Pentane	14/08/2012	0,05054	0,15	10
n-Pentane	14/08/2012	0,05093	0,13	10
n-Hexane	14/08/2012	0,02006	0,21	10
Methane	14/08/2012	96,09	0,01	10

Measurement № 3	Date dd/mm/yy	Result (10^{-2} mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	12/09/2012	1,0667	0,21	12
Carbon dioxide	12/09/2012	1,0141	0,02	12
Ethane	12/09/2012	0,9931	0,12	12
Propane	12/09/2012	0,5076	0,12	12
iso-Butane	12/09/2012	0,09989	0,12	12
n-Butane	12/09/2012	0,1007	0,12	12
iso-Pentane	12/09/2012	0,05045	0,11	12
n-Pentane	12/09/2012	0,05067	0,13	12
n-Hexane	12/09/2012	0,02009	0,16	12
Methane	12/09/2012	96,26	0,01	12

Results:

Gas mixture	Result 10^{-2} mol/mol	Coverage factor	Expanded uncertainty 10^{-2} mol/mol
Nitrogen	1,063	2	0,009
Carbon dioxide	1,004	2	0,005
Ethane	0,994	2	0,006
Propane	0,508	2	0,003
iso-Butane	0,1001	2	0,0008
n-Butane	0,1009	2	0,0007
iso-Pentane	0,0505	2	0,0006
n-Pentane	0,0508	2	0,0006
n-Hexane	0,0200	2	0,0003
Methane	96,17	2	0,09

Reference method

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

GC Model: Varian CP-3800 (ISO 6974 configuration) equipped with both TCD and FID detectors. The nitrogen, carbon dioxide and methane were determined using the TCD detector the other components were determined using FID detector.
Carrier gas: Helium.
Columns: 1.5 m x 1/8” ultimetal Molsieve 13X 80/100
0.5 m x 1/8” ultimetal Hayesep T 80/100
0.5 m x 1/8” ultimetal Hayesep Q 80/100
60 m x 0.25 mm CP-Sil 5 CB
Sample introduction: Multi position gas sampling valves
Data collection was performed using Star Chromatography Workstation 6.3.

Calibration Standards

Seven primary standard mixtures were used for natural gas analysis. Except for the measurement of i-pentane 4 primary standard mixtures were used, for the n-pentane and n-hexane 6 mixtures where used.
The mixtures were prepared according to International Standard ISO 6142:2001 by VSL and NPL.

PRM **D248644**

Component	Assigned value(x) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Methane	85,86	0,085
Ethane	7,005	0,014
Propane	0,978	0,002
iso-Butane	0,4926	0,0012
n-Butane	0,4880	0,0012
iso-Pentane	0,1044	0,0005
n-Pentane	0,03212	0,00016
Hexane	0,0502	0,00025
Nitrogen	1,012	0,002
Carbon dioxide	3,978	0,008

PRM **D248719**

Component	Assigned value(x) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Methane	89,83	0,085
Ethane	2,986	0,006
Propane	1,990	0,004
iso-Butane	0,2009	0,0005
n-Butane	0,1991	0,0005
iso-Pentane	0,02967	0,000145
n-Pentane	0,0676	0,0003
Hexane	0,2014	0,0010
Nitrogen	2,994	0,006
Carbon dioxide	1,501	0,003

PRM **D247751**

Component	Assigned value(*x*) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Methane	79,99	0,08
Ethane	3,991	0,006
Propane	3,004	0,0045
iso-Butane	0,5021	0,00125
n-Butane	0,4994	0,00125
iso-Pentane	0,1987	0,0010
n-Pentane	0,1968	0,0010
Hexane	0,1002	0,0005
Nitrogen	7,501	0,015
Carbon dioxide	4,017	0,008

PRM **D247726**

Component	Assigned value(*x*) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Methane	88,91	0,09
Ethane	1,017	0,0015
Propane	0,992	0,002
iso-Butane	0,3999	0,00095
n-Butane	0,3891	0,00095
iso-Pentane	0,0973	0,0005
n-Pentane	0,0984	0,0005
Hexane	0,0501	0,00025
Nitrogen	6,019	0,012
Carbon dioxide	2,027	0,004

PRM **D247718**

Component	Assigned value(*x*) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Methane	92,92	0,095
Ethane	1,491	0,002
Propane	0,5021	0,00075
iso-Butane	0,01017	0,000025
n-Butane	0,01002	0,000025
iso-Pentane	0,01991	0,00010
n-Pentane	0,01993	0,00010
Hexane	0,00998	0,00005
Nitrogen	2,524	0,005
Carbon dioxide	2,492	0,005

PRM **D523411**

Component	Assigned value(*x*) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Methane	68,82	0,05
Ethane	9,985	0,010
Propane	3,990	0,004
iso-Butane	0,994	0,002
n-Butane	1,206	0,0025
iso-Pentane		
n-Pentane		
Hexane		
Nitrogen	10,01	0,02
Carbon dioxide	5,002	0,0125

PRM **NG218A**

Component	Assigned value(*x*) 10^{-2} mol/mol	Standard uncertainty ($u(x)$) 10^{-2} mol/mol
Methane	98,057	0,010
Ethane	0,4992	0,00015
Propane	0,3034	0,0005
iso-Butane	0,05022	0,000125
n-Butane	0,04929	0,000125
iso-Pentane	0,01009	0,000035
n-Pentane	0,00988	0,000035
Hexane	0,02009	0,00005
Nitrogen	0,5066	0,00065
Carbon dioxide	0,4935	0,00075

Instrument Calibration

The standards used are described in the topic above.
Temperature and pressure correction were not take into calculation.
The measurement sequence was injection of the standards and then injection of the sample.
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 quadratic function.
For i-pentane a linear function was used because only 4 standards where available to calculate the curve.
At least 12 repeat analyses were performed to the first and the last day of analysis, but to second day, the two first of these was rejected.

Sample Handling

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

Evaluation of measurement uncertainty

The uncertainty of the unknown sample was calculated according to ISO 6143, using the software B_least. The measurements were carried out in three days under repeatability conditions. The final concentrations were a average of the results. Three sources of uncertainty were considered to estimate the uncertainty for each day of analysis:

- The uncertainty of the PRMs described on the certificates (type B)
- The uncertainty of the repeatability from the amount response (type A)
- The uncertainty from the calibration curve (type A)

The final standard uncertainty was the combination of the three days of analysis:

$$u_{comb} = \sqrt{u_{Day1}{}^2 + u_{Day2}{}^2 + u_{Day3}{}^2}$$

The final expanded uncertainty was calculated by multiply for the coverage factor: k = 2 with a confidence interval of 95%.

Annex C Measurement report from SMU

Supplementary comparison EURAMET.QM-S9

MEASUREMENT REPORT

Laboratory: SMU

Cylinder number: 0040F

Measurement № 1	Date dd/mm/yy	Result (10^{-2} mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	19/01/2012	1,0018	0,10	6
Carbon dioxide	19/01/2012	1,0322	0,10	6
Ethane	19/01/2012	0,98976	0,07	6
Propane	19/01/2012	0,50789	0,07	6
iso-Butane	19/01/2012	0,10011	0,08	6
n-Butane	19/01/2012	0,100952	0,08	6
iso-Pentane	19/01/2012	0,050567	0,09	6
n-Pentane	19/01/2012	0,053169	0,17	6
n-Hexane	19/01/2012	0,024342	0,14	6
Methane	19/01/2012	96,125	0,04	6

Measurement № 2	Date dd/mm/yy	Result (10^{-2} mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	10/09/2012	1,0036	0,13	6
Carbon dioxide	10/09/2012	1,0336	0,09	6
Ethane	10/09/2012	0,9874	0,09	6
Propane	10/09/2012	0,50758	0,12	6
iso-Butane	10/09/2012	0,10027	0,14	6
n-Butane	10/09/2012	0,10107	0,15	6
iso-Pentane	10/09/2012	0,05046	0,15	6
n-Pentane	10/09/2012	0,05315	0,18	6
n-Hexane	10/09/2012	0,024354	0,17	6
Methane	10/09/2012	96,139	0,04	6

Measurement № 3	Date dd/mm/yy	Result (10^{-2} mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	24/09/2012	1,0026	0,12	6
Carbon dioxide	24/09/2012	1,0303	0,11	6
Ethane	24/09/2012	0,9878	0,09	6
Propane	24/09/2012	0,50756	0,10	6
iso-Butane	24/09/2012	0,10021	0,14	6
n-Butane	24/09/2012	0,10095	0,15	6
iso-Pentane	24/09/2012	0,05067	0,17	6
n-Pentane	24/09/2012	0,05311	0,18	6
n-Hexane	24/09/2012	0,024381	0,17	6
Methane	24/09/2012	96,125	0,04	6

Results:

Gas mixture	Result 10^{-2} mol/mol	Coverage factor	Expanded uncertainty 10^{-2} mol/mol
Nitrogen	1,0027	2	0,0039
Carbon dioxide	1,0320	2	0,0047
Ethane	0,9883	2	0,0033
Propane	0,5077	2	0,0020
iso-Butane	0,10020	2	0,00040
n-Butane	0,10099	2	0,00040
iso-Pentane	0,05057	2	0,00031
n-Pentane	0,05314	2	0,00026
n-Hexane	0,02436	2	0,00013
Methane	96,130	2	0,111

Reference method

Analysis was accomplished according to ISO 6143:2001 against set of SMU PSM ´s using GC method.
Varian GC 3800 system in Laboratory of gases SMU contains:
- two detectors -TCD (in dual configuration) and FID
- multi-column system (molsieve 13 X packed 5 ft x1/8" S.S.,short DC 200/500 packed 30%, 2 ft x 1/8" S.S., long DC 200/500 packed 30%, 30 ft x 1/8" S.S., buffer packed 1.5% OV 101 CGHP 100/120, 2 ft x 1/8" S.S.).
Injection was accomplished through two sample loops with volume of 0.25 ml.
Carrier gas Helium.
The reverse flow of front carrier gas was used (back-flush).
The analysis was accomplished in iso-thermal way and last 20 minutes.
Multiposition valve was used for changing measuring position.
Analysis was operated in automated way, flow of the gas was controlled by mass flow controller Brooks.

Calibration Standards

All calibration standards were made gravimetrically according ISO 6142:2001 in SMU. Calculation of purity table was made automatically by 2.0 version ISO 6142 software with inputs from gravimetric preparation and purity measurements. Purity measurements of parent gases were made using following analytical instruments: GC FID- methaniser, GC TCD, FTIR and Dew-point meter. Mole fraction of undetected, but analysed component was calculated from detection limit of used method. Specifications of the manufacturer

were used for Ar, H_2 and O_2. Quality of used parent gases: Methane 4.5 Linde, Ethane 3.5 Messer, Propane 3.5 Messer, Isobutane 3.5 Linde, Butane 3.5 Linde, CO_2 5.5 Air Liquid, Nitrogen BIP Plus Air Products. Purity analysis of liquids C_5 and C_6 was made by GC MS. Quality of parent liquids: i-Pentane puriss p.a. Sigma Aldrich 2.5, n-Pentane puriss p.a. Sigma Aldrich 2.0, n-Hexane puriss p.a. Sigma Aldrich 2.0.

As calibrants were used 6 primary standard mixtures with following compositions and expanded uncertainties:

PSM 0014F_10

Component	Assigned value(*x*) mol/mol	Expanded uncertainty (*U*(*x*)) mol/mol
methane	0,9385	0,0011
ethane	0,007155	0,000019
iso-butane	0,0015053	0,0000057
iso-pentane	0,0001935	0,0000010
n-butane	0,0015365	0,0000057
n-hexane	0,0002179	0,0000009
n-pentane	0,0001993	0,0000007
neopentane	0,0001592	0,0000037
propane	0,006390	0,000018
CO_2	0,004491	0,000032
N_2	0,039671	0,000040

PSM 0025F_4

Component	Assigned value(*x*) mol/mol	Expanded uncertainty (*U*(*x*)) mol/mol
methane	0,9781	0,0012
ethane	0,008015	0,000027
iso-butane	0,0003740	0,0000016
iso-pentane	0,00016965	0,00000050
n-butane	0,0003637	0,0000012
n-hexane	0,0001736	0,0000006
n-pentane	0,0001693	0,0000005
neopentane	0,0000928	0,0000016
propane	0,0017702	0,0000050
CO_2	0,001113	0,000032
N_2	0,009648	0,000070

PSM 0018F_4

Component	Assigned value(*x*) mol/mol	Expanded uncertainty (*U*(*x*)) mol/mol
methane	0,9801	0,0009
ethane	0,004123	0,000011
izo-butane	0,0005791	0,0000012
izo-pentane	0,00012095	0,00000046
n-butane	0,0006033	0,0000014
n-hexane	0,0001235	0,0000006
n-pentane	0,0001233	0,0000004
neopentane	0,0000402	0,0000013
propane	0,0024648	0,0000036
CO_2	0,001855	0,000034
N_2	0,009864	0,000074

PSM 0094F_3

Component	Assigned value(*x*) mol/mol	Expanded uncertainty (*U*(*x*)) mol/mol
methane	0,9388	0,0010
ethane	0,006967	0,000019
iso-butane	0,0015248	0,0000130
iso-pentane	0,0001981	0,0000030
n-butane	0,0014204	0,0000080
n-hexane	0,0001951	0,0000022
n-pentane	0,0001997	0,0000006
neopentane	0,0001960	0,0000041
propane	0,006055	0,000060
CO_2	0,004516	0,000026
N_2	0,039875	0,000040

PSM 0030F_2

Component	Assigned value(*x*) mol/mol	Expanded uncertainty (*U*(*x*)) mol/mol
methane	0,8382	0,0010
ethane	0,035247	0,000076
izo-butane	0,0010213	0,0000014
izo-pentane	0,0002980	0,0000009
n-butane	0,0013948	0,0000020
n-hexane	0,0005136	0,0000019
n-pentane	0,0003074	0,0000006
neopentane	0,0001219	0,0000030
propane	0,007356	0,000009
CO_2	0,014078	0,000046
N_2	0,10150	0,00014

PSM 0706E_3

Component	Assigned value(*x*) mol/mol	Expanded uncertainty (*U*(*x*)) mol/mol
methane	0,8935	0,0008
ethane	0,039700	0,000087
izo-butane	0,003306	0,000008
izo-pentane	0,0005038	0,0000019
n-butane	0,004287	0,000012
n-hexane	0,0005286	0,0000014
n-pentane	0,0005065	0,0000022
neopentane	0,000982	0,000030
propane	0,014090	0,000022
CO_2	0,012913	0,000040
N_2	0,029642	0,000046

Instrument Calibration

Measurement method with 6 automated runs was used. All runs in first, third, fifth measurement sequence had rising molar fraction, second, fourth, processed in reverse order. From each run was made one calibration curve with sample signals. Data were subjected to the b_least program (weighted least square regression). The result of the measurement sequence was the average of molar fractions.
At b_least linear or quadratic models of analytical curves were used.
No corrections were used.

Sample Handling

All cylinders were at SMU kept at 17 – 22 °C before measurement. Measuring cylinders were equipped with pressure reducers. Samples were transferred to the instruments throw mass-flow controller and pressure controller automatically in sequences. No dilutions were used.

Evaluation of measurement uncertainty

Uncertainty of instrument response consisted from figure characterized roughly immediate repeatability and from signal drift estimated. From each run was made one calibration curve with sample signals. These figures together with molar fraction data with associated uncertainties were subjected to b_least program (weighted least square regression). Each run produced sample molar fraction with its standard uncertainty. From all runs results = average of molar fractions in one sequence were standard deviation found (uncertainty of type A) and from runs results uncertainties the mean (through squares) was found (uncertainty of type B). These 2 figures were combined to give result uncertainty.

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

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

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

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

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

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

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

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

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

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

Final result is average from 3 day results

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

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

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

Expanded uncertainty (k=2) of final result

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

Annex D Measurement report from VSL

Annex 1

Supplementary comparison EURAMET.QM-S9

MEASUREMENT REPORT

Laboratory: VSL Netherlands

Cylinder number: 0044 F

Measurement № 1	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	02/03/12	0.010241	0.01	5
Carbon dioxide	02/03/12	0.0099280	0.02	5
Ethane	02/03/12	0.011061	0.03	5
Propane	02/03/12	0.0050047	0.02	5
iso-Butane	02/03/12	0.00098635	0.02	5
n-Butane	02/03/12	0.00099344	0.02	5
iso-Pentane	02/03/12	0.00050916	0.02	5
n-Pentane	02/03/12	0.00051337	0.03	5
n-Hexane	29/02/12	0.00020229	0.01	5
Methane	02/03/12	0.96091	0.01	5

Measurement № 2	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	16/03/12	0.010221	0.05	5
Carbon dioxide	16/03/12	0.0099176	0.04	5
Ethane	16/03/12	0.011043	0.02	5
Propane	16/03/12	0.0050058	0.01	5
iso-Butane	16/03/12	0.00098717	0.01	5
n-Butane	16/03/12	0.00099409	0.01	5
iso-Pentane	16/03/12	0.00050940	0.01	5

n-Pentane	16/03/12	0.00051402	0.01	5
n-Hexane	27/03/12	0.00020220	0.01	4
Methane	16/03/12	0.96091	0.01	5

Measurement № 3	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	01/06/12	0.010233	0.03	5
Carbon dioxide	01/06/12	0.0099183	0.02	5
Ethane	01/06/12	0.011056	0.03	5
Propane	01/06/12	0.0049996	0.01	5
iso-Butane	01/06/12	0.00098632	0.00(3)	5
n-Butane	01/06/12	0.00099262	0.00(4)	5
iso-Pentane	01/06/12	0.00050909	0.01	5
n-Pentane	01/06/12	0.00051323	0.01	5
n-Hexane	05/06/12	0.00020222	0.02	5
Methane	01/06/12	0.96071	0.01	5

Measurement № 4	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	07/09/12	0.010245	0.04	5
Carbon dioxide	07/09/12	0.0099196	0.02	5
Ethane	07/09/12	0.011061	0.02	5
Propane	07/09/12	0.0050088	0.01	5
iso-Butane	07/09/12	0.00098602	0.00(5)	5
n-Butane	07/09/12	0.00099311	0.00(5)	5
iso-Pentane	07/09/12	0.00050905	0.01	5
n-Pentane	07/09/12	0.00051314	0.02	5
n-Hexane	07/09/12	0.00020196	0.01	5
Methane	19/09/12	0.96117	0.00(3)	5

Results:

Gas mixture	Result mol/mol	Coverage factor	Expanded uncertainty mol/mol
Nitrogen	0.01024	2	0.00004
Carbon dioxide	0.00992	2	0.00003
Ethane	0.011056	2	0.000027
Propane	0.005001	2	0.000015
iso-Butane	0.000987	2	0.000003
n-Butane	0.000994	2	0.000004
iso-Pentane	0.0005092	2	0.0000020
n-Pentane	0.0005134	2	0.0000021
n-Hexane	0.0002021	2	0.0000008
Methane	0.9609	2	0.0010

Reference method

The first GC is an Agilent 6890 N configured as Natural Gas Analyser (NGA). The column is a Porapak R , 3 m, 1/8" outer diameter, 80/100 mesh, and the GC is equipped with two detectors: the Flame Ionisation Detector (FID) placed at the exhaust of the thermal conductivity detector (TCD). There is one sampling valve with a 0.25 mL sample loop. The sample introduction is done using a multi-position gas valve at ambient pressure. The carrier gas is helium and the column temperature is programmed.

The measurements of hexane are taken on an Agilent 7890 GC, equipped with a DC200 column, 5 m, 1/8" outer diameter, 80/100 mesh and an FID detector. The sample loop has a volume of 1 mL and the oven temperature is kept at 75°C. The other conditions are the same as for the NGA.

Calibration Standards

The GCs are calibrated with a suite of primary standard gas mixtures (PSMs) for natural gas composition. The supplementary comparison mixture is measured in the same run as the PSMs. All peak areas are corrected for ambient pressure influence, which eliminates to a large part the systematic effects on the amount–of–substance fractions. This variation is observed between chromatograms and due to differences in the conditions under which the samples are taken: mostly pressure and to a far lesser extent temperature.

Instrument Calibration

The instrument is calibrated using for each component at least 7 primary standard gas mixtures (PSMs). 5 injections are used per mixture. The data are processed in accordance with ISO 6143, using a quadratic polynomial for all components.

Sample Handling

After acclimatization, the mixture is rehomogenised prior to analysis. The supplementary comparison mixture is treated further as any other natural gas mixture.

Evaluation of measurement uncertainty

The uncertainty evaluation was performed in accordance with ISO 6143. The results of the three runs were combined and the uncertainty associated with the amount–of–substance fraction value of the standards was assumed to be fully correlated between the three measurements.