International Key Comparison COOMET.QM-K23b (Natural Gas)

Final report

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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.

This comparison is organized by Technical Committee 1.8 “Physical Chemistry” COOMET. The comparison was registered in the international database on key comparison (KCDB), Appendix B of MRA, as COOMET.QM-K23b. Earlier the key comparison was carried out by Consultative Committee for Amount of Substance CCQM-К23b (Natural gas) [1].

Participants

Table 1 lists the participants of the key comparison.

Table 1: List of participants

Acronym	**Country**	**Institute**
VNIIM	RU	D.I.Mendeleyev Institute for Metrology, St-Petersburg, Russia
Ukrmetrteststandard	UA	All Ukrainian State Research-Industrial Center of Standardization, Metrology, Certification and Protection of Consumers, Kiev, Ukraine
BelGIM	BY	Belorussian State Institute for Metrology, Minsk, Belarus
BAM	DE	Federal Institute for Materials Research and Testing, Berlin, Germany
SMU	SK	Slovak Institute of Metrology, Bratislava, Slovak Republic
CMI	CZ	Czech Metrology Institute, Brno, Czech Republic

Measurement standards

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

Table 2: Nominal composition of the mixtures

Component	Mixture x (10^{-2} mol/mol)
Nitrogen	7
Carbon dioxide	3
Ethane	9.5
Propane	3.5
iso-Butane	0.8
n-Butane	1
Methane	balance

The mixtures have been prepared gravimetrically and subsequently verified by ISO 6142 and ISO 6143 [2,3]. The preparation of the mixtures has been carried out using the normal procedure for the preparation of gas mixtures.

After preparation, the mixtures have been verified using GC/TCD (nitrogen, carbon dioxide, ethane, propane), GC/FID and GC/TCD (iso-butane, n-butane).

After preparation of the mixtures the damage of one of a cylinder valve has been discovered. This cylinder was changed to another from another batch prepared for other purposes. Gas mixtures from the other batch were prepared and researched similarly to the first batch. The differences between molar fraction of the components in the other batch gas mixture from molar fraction of the components in the first batch gas mixtures are:

8,6 % for Nitrogen,
11 % for Carbon Dioxide,
5,1 % for Ethane,
6,5 % for Propane.
There are no differences for iso-butane and n-butane.

The indicated slight differences had not effect on the measurement procedure and uncertainty estimate.

Measurement protocol

The laboratories were requested to use their normal procedure for the measurement of the composition of the gas mixtures. 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. It was not required to reproduce all numerical data underlying the results reported and the uncertainties thereof, but the report of the evaluation of measurement uncertainty should at least allow addressing which components have been included in the evaluation, and what is their quantitative impact on the uncertainty of the results reported.

Schedule

The schedule of this key comparison was as follows:

Until November 2007	Preparation of gas mixtures
Until May 2008	Shipment of cylinders to participants
June 2008	Start of comparison
August 2008	Close of comparison
August 2008	Reports due to coordinating laboratory
October 2008	Cylinders due to coordinating 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

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

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

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

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

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

and its standard uncertainty as well. Furthermore, 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 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, the following expression is obtained

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

The validity of the mixtures has been demonstrated by verifying the composition as calculated from 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 [2]

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

The factor 2 is a coverage factor (normal distribution, 95 % level of confidence). The uncertainty associated with the verification highly depends on the experimental design followed. All mixtures prepared in this key comparison satisfy for all components the condition given in equation (7).

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

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

where

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

Since the amount of substance fraction from preparation is used at the basis, the expectation of the correction $<\Delta x_{i,ver}>$ due to verification can be taken as zero. 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

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[1] This definition of a reference value is consistent with the definition of a key comparison reference value, as stated in the mutual recognition arrangement (MRA) [3].

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

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

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

$$u^2_{i,ref} = u^2_{i,prep} + u^2_{i,ver}, \tag{12}$$

$$U_{i,ref} = k u_{i,ref}, \tag{13}$$

$k = 2$.

In order to determine the link between COOMET.QM-K23b and CCQM-K23b it is necessary to calculate $(U^*_{i,ref})^2$ taking into account deviation of VNIIM in CCQM-K23b:

$$(U^*_{i,ref})^2 = U^2_{i,prep} + U^2_{i,ver} + D_i^2{}_{CCQM-K23b} \tag{14}$$

where $\Delta_{CCQM-K23b}$ - deviation of VNIIM in CCQM-K23b from gravimetric value.

The values of $D_{iCCQM-K23b}$ for VNIIM the following:

VNIIM CCQM-K23b	$D_{iCCQM-K23b}$, 10^{-2} mol/mol
Nitrogen	0,0090
Carbon dioxide	- 0,0078
Ethane	- 0,0182
Propane	- 0,0087
iso-Butane	- 0,0021
n-Butane	- 0,0030
Methane	0,036

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

Measurement methods

A summary of the calibration methods and metrological traceability is given in table 3.

Table 3: Summary of calibration methods and metrological traceability

Laboratory	Calibration	Traceability
VNIIM	bracketing	Own standards
Ukrmetrteststandard	three points, linear	Own standards
BelGIM	three and four points, linear	Own standards
BAM	bracketing	Own standards
SMU	five points, quadratic	Own standards
CMI	two and five points, linear, quadratic	Own standards+ NMi VSL

All laboratories except BAM calculated methane mole fraction x_{CH4}, mol/mol according to the formula:

$$x_{CH4} = 1-\sum x_i,$$

x_i- mole fraction of mixture components, mol/mol. BAM analyzed methane value.

Supported CMC claims

Components and ranges supported by COOMET.QM-K23b are presented in Table 4.

Table 4: Components and ranges supported by COOMET.QM-K23b

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

Degrees of equivalence

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

$$\Delta x_i = D_i = x_i - x_{KCRV} , \tag{15}$$

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

$$\Delta x_i = D_i = x_i - x_{i,ref} . \tag{16}$$

The expanded uncertainty of D_i can be expressed as

$$U^2(\Delta x_i) = U_{i,lab}^2 + U_{i,prep}^2 + U_{i,ver}^2 + D_i^2{}_{CCQM-K23b} , \tag{17}$$

assuming that the aggregated error terms are uncorrelated.

In the figures 1-7, the degrees of equivalence for all participating laboratories are given relative to the gravimetric value. The uncertainties are, as required by the MRA [4], given as 95 % confidence intervals. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor k=2 was used.

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

Results

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 in view of deviation of VNIIM in the CCQM-K23b (10^{-2} mol/mol)
$D_{iCCQM-K23b}$	deviation of VNIIM in the CCQM-K23b (10^{-2} mol/mol)
x_{lab}	result of laboratory (10^{-2} mol/mol)
$x_{calculated}$	calculated value (for methane) (10^{-2} mol/mol)
U_{lab}	expanded 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	stated coverage factor
$U(\Delta x)$	expanded uncertainty of difference Δx, at 95 % level of confidence (10^{-2} mol/mol)

All results of this key comparison are presented in the tables 5 - 11 and shown in figures 1 - 7.

Table 5: Results for nitrogen

Laboratory	Cylinder	x_{prep}	U_{prep}	U_{ver}	$D_{iCCQM-K23b}$	U^*_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
VNIIM	D200273	7.11364	0.0024	0.01138	0.00900	0.01471	7.109	0.019	2	-0.0046	2	0.0237
Ukrmetrteststandard	D200292	6.40277	0.0024	0.01024	0.00900	0.01385	6.387	0.034	2	-0.0158	2	0.0367
BelGIM	D200278	7.10073	0.0024	0.01136	0.00900	0.01469	7.104	0.012	2	0.0033	2	0.0190
BAM	D200385	7.02603	0.0024	0.01124	0.00900	0.01460	7.039	0.021	2	0.0130	2	0.0256
SMU	D200368	7.32617	0.0024	0.01172	0.00900	0.01497	7.331	0.029	2	0.0048	2	0.0326
CMI	D200383	7.09918	0.0022	0.01136	0.00900	0.01466	7.084	0.110	2	-0.0152	2	0.1110

Table 6: Results for carbon dioxide

Laboratory	Cylinder	x_{prep}	U_{prep}	U_{ver}	$D_{iCCQM-K23b}$	U^*_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
VNIIM	D200273	2.92117	0.00156	0.00467	0.00780	0.00923	2.925	0.009	2	0.0038	2	0.0126
Ukrmetrteststandard	D200292	2.67252	0.00156	0.00428	0.00780	0.00903	2.663	0.014	2	-0.0095	2	0.0167
BelGIM	D200278	2.99103	0.00156	0.00479	0.00780	0.00928	2.992	0.008	2	0.0010	2	0.0123
BAM	D200385	3.00047	0.00156	0.00480	0.00780	0.00929	3.0029	0.009	2	0.0024	2	0.0129
SMU	D200368	2.93729	0.00156	0.00470	0.00780	0.00924	2.947	0.012	2	0.0097	2	0.0151
CMI	D200383	2.95492	0.00156	0.00473	0.00780	0.00925	2.912	0.05	2	-0.0429	2	0.0508

Table 7: Results for ethane

Laboratory	Cylinder	x_{prep}	U_{prep}	U_{ver}	$D_{iCCQM-K23b}$	U^*_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
VNIIM	D200273	9.38197	0.0024	0.01501	0.01820	0.02371	9.388	0.026	2	0.0060	2	0.0349
Ukrmetrteststandard	D200292	8.91803	0.0024	0.01427	0.01820	0.02325	8.906	0.019	2	-0.0120	2	0.0300
BelGIM	D200278	9.40949	0.0024	0.01506	0.01820	0.02374	9.431	0.012	2	0.0215	2	0.0266
BAM	D200385	9.44354	0.0024	0.01511	0.01820	0.02378	9.438	0.028	2	-0.0055	2	0.0367
SMU	D200368	9.12638	0.0024	0.01460	0.01820	0.02346	9.115	0.027	2	-0.0114	2	0.0358
CMI	D200383	9.38749	0.0022	0.01502	0.01820	0.02370	9.328	0.107	2	-0.0595	2	0.1096

Table 8: Results for propane

Laboratory	Cylinder	x_{prep}	U_{prep}	U_{ver}	$D_{iCCQM-K23b}$	U^*_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
VNIIM	D200273	3.41574	0.00152	0.00547	0.00870	0.01039	3.413	0.009	2	-0.0027	2	0.0135
Ukrmetrteststandard	D200292	3.17676	0.00152	0.00508	0.00870	0.01019	3.166	0.016	2	-0.0108	2	0.0190
BelGIM	D200278	3.45496	0.00152	0.00553	0.00870	0.01042	3.456	0.006	2	0.0010	2	0.0120
BAM	D200385	3.46743	0.00152	0.00555	0.00870	0.01043	3.4707	0.010	2	0.0033	2	0.0144
SMU	D200368	3.37998	0.00148	0.00541	0.00870	0.01035	3.378	0.014	2	-0.0020	2	0.0174
CMI	D200383	3.44095	0.00152	0.00551	0.00870	0.01041	3.400	0.041	2	-0.0410	2	0.0423

Table 9: Results for iso-butane

Laboratory	Cylinder	x_{prep}	U_{prep}	U_{ver}	$D_{iCCQM-K23b}$	U^*_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
VNIIM	D200273	0.78627	0.0006	0.00110	0.00210	0.00245	0.7853	0.002	2	-0.0010	2	0.0035
Ukrmetrteststandard	D200292	0.78893	0.0006	0.00110	0.00210	0.00245	0.7927	0.0054	2	0.0038	2	0.0059
BelGIM	D200278	0.78741	0.0006	0.00110	0.00210	0.00245	0.7875	0.0034	2	0.0001	2	0.0042
BAM	D200385	0.80445	0.00059	0.00113	0.00210	0.00245	0.8041	0.004	2	-0.0004	2	0.0047
SMU	D200368	0.78031	0.00058	0.00109	0.00210	0.00244	0.7785	0.0039	2	-0.0018	2	0.0046
CMI	D200383	0.80428	0.00059	0.00113	0.00210	0.00245	0.817	0.021	2	0.0127	2	0.0211

Table 10: Results for n-butane

Laboratory	Cylinder	x_{prep}	U_{prep}	U_{ver}	$D_{iCCQM-K23b}$	U^*_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
VNIIM	D200273	0.98172	0.0006	0.00137	0.00300	0.00335	0.9825	0.003	2	0.0008	2	0.0042
Ukrmetrteststandard	D200292	0.99569	0.0006	0.00139	0.00300	0.00336	0.993	0.0043	2	-0.0027	2	0.0055
BelGIM	D200278	0.9967	0.0006	0.00140	0.00300	0.00336	0.9993	0.0022	2	0.0026	2	0.0040
BAM	D200385	0.98637	0.00059	0.00138	0.00300	0.00335	0.9903	0.005	2	0.0039	2	0.0060
SMU	D200368	0.9748	0.00058	0.00136	0.00300	0.00335	0.9725	0.0049	2	-0.0023	2	0.0059
CMI	D200383	0.99497	0.00059	0.00139	0.00300	0.00336	0.990	0.016	2	-0.0050	2	0.0163

Table 11: Results for methane

Laboratory	Cylinder	$x_{calculated}$	U^*_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
VNIIM	D200273	75.3995	0.031	75.397	0.034	2	-0.0023	2	0.0464
Ukrmetrtestandard	D200292	77.0453	0.031	77.092	0.045	2	0.0467	2	0.0544
BelGIM	D200278	75.2597	0.031	75.230	0.02	2	-0.0297	2	0.0373
BAM	D200385	75.2717	0.031	75.2549	0.045	2	-0.0168	2	0.0549
SMU	D200368	75.4751	0.031	75.478	0.046	2	0.0029	2	0.0557
CMI	D200383	75.3182	0.031	75.470	0.454	2	0.1518	2	0.4551

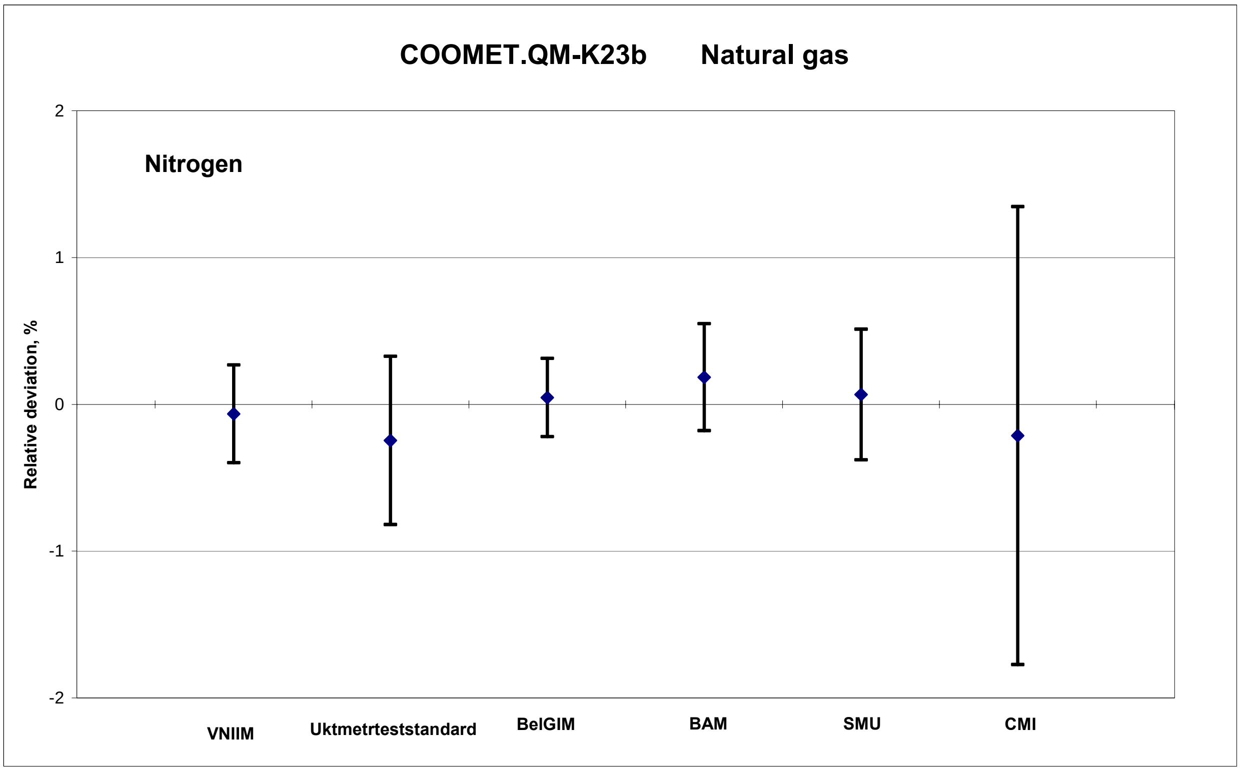

Figure 1 Degrees of equivalence
Nitrogen

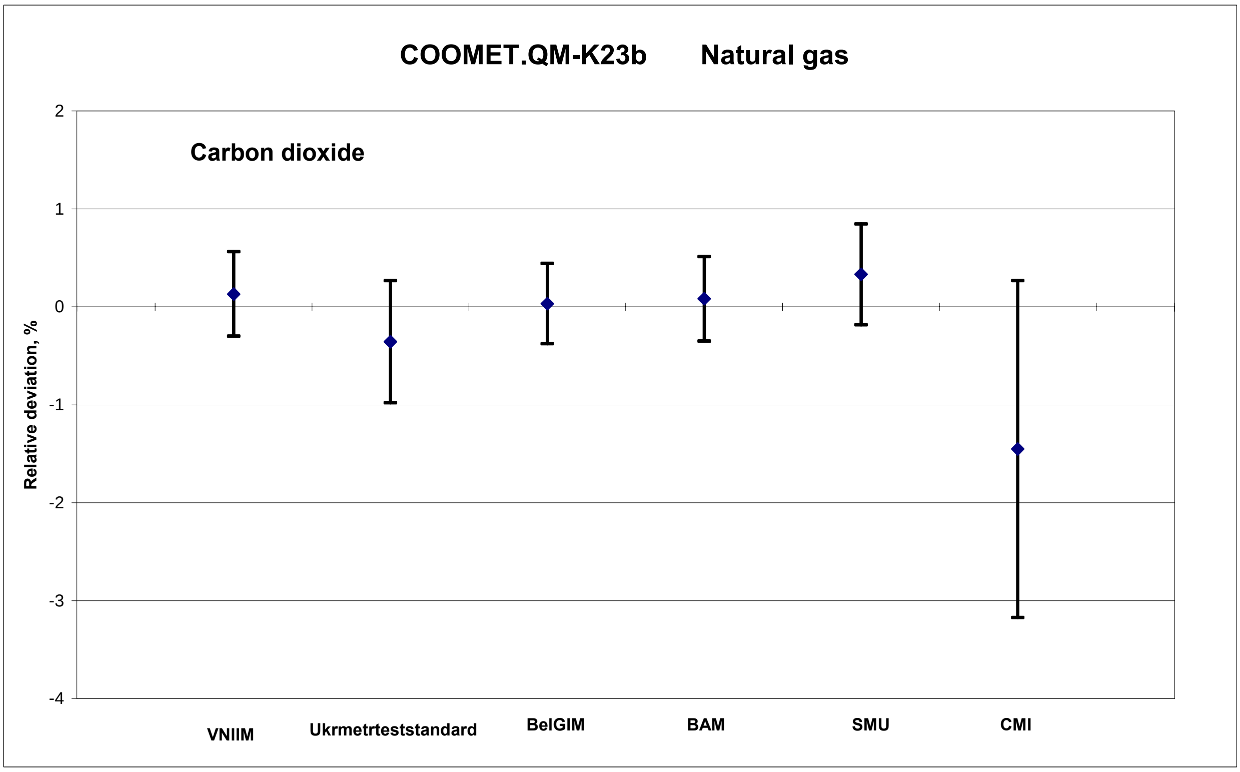

Figure 2 Degrees of equivalence
Carbon dioxide

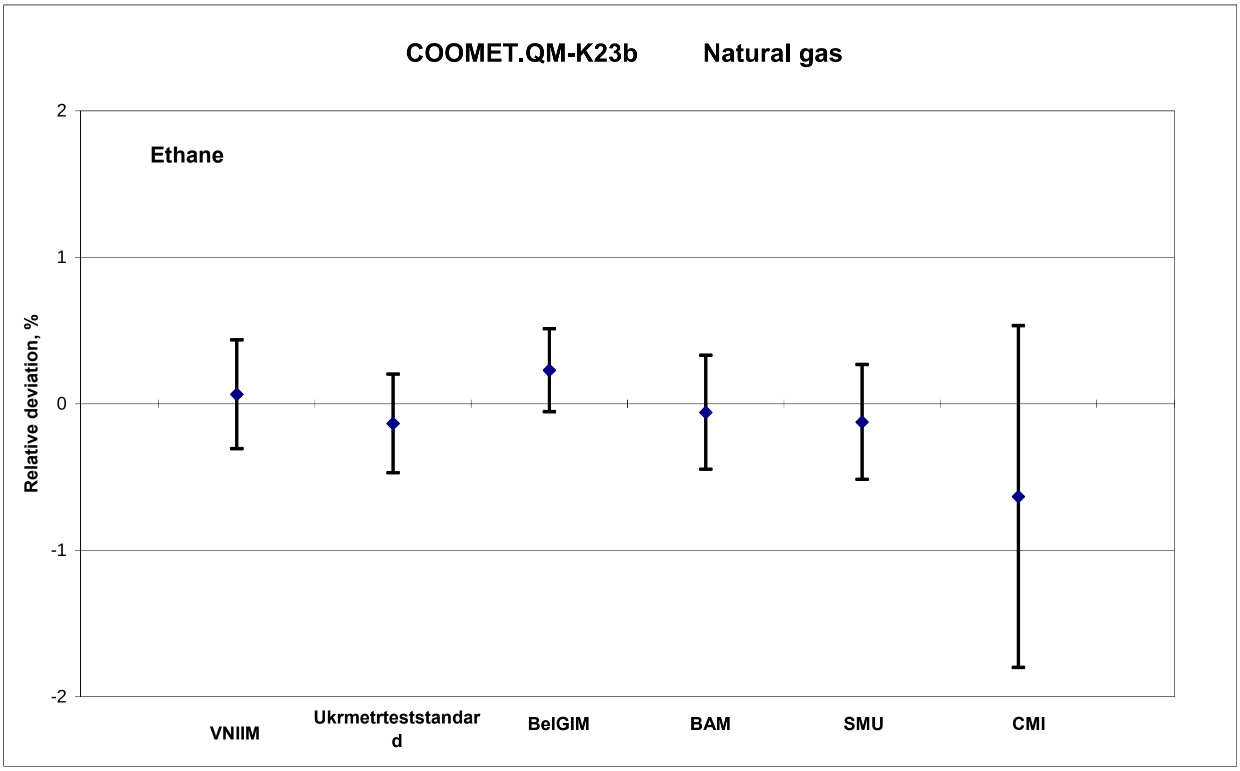

Figure 3 Degrees of equivalence
Ethane

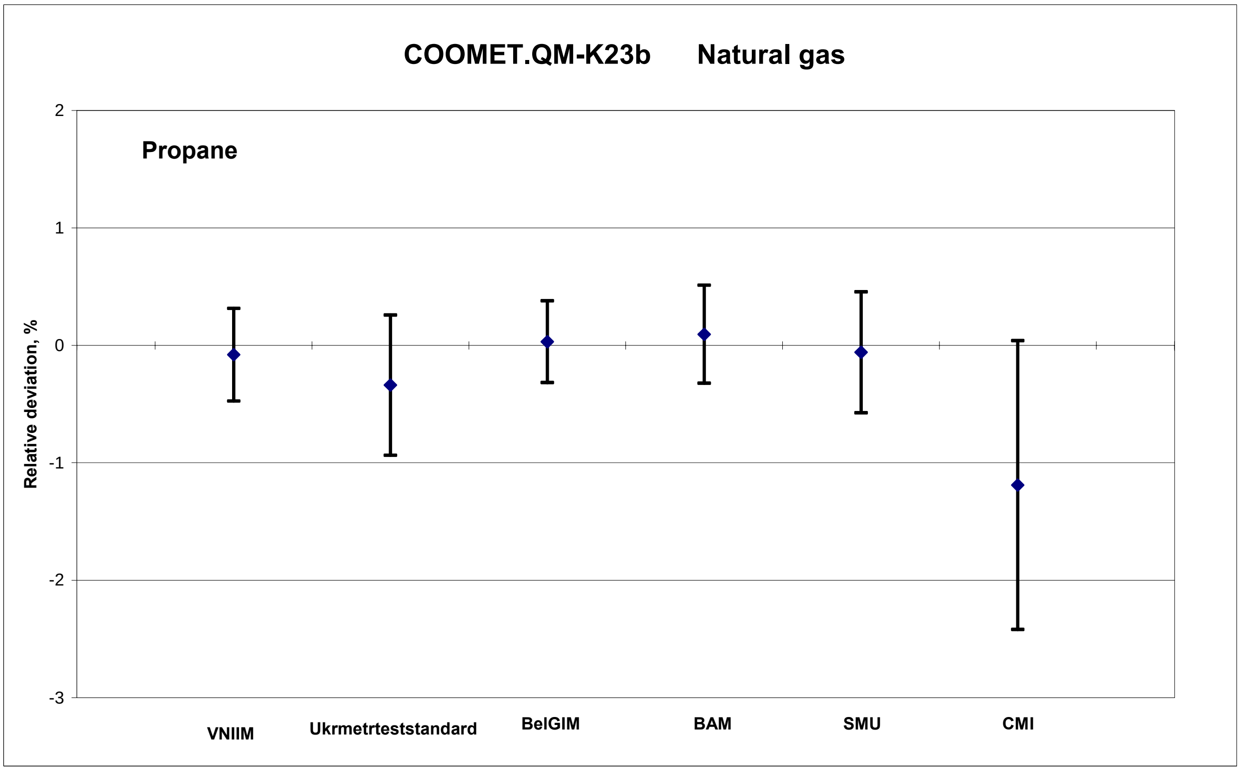

Figure 4 Degrees of equivalence
Propane

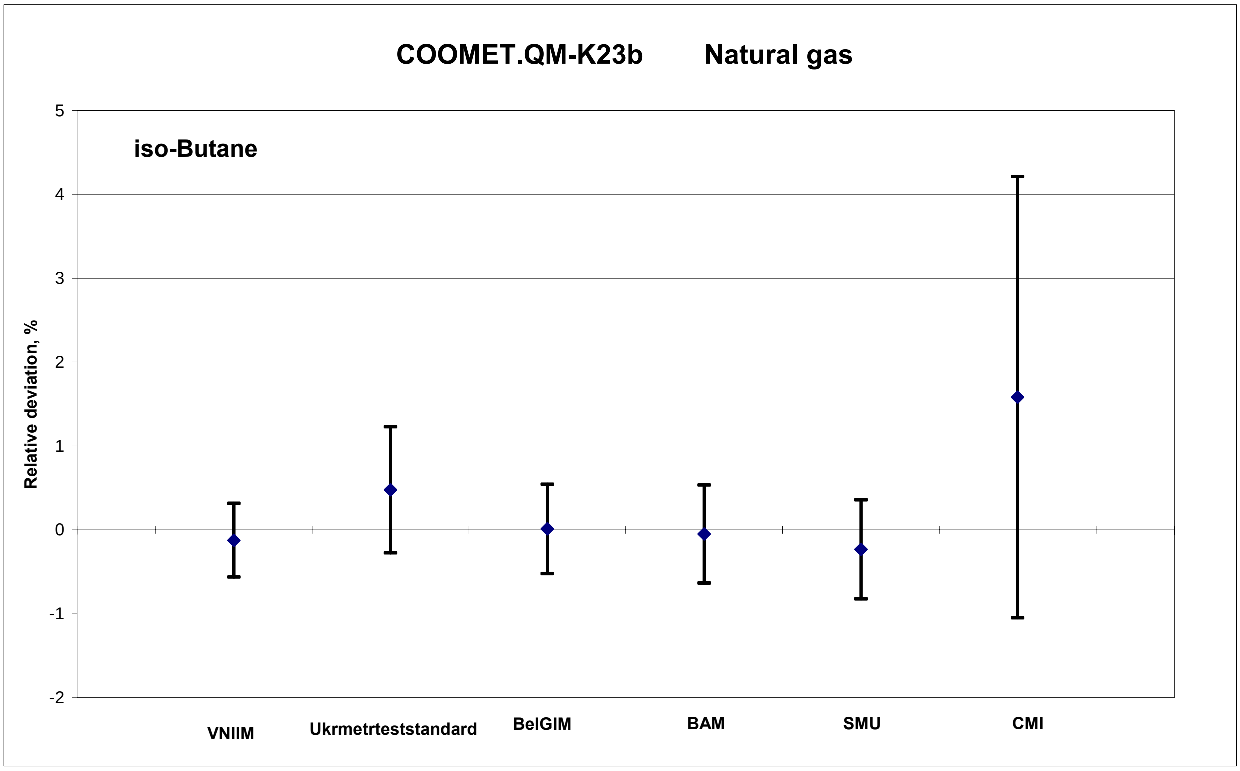

Figure 5 Degrees of equivalence
iso-Butane

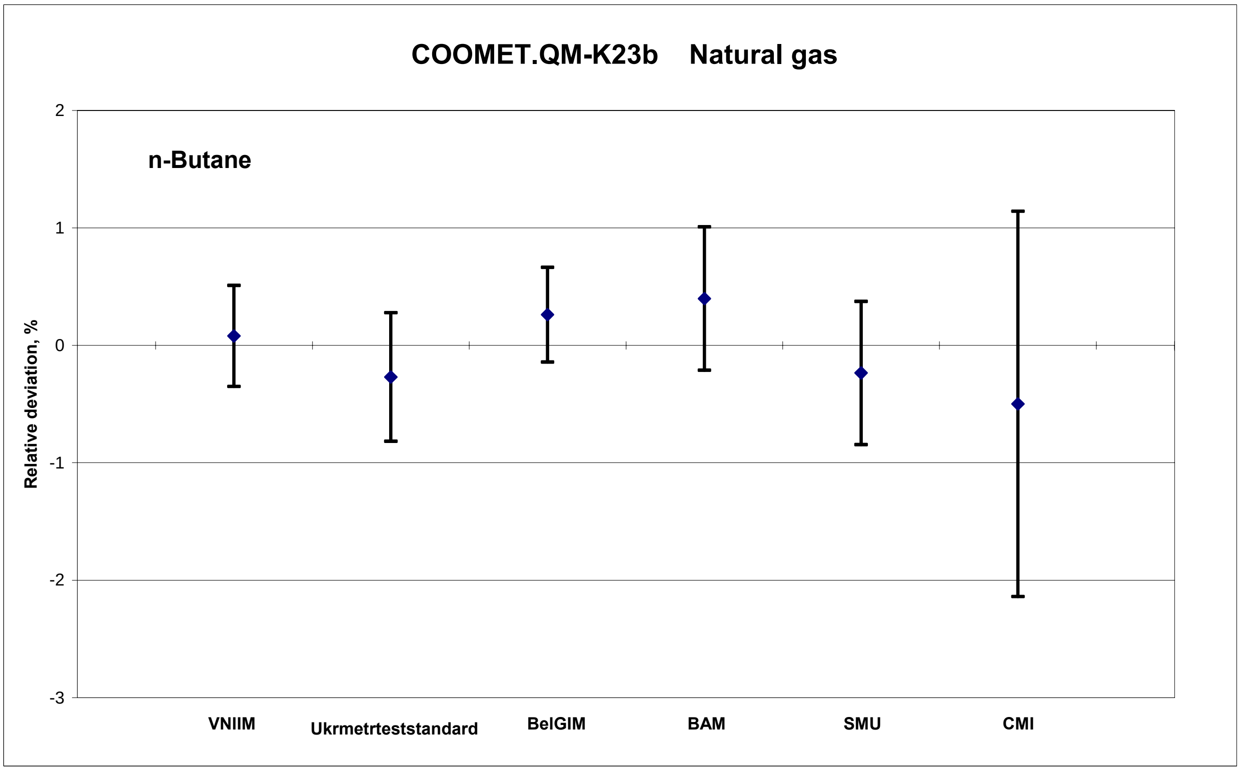

Figure 6 Degrees of equivalence
n-Butane

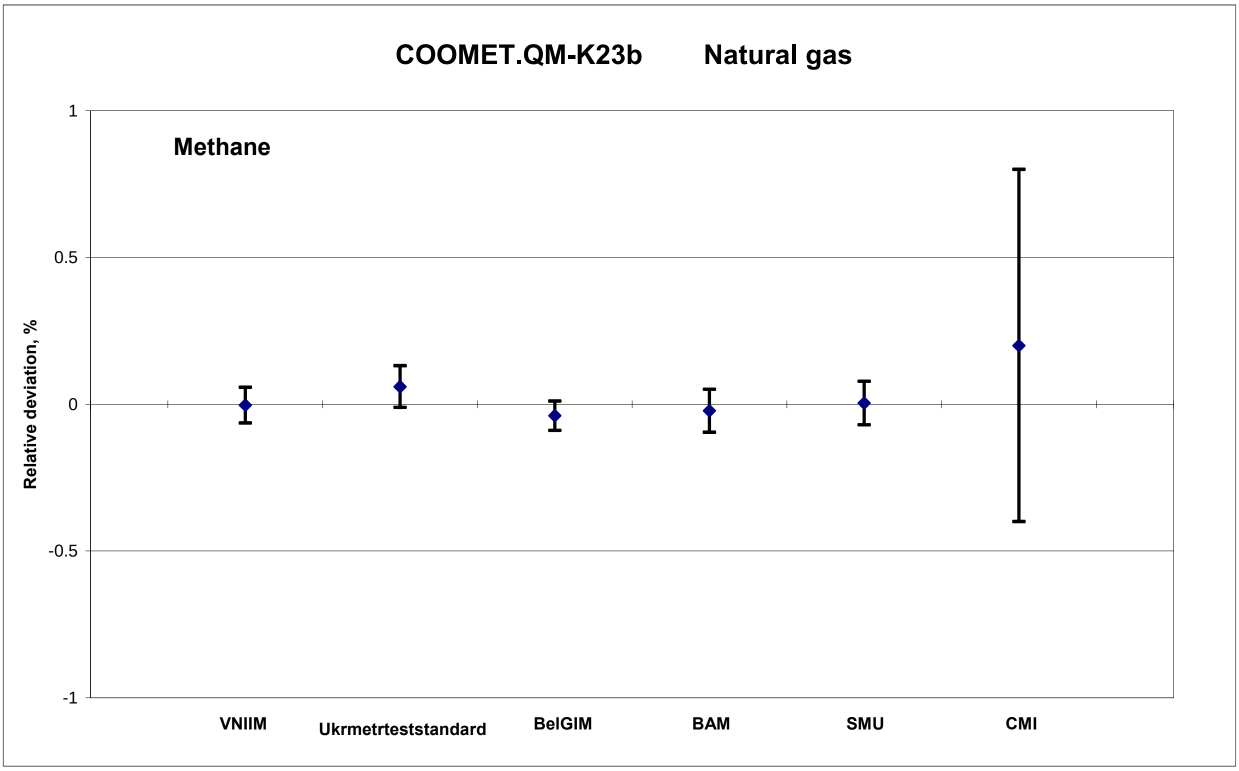

Figure 7 Degrees of equivalence
Methane

Discussion and conclusions

The reported results for nitrogen (figure 1) agree with KCRV within 0.25 % relative. For carbon dioxide and propane (figure 2, 4) most results agree with KCRV within 0.4 % relative (except CMI). For ethane (figure 3) most results agree with KCRV within 0.23 % relative (except CMI). In the case of iso-butane and n-butane (figure 5, 6) results agree with KCRV within 0.5 % relative (except CMI for iso-butane). For methane (figure 7) most results agree with KCRV within 0.07 % relative (except CMI).

The agreement of the results in this key comparison is very good. Most of the NMIs (VNIIM, BAM, SMU, CMI) participated in CCQM-K23b. BelGIM and Ukrmetrteststandard participated in a comparison of natural gas for the first time, and both laboratories performed well in this key comparison. CMI obtained better results than in CCQM-K23b.

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Annex 1: Measuring reports as submitted by participating laboratories

D.I.MENDELEYEV INSTITUTE FOR METROLOGY (VNIIM)
RESEARCH DEPARTMENT FOR THE STATE MEASUREMENT STANDARDS IN THE FIELD OF PHYSICO-CHEMICAL MEASUREMENTS

Key Comparison COOMET.QM-K23b

SYNTHETIC NATURAL GAS

REPORT

L.A.Konopelko, Y.A.Kustikov, T.A.Popova, V.V.Pankratov, E.V.Gromova

Report form

Cylinder number: D200273

Measurement # 1

Component	Date (dd/mm/yy)	Result (10^{-2} mol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	15/07/08	7,101	0,2	6
Carbon dioxide		2,925	0,2	6
Ethane		9,378	0,3	6
Propane		3,416	0,3	6
iso-Butane		0,7850	0,2	6
n-Butane		0,9821	0,1	6
Methane		75,4129	-	-

Measurement # 2

Component	Date (dd/mm/yy)	Result (10^{-2} mol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	21/07/08	7,114	0,4	6
Carbon dioxide		2,922	0,3	6
Ethane		9,390	0,3	6
Propane		3,413	0,2	6
iso-Butane		0,7847	0,2	6
n-Butane		0,9819	0,2	6
Methane		75,3944	-	-

Measurement # 3

Component	Date (dd/mm/yy)	Result (10^{-2} mol/mol)	Standard deviation (% relative)	Number of replicates
Nitrogen	25/07/08	7,112	0,2	6
Carbon dioxide		2,928	0,3	6
Ethane		9,396	0,3	6
Propane		3,410	0,2	6
iso-Butane		0,7862	0,2	6
n-Butane		0,9834	0,3	6
Methane		75,3844	-	-

Final results

Component	**Result (assigned value), 10^{-2} mol/mol**	**Expanded uncertainty, 10^{-2} mol/mol**	**Relative expanded uncertainty, %**	**Coverage factor**
Nitrogen	**7,109**	**0,019**	**0,27**	**2**
Carbon dioxide	**2,925**	**0,009**	**0,31**	**2**
Ethane	**9,388**	**0,026**	**0,28**	**2**
Propane	**3,413**	**0,009**	**0,26**	**2**
iso-Butane	**0,7853**	**0,002**	**0,25**	**2**
n-Butane	**0,9825**	**0,003**	**0,31**	**2**
Methane	**75,397**	**0,034**	**0,05**	**2**

Method description form

Reference method

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

Instrument	Detectors	Columns	
Crystal-5000.1 ("Chromatec", Russia)	TCD	NaX	l= 2m, d_{int}=2mm
	TCD	Haye Sep R	l= 2m, d_{int}=2mm
	FID	Haye Sep R	l= 2m, 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, 10^{-6} mol/mol	Standard uncertainty, 10^{-6} mol/mol
Nitrogen	999998	0,7
Carbon dioxide	999982	1,5
Ethane	999109	43
Propane	999997	6,5
iso-Butane	997779	62,5
n-Butane	997717	57,8
Methane	999925	4,4

Preparation of standard gas mixtures was carried out gravimetrically in 1 stage.

All mixtures were prepared in aluminium cylinders, V=10 dm^3.

There were prepared 2 standard gas mixtures by gravimetric method according to ISO 6142. The concentrations of the components in the calibration standards closely bracketed the expected concentrations in analyzed gas mixture.

Verification of molar fraction in prepared mixtures was carried out chromatographically. Relative standard deviation for each measurement series was not more than 0,4 % for every component.

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

Table 2

Cylinder №	Component	Assigned value, 10^{-2} mol/mol	Relative standard uncertainty (gravimetry), %
D152712	Nitrogen	7,229	0,02
	Carbon dioxide	2,925	0,03
	Ethane	9,322	0,02
	Propane	3,618	0,02
	iso-Butane	0,8131	0,09
	n-Butane	1,003	0,07
	Methane	75,090	-
D152728	Nitrogen	7,102	0,02
	Carbon dioxide	3,015	0,03
	Ethane	9,414	0,02
	Propane	3,479	0,02
	iso-Butane	0,8021	0,09
	n-Butane	1,116	0,07
	Methane	75,072	-

Instrument calibration

Bracketing was used as calibration method.

There were made 3 independent measurements under repeatability conditions with 3 independent calibrations.

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

Sample handling

Prior to measurements cylinders were stabilized to room temperature.

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

Evaluation of measurement uncertainty

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

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

Uncertainty budget for components mole fraction in the studied gas mixture in cylinder № D200273 are shown in the tables 3-8.

Table 3 Uncertainty budget for Nitrogen mole fraction

Source of uncertainty	Type of evaluation	Standard uncertainty, 10^{-2} mol/mol
Preparation of the standard gas mixtures	B	0,0012
Standard deviation of calibration	A	0,006
Standard deviation of measurement results	A	0,007
Total standard uncertainty		0,0093
Expanded uncertainty (*k*=2)		0,019

Table 4 Uncertainty budget for Carbon Dioxide mole fraction

Source of uncertainty	Type of evaluation	Standard uncertainty, 10^{-2} mol/mol
Preparation of the standard gas mixtures	B	0,00078
Standard deviation of calibration	A	0,003
Standard deviation of measurement results	A	0,003
Total standard uncertainty		0,0043
Expanded uncertainty (*k*=2)		0,009

Table 5 Uncertainty budget for Ethane mole fraction

Source of uncertainty	Type of evaluation	Standard uncertainty, 10^{-2} mol/mol
Preparation of the standard gas mixtures	B	0,0012
Standard deviation of calibration	A	0,009
Standard deviation of measurement results	A	0,009
Total standard uncertainty		0,013
Expanded uncertainty (*k*=2)		0,026

Table 6 Uncertainty budget for Propane mole fraction

Source of uncertainty	Type of evaluation	Standard uncertainty, 10^{-2} mol/mol
Preparation of the standard gas mixtures	B	0,00076
Standard deviation of calibration	A	0,003
Standard deviation of measurement results	A	0,003
Total standard uncertainty		0,0043
Expanded uncertainty (*k*=2)		0,009

Table 7 Uncertainty budget for iso-Butane mole fraction

Source of uncertainty	Type of evaluation	Standard uncertainty, 10^{-2} mol/mol
Preparation of the standard gas mixtures	B	0,0006
Standard deviation of calibration	A	0,0007
Standard deviation of measurement results	A	0,0008
Total standard uncertainty		0,0012
Expanded uncertainty (*k*=2)		0,002

Table 8 Uncertainty budget for n-Butane mole fraction

Source of uncertainty	Type of evaluation	Standard uncertainty, 10^{-2} mol/mol
Preparation of the standard gas mixtures	B	0,0006
Standard deviation of calibration	A	0,0008
Standard deviation of measurement results	A	0,0008
Total standard uncertainty		0,0013
Expanded uncertainty (*k*=2)		0,003

Methane mole fraction $\mathbf{x_{CH4}}$, 10^{-2} mol/mol, was calculated according to the formula:

$$x_{CH4} = 100 - \sum x_i \, .$$

Total standard uncertainty of methane mole fraction u_{CH4}, 10^{-2} mol/mol, was calculated according to formula

$$u_{CH4} = \sqrt{\sum u_{Ai}^2 + \sum u_{Bi}^2}$$

x_i – mole fraction of mixture components, 10^{-2} mol/mol.

u_{Ai} and u_{Bi} - standard uncertainties of type A and B of components mole fraction, 10^{-2} mol/mol.

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ЕВРО-АЗИАТСКОЕ СОТРУДНИЧЕСТВО
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МЕТРОЛОГИЧЕСКИХ УЧРЕЖДЕНИЙ

COOMET **КООМЕТ**

KEY COMPARISON COOMET 400/RU/07

“COMPARISON OF NATURAL GAS COMPOSITION STANDARDS”

MEASUREMENT REPORT

I. Results of experimental study

Laboratory: Ukrmetrteststandart, Kiev, Ukraine

NOMINAL COMPOSITION VALUES:

Nitrogen	70 mmol/mol
Carbon dioxide	30 mmol/mol
Ethane	95 mmol/mol
Propane	35 mmol/mol
iso-Butane	8 mmol/mol
n-Butane	10 mmol/mol
Methane	balance

Cylinder number: 0292

Measurement No1	Date	Results (mol/mol)	Relative standard deviation (%)	Number of sub-measurements
Nitrogen	12.02.2008	0,06382	0,4	5
Carbon dioxide	12.02.2008	0,02661	0,3	5
Ethane	12.02.2008	0,08906	0,1	5
Propane	12.02.2008	0,03166	0,4	5
iso-Butane	12.02.2008	0,007930	0,2	5
n-Butane	12.02.2008	0,009930	0,3	5
Methane	balance			

Measurement No2	Date	Results (mol/mol)	Relative standard deviation (%)	Number of sub-measurements
Nitrogen	13.02.2008	0,06388	0,3	5
Carbon dioxide	13.02.2008	0,02661	0,2	5
Ethane	13.02.2008	0,08885	0,1	5
Propane	13.02.2008	0,03159	0,2	5
iso-Butane	13.02.2008	0,007922	0,3	5
n-Butane	13.02.2008	0,009913	0,3	5
Methane	balance			

Measurement No3	Date	Results (mol/mol)	Relative standard deviation (%)	Number of sub-measurements
Nitrogen	14.02.2008	0,06408	0,2	5
Carbon dioxide	14.02.2008	0,02666	0,3	5
Ethane	14.02.2008	0,08926	0,1	5
Propane	14.02.2008	0,03174	0,2	5
iso-Butane	14.02.2008	0,007930	0,3	5
n-Butane	14.02.2008	0,009947	0,2	5
Methane	balance			

Final results:

Gas mixture	Result (mol/mol)	Coverage factor	Expanded uncertainty (mol/mol)
Nitrogen	0,06387	2	0,00034
Carbon dioxide	0,02663	2	0,00014
Ethane	0,08906	2	0,00019
Propane	0,03166	2	0,00016
iso-Butane	0,007927	2	0,000054
n-Butane	0,009930	2	0,000043
Methane	0,77092	2	0,00045

II. Description of the study

Instrument(s)

Gas chromatographs HP 6890 belonging to the Ukrainian national primary standard of mole fraction unit of gaseous components (DETU 05-01-2003) were used for analysis.

Mode of data acquisition: automatic.

Calibration standards

All the primary standard gas mixtures (PSGM) used for calibration were prepared gravimetrically from pure gases according to ISO 6142 using Mettler Toledo electronic balance KA-20-3, maximum capacity 20 kg, minimum weighing limit 0,1 g, standard deviation is 0,006 g.

Purity analysis of parent gases was carried out using HP6890N chromatographs with HID, FID, TCD and MSD detectors, as well as GIAM-15M and Onix gas analyzers.

Prepared PSGMs have been verified by analytical comparisons with existing gravimetrically prepared PSGMs according to ISO 6143.

Calibration Standards

Calibration standards – primary standard gas mixtures (PSGM) used for measurements by comparison method:

Composition	PSGM -1 cylinder No D340089		PSGM -2 cylinder No 5672A		PSGM -3 cylinder No 8318	
	x, %	u(x) , %	*x*, %	u(x) , %	*x*, %	u(x) , %
Nitrogen	6,012	0,03	6,282	0,03	6,618	0,03
Carbon dioxide	2,542	0,04	2,630	0,04	2,817	0,04
Ethane	8,413	0,02	8,901	0,02	9,363	0,02
Propane	3,045	0,03	3,174	0,03	3,342	0,03
iso-Butane	0,9379	0,1	0,9882	0,1	1,0384	0,1
n-Butane	0,7592	0,1	0,7925	0,1	0,8398	0,1
Methane	balance	–	balance	–	balance	–

Note: *x* – mole fraction, *u(x)* – relative standard uncertainty, %

Calibration and measurements

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

Calibration and measurement methods

Laboratory	Measurement method	Type of calibration curve
Ukrmetrteststandart	GC/TCD	3 points, linear

GC/TCD – gas chromatographic with thermal-conductivity detector

Sample Handling

Handing with PSGM and samples – according to ISO 16664:2003.

The cylinders were kept for 24 hrs in the room where comparators were located. The room was thermostatted at t = (20 ± 2) ºC.

Uncertainty calculation

Uncertainty table:

Uncertainty source X_j	Type of evaluation	Relative standard uncertainty $u(x_j)$, %	Sensitivity factor c_j	Contribution to relative standard uncertainty $u_j(y)$, %
Calibration PSGM				
Nitrogen	B	0,03	1	0,03
Carbon dioxide	B	0,04	1	0,04
Ethane	B	0,02	1	0,02
Propane	B	0,03	1	0,03
iso-Butane	B	0,1	1	0,1
n-Butane	B	0,1	1	0,1
Comparison				
Nitrogen	A, B	0,2	1	0,2
Carbon dioxide	A, B	0,3	1	0,3
Ethane	A, B	0,1	1	0,1
Propane	A, B	0,2	1	0,2
iso-Butane	A, B	0,2	1	0,2
n-Butane	A, B	0,3	1	0,3

Coverage factor: 2

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COOMET **КООМЕТ**

Key comparison COOMET.QM-K23.b

« STANDARD REFERENCE MATERIALS – SYNTHETIC NATURAL GAS»

MEASUREMENT REPORT

I. Result of Study

Laboratory: Belarus, BelGIM, department for physicochemical and optical measurements, section for measurement standards and gas mixtures, Minsk, Serova street 8.

Cylinder no.: 0278, aluminum, 10 dm^3

Measurement No. 1	Date (dd/mm/yy)	Result, x, mole/mole $\cdot 10^{-2}$	Standard Deviation, % rel.	Number of Sub-Measurements n
Nitrogen	26.03.2008	7,114	0,07	6
Carbon dioxide		3,000	0,14	6
Ethane		9,440	0,1	6
Propane		3,452	0,08	6
i-Butane		0,7908	0,1	6
n-Butane		1,0010	0,13	6

Measurement No. 2	Date (dd/mm/yy)	Result, x, mole/mole $\cdot 10^{-2}$	Standard Deviation, % rel.	Number of Sub-Measurements n
Nitrogen	28.03.2008	7,103	0,14	6
Carbon dioxide		2,990	0,07	6
Ethane		9,422	0,09	6
Propane		3,455	0,11	6
i-Butane		0,7877	0,11	6
n-Butane		0,9988	0,1	6

Measurement No. 3	Date (dd/mm/yy)	Result, x, mole/mole $\cdot 10^{-2}$	Standard Deviation, % rel.	Number of Sub-Measurements n
Nitrogen	31.03.2008	7,107	0,17	6
Carbon dioxide		2,986	0,07	6
Ethane		9,427	0,04	6
Propane		3,454	0,04	6
i-Butane		0,7858	0,05	6
n-Butane		0,9983	0,05	6

Measurement No. 4	Date (dd/mm/yy)	Result, ***x***, mole/mole $\cdot 10^{-2}$	Standard Deviation, % rel.	Number of Sub-Measurements n
Nitrogen	02.04.2008	7,105	0,16	6
Carbon dioxide		2,995	0,14	6
Ethane		9,438	0,11	6
Propane		3,459	0,08	6
i-Butane		0,7850	0,09	6
n-Butane		1,0000	0,18	6

Measurement No. 5	Date (dd/mm/yy)	Result, ***x***, mole/mole $\cdot 10^{-2}$	Standard Deviation, % rel.	Number of Sub-Measurements n
Nitrogen	04.04.2008	7,092	0,08	6
Carbon dioxide		2,994	0,12	6
Ethane		9,430	0,05	6
Propane		3,456	0,04	6
i-Butane		0,7907	0,03	6
n-Butane		0,9990	0,03	6

Measurement No. 6	Date (dd/mm/yy)	Result, ***x***, mole/mole $\cdot 10^{-2}$	Standard Deviation, % rel.	Number of Sub-Measurements n
Nitrogen	07.04.2008	7,105	0,05	6
Carbon dioxide		2,989	0,07	6
Ethane		9,429	0,06	6
Propane		3,457	0,04	6
i-Butane		0,7852	0,08	6
n-Butane		0,9987	0,08	6

Results:

Gas Mixture	Result, $\overline{x}$ mole/mole $\cdot 10^{-2}$	Coverage Factor, ***k***	Expanded Uncertainty, mole/mole $\cdot 10^{-2}$
Nitrogen	7,104	2	0,012
Carbon dioxide	2,992		0,008
Ethane	9,431		0,012
Propane	3,456		0,006
i-Butane	0,7875		0,0034
n-Butane	0,9993		0,0022
Methane	75,23		0,02

II. Description of Study

Equipment

Measurements were performed on a gas chromatographer "Crystal 5000" (subsequently referred to as chromatographer) fitted with a thermal conductivity detector (subsequently referred to as DTP-1) having a detection limit of $5 \cdot 10^{-9}$ g/ml for propane (gas-carrier is helium) and a thermal conductivity detector (subsequently referred to as DTP-2) having a detection limit of $5 \cdot 10^{-9}$ g/ml for propane (gas-carrier is argon).

A PC with "Chromatek Analytic" v. 2.5 installed was applied to control the chromatographer and to acquire and handle the chromatographic data.

During the measurements following auxiliaries and materials were used:

1. Metallic packed column of 3m x 3mm x 2mm - HayeSep N 80/100, metallic packed column of 1m x 4mm x 2mm - CaA 0,16/0,25, metallic packed column of 3m x 4mm x 2mm - CaA 0,16/0,25.
2. Gaseous helium, grade "6, 0".
3. Multicomponent calibration gas mixtures - Calibration Standards (subsequently referred to as CS), prepared and certified by a gravimetric method.

Calibration Standards (CS).

The quantitative composition of CS was determined by a gravimetric method according to ISO 6142:2001.

The contents of components in CS are expressed in molar fractions. The uncertainty of CS composition is expressed as a standard uncertainty. Molar masses of components and their associated uncertainties are derived from ISO 14912:2003 (E).

Technical and metrological performance of the equipment applied for gravimetric preparation of gas mixtures is shown in Table 1.

Table 1 – CS Preparation equipment.

Equipment Name	Manufacturer	Metrological Performance
Mass comparator scales SSE40K3	Sartorius, Germany	Measuring limit: 41 kg Readout range (scale interval): 2 mg RMS deviation 4,4 mg at maximum load Operating temperature range +10÷30°C 1 hour temperature variation: ±0,5 °C or less.
Gas mixing facility based on static pressure method	Belarus, KB "Akademicheskoye"	Measuring limit: 0,00025 ÷ 10,0 MPa Accuracy class of the manometers – 0,15; Accuracy class of the vacuum meter – 0,25.

Purity analysis of initial gases

Data about purity of initial gases are taken from supplier's specifications and from results of analysis of gas impurity levels according to procedures (MVIs) developed by BelGIM.

Composition of "pure" gases used for calibration mixtures is given in Table 2.

Table 2 –Purity of initial gases

Initial gas 1: iC_4H_{10}

Component	Molar Fraction, %	Standard Uncertainty, m. f., %
N_2	0,0002	0,00005
C_3H_8	0,0740	0,0010
iC_4H_{10}	99,9200	0,0010
C_3H_6	0,0060	0,0005

Initial gas 2: nC_4H_{10}

Component	Molar Fraction, %	Standard Uncertainty, m. f., %
C_3H_8	0,2120	0,0090
nC_4H_{10}	99,6100	0,0011
iC_4H_{10}	0,0880	0,0010
$isoC_5H_{12}$	0,0010	0,0001
$neoC_5H_{12}$	0,0920	0,0050

Initial gas 3: C_3H_8

Component	Molar Fraction, %	Standard Uncertainty, m. f., %
CO_2	0,001	0,00005
CH_4	0,001	0,0002
C_2H_6	0,0440	0,0020
C_3H_8	99,9500	0,0020
nC_4H_{10}	0,0003	0,00001
iC_4H_{10}	0,0002	0,00001
nC_5H_{12}	0,0002	0,000005
nC_6H_{14}	0,00005	0,000005

Initial gas 4: CO_2

Component	Molar Fraction, %	Standard Uncertainty, m. f., %
N_2	0,0043	0,0004
O_2	0,0026	0,0002
CO_2	99,9884	0,0005
H_2O	0,0047	0,0002

Initial gas 5: C_2H_6

Component	Molar Fraction, %	Standard Uncertainty, m. f., %
C_2H_6	99,999	0,000006
nC_4H_{10}	0,0002	0,000006

Initial gas 6: N_2

Component	Molar Fraction, %	Standard Uncertainty, m. f., %
H_2	0,0002	0,00005
N_2	99,9990	0,0005
O_2+Ar	0,0005	0,00005

Initial gas 7: Methane

Component	Molar Fraction, %	Standard Uncertainty, m. f., %
CH_4	99,991	0,0003
N_2	0,0002	0,00007
O_2	0,0009	0,00005
C_2H_6	0,0059	0,0002
H_2O	0,0020	0,0002

Chromatographer calibration and standard reference materials measuring

1. When carrying out chromatographer calibration, CS were used the composition of which was identical to the composition of the sample being analyzed. Each component contents with associated standard uncertainties are given in Table 3.

Table 3 – the CS used during calibration.

Cylinder, Volume, Material, Preparation Date	Component	Content, **x**, mole/mole $\cdot 10^{-2}$	Standard uncertainty, **$u(x)$**, mole/mole $\cdot 10^{-2}$
267581, 4 dm^3, steel 03.12.2007	N_2	6,3570	0,0015
	CO_2	2,695	0,001
	C_2H_6	10,0128	0,0016
	C_3H_8	2,9354	0,0011
	i-C_4H_{10}	0,4704	0,0008
	n-C_4H_{10}	0,8558	0,0008
	CH_4	balance	
1476, 4 dm^3, aluminum, 04.12.2007	N_2	8,1836	0,0012
	CO_2	4,4468	0,0008
	C_2H_6	7,9742	0,0012
	C_3H_8	5,1571	0,0008
	i-C_4H_{10}	0,7272	0,0006
	n-C_4H_{10}	1,4117	0,0006
	CH_4	balance	
5006, 4 dm^3, aluminum, 05.12.2007	N_2	6,9716	0,0012
	CO_2	3,5347	0,0008
	C_2H_6	11,1349	0,0013
	C_3H_8	3,4702	0,0008
	i-C_4H_{10}	0,5742	0,0006
	n-C_4H_{10}	1,0712	0,0006
	CH_4	balance	
363, 2 dm^3, steel, 24.03.2008	i-C_4H_{10}	0,8257	0,0011
	n-C_4H_{10}	1,0462	0,0011
	CH_4	balance	

2. Number of sub-measurements for each calibration sample – 3.

3. Analytical function (subsequently referred to as AF) used to determine the content of components in a sample being analyzed is written as follows:

$$x(y) = b_1 y + b_0, \qquad (1)$$

where: x – certain content, % of a mole fraction;

y – value of the chromatographer response for this component, mV*s;
b_1 – slope coefficient;
b_0 – intercept coefficient.

4. Upon completion of calibration calculations of analytical function coefficients were made according to ISO 6143: 2001, and also uncertainties of values of angular coefficients and their covariation were calculated using the program recommended in the above-mentioned standard.

5. The method of transfer standard sample introduction is identical to that used for each CS, i.e. automatic, with pressure (flow) stabilization.

6. The cylinder containing the standard reference material was conditioned in the room where the measurement facility is allocated for no less than 1 day at the temperature t=20±2°C.

Uncertainty calculation

Generally, the total standard uncertainty related to results of 5 individual measurements, is evaluated by following formula:

$$u(x) = \sqrt{u^2{}_A + u^2{}_B}\ , \tag{2}$$

where u_A –uncertainty associated with results of individual measurements;
u_B – uncertainty due to chromatographer calibration and to the uncertainty of CS component contents.

A-type uncertainty evaluation

The A-type uncertainty $\boldsymbol{u_A}$ of the results of n=5 measurement series is evaluated by the formula:

$$u_A = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n(n-1)}}\ , \tag{3}$$

where: x_i – result of i measurement series;
$\bar{x}$ – arithmetic mean for five measurement series.

Table 4 – A-type uncertainty evaluation results.

Component	Measurement 1	Measurement 2	Measurement 3	Measurement 4	Measurement 5	Measurement 6	Mean	u_A
Nitrogen	7,114	7,103	7,107	7,105	7,092	7,105	7,104	0,003
Carbon dioxide	3,000	2,990	2,986	2,995	2,994	2,989	2,992	0,002
Ethane	9,440	9,422	9,427	9,438	9,430	9,431	9,431	0,003
Propane	3,452	3,455	3,454	3,459	3,456	3,457	3,456	0,001
i-Butane	0,7908	0,7877	0,7858	0,7850	0,7907	0,7852	0,7875	0,0009
n-Butane	1,0010	0,9988	0,9983	1,0000	0,9990	0,9987	0,9993	0,0005

B-type uncertainty evaluation

B-type uncertainty $\boldsymbol{u_B}$ due to the uncertainty of CS component contents and to the uncertainty of the chromatographer response to these contents during its calibration was evaluated on the basis of results of calibration measurements for each measurement series.

Generally, the uncertainty of results of component determination for each series of measurements is evaluated by the following formula:

$$u(x) = \sqrt{(b_1)^2 \cdot u^2(y) + u^2(b_0) + y^2 \cdot u^2(b_1) + 2 \cdot y \cdot u(b_1, b_0)}\ , \qquad (4)$$

Where *u (y)* – standard uncertainty of the chromatographer response *y*;

u (b_1) – standard uncertainty of the AF slope coefficient;

u (b_0) – standard uncertainty of the AF intercept;

u (b_1, b_0) – covariation of the AF arguments b_0 and b_1.

Table 5 - B-type uncertainty evaluation results.

	u_B, mole/mole·10^{-2}						
Measurement, №	1	2	3	4	5	6	Max.
Nitrogen	0,0045	0,0023	0,0046	0,0053	0,0035	0,0022	0,0053
Carbon dioxide	0,0027	0,0018	0,0020	0,0031	0,0011	0,0022	0,0031
Ethane	0,0053	0,0028	0,0036	0,0041	0,0041	0,0029	0,0053
Propane	0,0022	0,0013	0,0014	0,0015	0,0011	0,0016	0,0022
i-Butane	0,0010	0,0007	0,0014	0,0009	0,0009	0,0009	0,0014
n-Butane	0,0008	0,0006	0,0010	0,0009	0,0005	0,0007	0,0010

Table 6 – Total standard uncertainty evaluation results.

Component	x, mole/mole·10^{-2}	u_A, mole/mole·10^{-2}	u_B, mole/mole·10^{-2}	$u(x)$, mole/mole·10^{-2}
Nitrogen	7,104	0,003	0,0053	0,006
Carbon dioxide	2,992	0,002	0,0031	0,004
Ethane	9,431	0,003	0,0053	0,006
Propane	3,456	0,001	0,0022	0,003
i-Butane	0,7875	0,0009	0,0014	0,0017
n-Butane	0,9993	0,0005	0,0010	0,0011

Methane determination

The methane content in a comparison sample is determined by the following formula:

$$x_{CH_4} = 100 - \sum x_i \,, \qquad (5)$$

where: x_i –content of each individual component, mole/mole·10^{-2}.

Evaluation of the total standard uncertainty for methane

Uncertainty of the methane content is evaluated by the following formula:

$$u(x_{CH_4}) = \sqrt{\sum u^2(x_i)} \,, \qquad (6)$$

where: $u(x_i)$ – uncertainty of each individual component content, mole/mole·10^{-2}.

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ЕВРО-АЗИАТСКОЕ СОТРУДНИЧЕСТВО
ГОСУДАРСТВЕННЫХ
МЕТРОЛОГИЧЕСКИХ УЧРЕЖДЕНИЙ

COOMET **КООМЕТ**

Annex 1

Key comparison COOMET 400/RU/07

“Standard Reference Materials – Synthetic Natural Gas”

MEASUREMENT REPORT

I. Results of Study

Laboratory: BAM Bundesanstalt fuer Materialforschung und -pruefung

Cylinder number: D200385

Measurement № 1	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	23/06/08	0,070404	0,16	5*3
Carbon dioxide	23/06/08	0,030033	0,15	5*3
Ethane	23/06/08	0,094336	0,15	5*3
Propane	23/06/08	0,034707	0,15	5*3
iso-Butane	23/06/08	0,008047	0,19	5*3
n-Butane	23/06/08	0,009905	0,19	5*3
Methane	23/06/08	0,752568	0,03	5*3

Measurement № 2	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	24/06/08	0,070394	0,13	10*3
Carbon dioxide	24/06/08	0,030033	0,14	10*3
Ethane	24/06/08	0,094315	0,16	10*3
Propane	24/06/08	0,034706	0,15	10*3
iso-Butane	24/06/08	0,008041	0,17	10*3
n-Butane	24/06/08	0,009905	0,17	10*3
Methane	24/06/06	0,752607	0,03	10*3

Measurement № 3	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	25/06/08	0,070390	0,15	10*3
Carbon dioxide	25/06/08	0,030026	0,14	10*3
Ethane	25/06/08	0,094380	0,15	10*3
Propane	25/06/08	0,034708	0,16	10*3
iso-Butane	25/06/08	0,008039	0,19	10*3
n-Butane	25/06/08	0,009902	0,20	10*3
Methane	25/06/08	0,752555	0,03	10*3

Measurement № 4	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	26/06/08	0,070381	0,13	10*3
Carbon dioxide	26/06/08	0,030027	0,15	10*3
Ethane	26/06/08	0,094470	0,13	10*3
Propane	26/06/08	0,034705	0,14	10*3
iso-Butane	26/06/08	0,008039	0,18	10*3
n-Butane	26/06/08	0,009902	0,16	10*3
Methane	26/06/08	0,752476	0,03	10*3

Measurement № 5	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	27/06/08	0,070382	0,14	10*3
Carbon dioxide	27/06/08	0,030027	0,14	10*3
Ethane	27/06/08	0,094399	0,14	10*3
Propane	27/06/08	0,034708	0,15	10*3
iso-Butane	27/06/08	0,008041	0,17	10*3
n-Butane	27/06/08	0,009904	0,15	10*3
Methane	27/06/08	0,752540	0,03	10*3

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	0,070390	2	0,000211
Carbon dioxide	0,030029	2	0,000090
Ethane	0,094380	2	0,000283
Propane	0,034707	2	0,000104
iso-Butane	0,008041	2	0,000040
n-Butane	0,009903	2	0,000050
Methane	0,752549	2	0,000452

II. Method description forms

Instrument(s) (principles, make, type, configuration, data collection etc.)

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: Siemens Maxum edition II (6 channel system) with a stream,
selection valve for 8 streams and 6 gas sampling valves,
Oven: fixed temperature = 60 °C.

Channel T2l: for the determination of CH_4.
Carrier Gas: Helium
Detector: TCD
Data Collection: Eazy Chrom

Channel T2r: for the determination of N_2,
Carrier Gas: Helium
Detector: TCD
Data Collection: Eazy Chrom

Channel T3l: for the determination of CO_2
Carrier Gas: Helium
Detector: TCD
Data Collection: Eazy Chrom

Channel T1r: for the determination of C_3H_8
Carrier Gas: Helium
Detector: TCD
Data Collection: Eazy Chrom

Channel T3r: for the determination of n-C_4H_{10} and I-C_4H_{10}
Carrier Gas: Helium
Detector: TCD
Data Collection: Eazy Chrom

Calibration Standards

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

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

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

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

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

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

BAM 6028-050808

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*)) (k=2) $\%_{rel}$
Nitrogen	6,6583	0,04
Carbon dioxide	2,8466	0,04
Ethane	8,8876	0,08
Propane	3,2294	0,08
iso-Butane	0,80434	0,10
n-Butane	0,98565	0,10
(any relevant impurities)		
Methane	Balance (76,58806)	0,025

C49331-050507

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*)) (k=2) $\%_{rel}$
Nitrogen	7,5703	0,04
Carbon dioxide	3,2365	0,04
Ethane	9,3690	0,08
Propane	3,4001	0,08
iso-Butane	0,81847	0,10
n-Butane	1,00434	0,10
(any relevant impurities)		
Methane	Balance (74,60126)	0,025

C49360-050608

Component	Assigned value(*x*)	Standard uncertainty (*u*(*x*)) (k=2) $\%_{rel}$
Nitrogen	7,4032	0,04

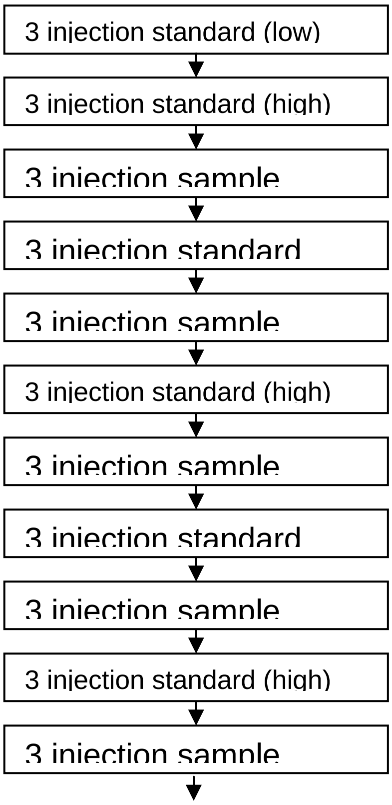
Carbon dioxide	3,1650	0,04
Ethane	9,8955	0,08
Propane	3,5932	0,08
iso-Butane	0,79930	0,10
n-Butane	1,02413	0,10
(any relevant impurities)		
Methane	Balance (74,11979)	0,025

Instrument Calibration

Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.)

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

Measurement sequence



Sample Handling

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)

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.

Uncertainty

How the uncertainty of measurement associated with the final result has been evaluated? The main components of uncertainty addressed in the uncertainty of the calibrants, sample handling, calibration of the equipment, and the measurement. If deemed useful, raw measurement data can be given as well in this section.

The uncertainty 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 $U_{(residual)}$

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

- Uncertainty of the grav. prepared calibration gas $U_{cal\ gas}$
- Standard deviation (GC-Sample) $U_{GC(sample)}$
- Standard deviation (GC-Calibration) $U_{GC(analysis)}$
- Residual-uncertainty of non-recovery errors $U_{residual}$

Key comparison COOMET.QM-K23.b

“Standard Reference Materials – Synthetic Natural Gas”

MEASUREMENT REPORT

I. Results of Study

Laboratory: Slovak Institute of Metrology

Cylinder number: D200368

Measurement № 1	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	07/07/08	0.07321	0.08	6
Carbon dioxide	07/07/08	0.02946	0.08	6
Ethane	07/07/08	0.09114	0.06	6
Propane	07/07/08	0.03376	0.14	6
iso-Butane	07/07/08	0.007784	0.14	6
n-Butane	07/07/08	0.009723	0.12	6
Methane	07/07/08	0.7544	0.05	6

Measurement № 2	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	10/07/08	0.07339	0.10	6
Carbon dioxide	10/07/08	0.02949	0.09	6
Ethane	10/07/08	0.09119	0.06	6
Propane	10/07/08	0.03378	0.09	6
iso-Butane	10/07/08	0.007787	0.09	6

n-Butane	10/07/08	0.009727	0.09	6
Methane	10/07/08	0.7543	0.05	6

Measurement № 3	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	15/07/08	0.07334	0.09	5
Carbon dioxide	15/07/08	0.02947	0.08	5
Ethane	15/07/08	0.09113	0.05	5
Propane	15/07/08	0.03380	0.14	5
iso-Butane	15/07/08	0.007783	0.14	5
n-Butane	15/07/08	0.009726	0.14	5
Methane	15/07/08	0.7545	0.05	5

Results:

Gas mixture	Result (mol/mol)	Coverage factor	Expanded uncertainty (mol/mol)
Nitrogen	**0.07331**	2	**0.00029**
Carbon dioxide	**0.02947**	2	**0.00012**
Ethane	**0.09115**	2	**0.00027**
Propane	**0.03378**	2	**0.00014**
iso-Butane	**0.007785**	2	**0.000039**
n-Butane	**0.009725**	2	**0.000049**
Methane	**0.75478***	2	**0.00046****

* Methane mole fraction $x_{CH4,}$ mol/mol was calculated according to formula:

$$x_{CH4} = 1-\sum x_i$$

x_i- mole fraction of mixture components, mol/mol.

** Calculation of expanded uncertainty of methane mole fraction is described on page 7.

II. Method description forms

Measured on Gas Chromatograph Varian 3 800, with using Porapack and molsieve packed columns, 2x 1mL sample loops, TCD and FID detectors, oven temperature 108 °C, carrier gas Helium. All measurements were done in automatic way. Before entering sample loops all gas mixtures went through a mass flow controller and pressure controller.

Calibration Standards

All SMU calibration standards were made gravimetrically according to ISO 6142 and ISO 6143, impurities of parent gases were analysed on hydrocarbons, CO, CO_2, N_2 and water by SMU on GC and FTIR spectrometer. Quality of 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.

As calibrants were used 5 primary standard mixtures with following compositions and uncertainties in non extended form:

0011F_5

Component	Assigned value (mol/mol)	Standard uncertainty (mol/mol)
Nitrogen	0.13320	0.00014
Carbon dioxide	0.029921	0.000034
Ethane	0.084755	0.000088
Propane	0.038550	0.000051
iso-Butane	0.005562	0.000010
n-Butane	0.006775	0.000012
Methane	0.70123	0.00070

0717E_3

Component	Assigned value (mol/mol)	Standard uncertainty (mol/mol)
Nitrogen	0.072976	0.000086
Carbon dioxide	0.029560	0.000033
Ethane	0.089642	0.000093
Propane	0.033579	0.000045
iso-Butane	0.007706	0.000016

n-Butane	0.007489	0.000016
Methane	0.75904	0.00076

0715E_5

Component	Assigned value (mol/mol)	Standard uncertainty (mol/mol)
Nitrogen	0.10468	0.00012
Carbon dioxide	0.031946	0.000045
Ethane	0.082555	0.000095
Propane	0.035614	0.000048
iso-Butane	0.007281	0.000016
n-Butane	0.009566	0.000019
Methane	0.72835	0.00073

9328E_2

Component	Assigned value (mol/mol)	Standard uncertainty (mol/mol)
Nitrogen	0.071268	0.000087
Carbon dioxide	0.031077	0.000043
Ethane	0.09553	0.00010
Propane	0.033909	0.000051
iso-Butane	0.007956	0.000016
n-Butane	0.010313	0.000019
Methane	0.74994	0.00075

0099F_2

Component	Assigned value (mol/mol)	Standard uncertainty (mol/mol)
Nitrogen	0.012306	0.000017
Carbon dioxide	0.013200	0.000017
Ethane	0.046611	0.000049
Propane	0.018658	0.000025
iso-Butane	0.004259	0.000010
n-Butane	0.004361	0.000010
Methane	0.90060	0.00090

Instrument Calibration

All runs in first, third, fifth measurement sequence had rising molar fraction, second, fourth, sixth processed in reverse order. All calibration standards in previous tables were used at each run. Uncertainty of response consisted from figure characterised roughly immediate repeatability and from signal drift estimated. From each run was made one calibration curve with sample signals. These figures together with molar fraction data were subjected to b_least program (weighted least square regression). Each run produced sample molar fraction with its standard uncertainty. From all runs results = average of molar fractions in one sequence were standard deviation found (uncertainty of type A) and from runs results uncertainties the mean (through squares) was found (uncertainty of type B). These 2 figures were combined to give result uncertainty.

At b_least these models of analytical curves were used:

Nitrogen	TCD	2-polynomial
Carbon dioxide	TCD	2-polynomial
Ethane	TCD	2-polynomial
Propane	FID	2-polynomial
iso-Butane	FID	2-polynomial
n-Butane	FID	2-polynomial

Sample Handling

Cylinders with natural gas were at SMU kept at 17 – 22 °C. Only automated measurements with mass flow controller were used.

Uncertainty

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

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

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

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

Following estimation of result uncertainty (except methane) keeps “Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method" (Annual Book of ASTM Standards E 691-87) with some approximations.

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

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

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

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

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

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

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

p – number of days (3)
n – number of measurements in 1 day

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

Uncertainty source	Contribution (%)
Type A (stand. deviation)	26 %
Type B (response drift, uncertainty of calibration RM)	74 %

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

Uncertainty source	Contribution (%)
Type A (stand. deviation)	23.5 %
Type B (response drift, uncertainty of calibration RM)	76.5 %

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

Uncertainty source	Contribution (%)
Type A (stand. deviation)	22 %
Type B (response drift, uncertainty of calibration RM)	78 %

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

Uncertainty source	Contribution (%)
Type A (stand. deviation)	35 %
Type B (response drift, uncertainty of calibration RM)	65 %

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

Uncertainty source	Contribution (%)
Type A (stand. deviation)	29 %
Type B (response drift, uncertainty of calibration RM)	71 %

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

Uncertainty source	Contribution (%)
Type A (stand. deviation)	27 %
Type B (response drift, uncertainty of calibration RM)	73 %

Evaluation of the measurement uncertainty for **methane**:
Total standard uncertainty of methane mole fraction u_{CH4}, mol/mol was calculated according to formula

$$u_{CH4}=\sqrt{\sum u_{Ai}^2 + u_{Bi}^2}$$

u_{Ai} and u_{Bi}- standard uncertainties of type A and B of components mole fraction, mol/mol.
Expanded uncertainty U(k=2) was calculated from standard uncertainty $2*u_{CH4}$.
Reported uncertainties of SMU primary standard mixtures and measurement values are in accordance with SMU CMC´s (BIPM KCDB) for synthetic natural gas.

Ing. Miroslava Valkova, Laboratory of gases

Ing. Stanislav Musil, PhD., Deputy for research

SMU Bratislava, Slovakia Date: 31.07.2008

Annex 1

Key comparison COOMET.QM-K23.b

"Standard Reference Materials – Synthetic Natural Gas"

MEASUREMENT REPORT

I. Results of Study

Laboratory: Czech Metrology Institute

Cylinder number: D200383

Measurement № 1	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	20/05/08	7,019	0,37	10
Carbon dioxide	20/05/08	2,905	0,31	10
Ethane	20/05/08	9,354	0,70	10
Propane	20/05/08	3,392	0,35	10
iso-Butane	20/05/08	0,816	0,42	10
n-Butane	20/05/08	0,992	0,43	10
Methane	20/05/08	75,521	0,27	10

Measurement № 2	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	27/05/08	7,119	1,32	5
Carbon dioxide	27/05/08	2,925	0,45	5
Ethane	27/05/08	9,342	0,47	5
Propane	27/05/08	3,405	0,67	5
iso-Butane	27/05/08	0,821	0,53	5
n-Butane	27/05/08	0,993	0,48	5
Methane	27/05/08	75,395	0,47	5

Measurement № 3	Date dd/mm/yy	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements n
Nitrogen	24/07/08	7,113	0,44	8
Carbon dioxide	24/07/08	2,907	0,31	8
Ethane	24/07/08	9,286	0,15	8
Propane	24/07/08	3,404	0,30	8
iso-Butane	24/07/08	0,814	0,28	8
n-Butane	24/07/08	0,984	0,23	8
Methane	24/07/08	75,492	0,16	8

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	7,084	2	0,110
Carbon dioxide	2,912	2	0,050
Ethane	9,328	2	0,107
Propane	3,400	2	0,041
iso-Butane	0,817	2	0,021
n-Butane	0,990	2	0,016
Methane	75,470	2	0,454

II. Method description forms

Instrument(s) (principles, make, type, configuration, data collection etc.)

Instrument: Gas Chromatograph, type DANI 1000,

Detector: microTCD, detector measurement temperature: 200 °C

Column: Rt-Q PLOT, length 30 m, inside diameter 0,53 mm

Method: optimal method for hydrocarbons analysis used (name: 0703uTCD.met)

time of analysis – 15 min.

oven temperature program from 40 °C to 230 °C

Calibration Standards

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

For calibrations were used the own CMI standards: cylinder number 56610 (nitrogen, carbon dioxide, ethane, propane in methane) and cylinder number 56611 (n-butane, iso-butane in methane). Both mixtures were prepared gravimetrically. It was used for preparation the special balance (AVZP) in the property of CMI, filling equipment in Linde Gas Praha factory, pure gases and pre-mixtures. Impurities of source gases were analysed in SMU laboratory by GC/MS and FTIR.

These reference materials were analysed in CMI laboratory and verified in SMÚ laboratory.

Composition of calibrants may be reported in the following format:

Component	Assigned value	Standard uncertainty
Nitrogen	7,104	0,013
Carbon dioxide	2,980	0,0014
Ethane	9,340	0,005
Propane	3,377	0,002
iso-Butane	0,797	0,003
n-Butane	0,997	0,004
(any relevant impurities)		

Instrument Calibration

Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.)

Calibration were performed by GC DANI calibration possibilities. Each calibration standard was measured 5-times for AREA value assignment. AREA average of these measurements were allocated the reference value. These values were used as a calibration point.

The equitation of measurement is:

$$c_{\text{sample}} = c_{RM} * \frac{A_{sample}}{A_{RM}}$$

where A – Area (mV s), c – concentration (mol %)

In the first and second measurement were used two-point calibration of seven components. Reference values come from NMi Primary Reference Material (cylinder No: 8670E) and CMI reference standard: (cylinder No: 56610 and 56611).

Calibration files used for measurement:

1st measurement: 56610-1.cal

2nd measurement: 56610-2.cal

1rd measurement: Celkova kal-multi.cal (multi-level calibration)

Calibration file (56610-2.cal) - given here as an example:

Bellow are given calibration points tables with using models and equations for each components

Comp.	Level	Area	Amount	Type	Equation	R corr.coef.	Curve from "0"
Nitrogen	1	121,0299	7,104	Quadr.	$Y= -0{,}3165\ X^2 + 19{,}2508\ X$	1,00000	yes
	2	55,4687	3,03				

Comp.	Level	Area	Amount	Type	Equation	R corr.coef.	Curve from “0”
CO_2	1	60,5116	2,980	linear	Y= 20,30859 X	0,9999999	yes
	2	55,4687	3,03				

Comp.	Level	Area	Amount	Type	Equation	R corr.coef.	Curve from “0”
Ethane	1	202,3120	9,340	Quadr.	$Y= -0{,}09506 X^2 + 22{,}54869 X$	1,00000	yes
	2	22,4313	0,999				

Comp.	Level	Area	Amount	type	equation	R corr.coef.	Curve from “0”
Propane	1	96,4761	3,377	Quadr.	$Y= -0{,}25617 X^2 + 29{,}43366 X$	1,00000	yes
	2	14,682	0,501				

Comp.	Level	Area	Amount	Type	Equation	R corr.coef.	Curve from “0”
i-butane	1	26,4462	0,797	linear	Y= 33,24431 X	0,999974	yes
	2	6,9107	0,202				

Comp.	Level	Area	Amount	Type	Equation	R corr.coef.	Curve from "0"
n-butane	1	34,5795	0,997	linear	Y= 34,75528 X	0,9999724	yes
	2	10,6302	0,202				

In the third measurement were used multi-level calibration from 5 standards: 5 calibration points (various concentration).

The calibration graphs could be available in the paper form as an enclosure.

Given calibration files were tested on known gas mixtures, which we use for studies of stability, repeatability and reproducibility.

In the case of classical linear model of one-point calibration we had problems with analysis of higher concentration in the case of Ethane, Propane and Nitrogen. That is a reason for using of quadratic model. We had also problem with very low concentration of Nitrogen, that is why here the calibration curve ignores "zero" point.

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)

CMI laboratory for gas analysis is done in the special container that has two parts. One is laboratory with chromatographs and PC, second one is a storage of cylinders.

Special sampling system leads from the storage to the laboratory with pressure measurement by manometers, flow measurement. The exit pressure from bottles is reduced to five bars, entrance pressure to the chromatograph is reduced to two bars.

The Swagelok valves and capillary tubes are used in the whole sampling system.

Samples are held in the storage, temperature is stable between 15°C and 30°C.

Sample should be mixed by special heating equipment that can be connected at the bottom of bottle.

The process of samples transfer to the instruments is described in methodical procedure. At first is necessary to prepare right journey of sample to GC. After that is open (and then closed) button on GC DANI. Other chromatographs dose sample automatically.

Uncertainty

How the uncertainty of measurement associated with the final result has been evaluated? The main components of uncertainty addressed in the uncertainty of the calibrants, sample handling, calibration of the equipment, and the measurement. If deemed useful, raw measurement data can be given as well in this section.

Uncertainty estimation is given bellow:

expanded uncertainty (U):

$U = k\, u_c$

u_c - combined uncertainty

k - coverage factor

combined uncertainty (u_c)

$$u_c(i) = \sqrt{u^2{}_{s,CRM}(i) + u_{cal}^2(i) + u_{s,repeat}^2(i)}$$

where:

$$u_{s,repeat}(i) = \frac{s(x_i)}{\sqrt{n}}$$

$$s(x_i) = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{(n-1)}}$$

x_i	value of measured quantity
$\bar{x}$	average value of measured quantity
$u_{s,repeat.}$	standard uncertainty of repeatability
$u_{s\ cal..}$	standard uncertainty of calibration measurement

$u_{s\ CRM.}$ standard uncertainty of certified reference material

$s(x_i)$ standard deviation

Combined uncertainty is calculated from three particular standard uncertainties: coming from repeatability of measurement, repeatability of calibration source measurement and uncertainty of CRM (gravimetric preparation).

Note:
For routine analysis is used standard uncertainty of repeatability as a most important source of combined uncertainty .
The results of known mixtures are compared with certificates and older analysis one by absolute and relative deviation.

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Enclosure No 1:

Calibration graphs (multilevel calibration – 5 calibration points)
(in hard copy – "paper" only)