International Supplementary Comparison

COOMET.QM-S5 (COOMET project № 576/RU/12)

“Supplementary comparison of national standards in the field of analysis of gas mixtures containing CO_2, CO, C_3H_8 in nitrogen (“automotive” gas mixtures)”

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Supplementary Comparison COOMET.QM-S5 (COOMET 576/RU/12)

Final report

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Field

Amount of substance: gas analysis

Subject

Supplementary comparison of national measurement standards in the field of analysis of gas mixtures of carbon dioxide (CO_2), carbon monoxide (CO) and propane (C_3H_8) in nitrogen (automotive gas mixtures).

Participants:

Institute	City	Country
VNIIM	St. Petersburg	Russia
Ukrmetrteststandard	Kiev	Ukraine
BelGIM	Minsk	Belarus
BAM	Berlin	Germany
KazInMetr	Karaganda	Kazakhstan

Organising body

TC 1.8 «Physical Chemistry» COOMET

Rationale

The relevance of the comparison is founded on tightening of requirements to a control of automobile emissions (realization of environmental standards of EURO 4, EURO-5).
Discussions at the 30-th GAWG meeting (November 2013) led to decision to give status of “supplementary comparison” to this study because the appropriate CCQM key comparison (CCQM-K3) was carried out about 10 years ago.

There have been four previous key comparisons in this field: CCQM-K3 (the results were published in November 2001), EUROMET.QM-K3 (the results were published in July 2002), APMP.QM-K3 (the results were published in November 2003) and COOMET.QM-K3 (the results were published in August 2006).

Supported claims

This supplementary comparison can be used to support CMC claims for:
CO_2 in the range (4 - 16) $\cdot 10^{-2}$ mol/mol;
CO in the range (0.5- 5) $\cdot 10^{-2}$ mol/mol;
C_3H_8 in the range (0.01 – 0.3) $\cdot 10^{-2}$ mol/mol.

Measurement standards

The nominal amount of substance fraction of components in gas mixtures was as follows:

CO_2	13.5 $\cdot 10^{-2}$ mol/mol
CO	3.0 $\cdot 10^{-2}$ mol/mol
C_3H_8	0.2 $\cdot 10^{-2}$ mol/mol
N_2	balance

The total number of gas mixtures that took part in these comparisons was 8. Two gas mixtures were prepared during COOMET.QM-K3 and showed good stability results and six gas mixtures were newly prepared. Four newly prepared gas mixtures were sent to participants for study. Stability of all measurement standards before and after shipment was checked against one of the newly prepared mixtures.

Schedule

The cylinders containing the comparison mixtures were shipped to all the participants in February 2014. The measurement results were submitted by the participants in May–August 2014. Almost all cylinders containing the measurement gas mixtures were returned to the coordinating laboratory in the period May – October 2014. Due to the customs clearance delay for the Kazakhstan measurement mixture, re-analysis of their cylinder was postponed to November 2014.

Measurement protocol

The protocol informed the participants about the ranges of nominal concentration of the components in the gas mixtures. The measurement protocol requested each laboratory to perform at least 3 measurements obtained under repeatability conditions including at least three separate calibrations. Reports of the laboratories were to contain information on the methods that were used for analyzing the comparison gas mixtures, calibration methods, methods of preparation of calibration mixtures, and also a detailed uncertainty budget.

Measurement model

The measurement model has been taken from the key comparison CCQM-K3 [1].The gas mixtures for the comparison were prepared gravimetrically in accordance with the requirements of ISO 6142 [1] and were studied regarding their composition and stability at the coordinating laboratory (VNIIM) in accordance with requirements of ISO 6143 [2].

The amount–of–substance fractions as obtained from gravimetry and purity analysis of the parent substances were used as reference values.
The combined standard uncertainty of a component reference value $u_{i,ref}$ (for a mixture i) was calculated using the following equation:

$$u_{\mathrm{i,ref}} = \sqrt{u_{i,grav}^2 + u_{\mathrm{i,ver}}^2 + u_{i,stab}^2} \qquad (1)$$

where
$u_{i,grav}$ – is the standard uncertainty of gravimetric preparation.

The following equation is used to calculate the combined uncertainty of the gravimetric uncertainty:

$$u_{\mathrm{i,grav}} = \sqrt{u_{i,weighing}^2 + u_{i,purity}^2} \qquad (2)$$

$u_{i,weighing}$ - is the standard uncertainty of weighing process;
$u_{i,purity}$ - is the standard uncertainty due to the purity of the parent gases;
$u_{i,ver}$ - is the standard uncertainty from verification;
$u_{i,stab}$ - is the standard uncertainty concerned with stability.

Long-term stability measurements did not show any change in the concentration of the target components within the precision of these measurements, so that there was not any corrections due to instability.
The standard uncertainty concerned with stability was taken as zero $u_{i,stab} = 0$.
The expression for the combined standard uncertainty of a reference value becomes thus:

$$u_{\mathrm{i,ref}} = \sqrt{u_{i,grav}^2 + u_{\mathrm{i,ver}}^2} \qquad (3)$$

Measurement methods and calibration procedures

The following methods of measurement and calibration methods have been employed (table 1).

Table 1 Measurement and calibration methods

Laboratory	Measurement method	Calibration method	Total number of measurements
VNIIM	NDIR analyzer	CO: linear, two points; CO_2: calibration curve, five points; C3H8: linear, two points	3 measurements 10 sub-measurements
Ukrmetrtest standard	GC-TCD (CO,CO_2) GC-FID (C_3H_8)	linear, three points; linear, three points	3 measurements 10 sub-measurements
BelGIM	GC-TCD (CO,CO_2) GC-FID (C_3H_8)	linear, three points; linear, three points	5 measurements with 6 observations
BAM	GC-TCD (CO,CO_2) GC-FID (C_3H_8)	calibration curve by three points and method of bracketing	3 measurements with 3-5 observations in each measurement
KazInMetr	GC-TCD (CO,CO_2) GC-FID (C_3H_8)	one point	3 measurements 5 sub-measurements

Degrees of equivalence

The degree of equivalence (D_i) for each participating laboratory (and each component) in the comparison is defined in accordance with the equation:

$$D_i = x_{i,lab} - x_{KCRV} \tag{4}$$

Since the comparison gas mixtures had slightly different concentrations (see Tables 2-4) and taking into account the fact, that the pilot laboratory prepared the mixtures using the same methods and materials, the individual values based on gravimetry and purity analysis can be adopted as reference values.
Hence the degree of equivalence can be expressed as:

$$D_i = x_{i,lab} - x_{i,,ref} \tag{5}$$

The combined standard uncertainty of the degree of equivalence can be expressed as

$$u(D_i) = \sqrt{u^2_{i,lab} + u^2_{i,grav} + u^2_{i,ver}} \tag{6}$$

The expanded uncertainty $U(D_i)$ at a 95 % confidence level is calculated using the following equation:

$$U(D_i) = k\sqrt{u^2_{i,lab} + u^2_{i,grav} + u^2_{i,ver}} \tag{7}$$

where k is the coverage factor, ($k=2$).

The degrees of equivalence for the participating laboratories are shown relative to the gravimetric values in figures 1-3. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed. 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.

Results

In this section the results of the comparison are summarized. In the Tables 2-4 the following data is presented:

$x_{i,ref}$	reference value (amount of substance fraction from gravimetric preparation), $\cdot 10^{-2}$ mol/mol;
$u_{i,ref}$	uncertainty of the reference value, $\cdot 10^{-2}$ mol/mol;
$x_{i,lab}$	result of laboratory, $\cdot 10^{-2}$ mol/mol;
$u_{i,lab}$	stated standard uncertainty of laboratory, $\cdot 10^{-2}$ mol/mol;
D_i	degree of equivalence (difference between laboratory result and reference value), $\cdot 10^{-2}$ mol/mol;
$U(D_i)$	expanded uncertainty of D_i, at 95 % level of confidence, $\cdot 10^{-2}$ mol/mol;
k	assigned coverage factor for degree of equivalence;
$D_{i,rel}$	relative form for degree of equivalence ($D_{i,rel} = D_i * 100 / x_{i,ref}$), $\cdot$%;
$U(D_i)_{rel}$	relative form for expanded uncertainty of D_i ($U(D_i)_{rel} = U(D_i) * 100 / x_{i,ref}$), $\cdot$%.

Table 2: Results for CO

Laboratory	Cylinder	$x_{i,ref}$ (10^{-2} mol/mol)	$u_{i,ref}$ (10^{-2} mol/mol)	$x_{i,lab}$ (10^{-2} mol/mol)	$u_{i,lab}$ (10^{-2} mol/mol)	D_i (10^{-2} mol/mol)	$D_{i,rel}$ %	k	$U(D_i)$ (10^{-2} mol/mol)	$U(D_i)_{rel}$ %
VNIIM	M365633	2.9933	0.00125	2.9928	0.0013	-0.0005	-0.016	2	0.0036	0.121
BAM	M365611	3.0049	0.00125	3.002	0.0075	-0.0029	-0.096	2	0.0152	0.506
BelGIM	M365612	3.0175	0.00125	3.010	0.003	-0.0075	-0.248	2	0.0065	0.215
Ukrmetrteststandard	M365623	3.0028	0.00125	3.004	0.0025	0.0012	0.040	2	0.0056	0.186
KazInMetr	M365622	2.9980	0.00125	3.0254	0.0212	0.027	0.91	2	0.042	1.42

Table 3: Results for CO_2

Laboratory	Cylinder	$x_{i,ref}$ (10^{-2} mol/mol)	$u_{i,ref}$ (10^{-2} mol/mol)	$x_{i,lab}$ (10^{-2} mol/mol)	$u_{i,lab}$ (10^{-2} mol/mol)	D_i (10^{-2} mol/mol)	$D_{i,rel}$ %	k	$U(D_i)$ (10^{-2} mol/mol)	$U(D_i)_{rel}$ %
VNIIM	M365633	13.6501	0.00095	13.6571	0.0046	0.0069	0.051	2	0.0092	0.068
BAM	M365611	13.5450	0.0010	13.553	0.020	0.008	0.059	2	0.040	0.296
BelGIM	M365612	13.5241	0.00095	13.50	0.01	-0.024	-0.178	2	0.020	0.148
Ukrmetrteststandard	M365623	13.4885	0.00095	13.479	0.010	-0.010	-0.075	2	0.020	0.148
KazInMetr	M365622	13.6735	0.0010	13.6319	0.0968	-0.042	-0.30	2	0.194	1.42

Table 4: Results for C_3H_8

Laboratory	Cylinder	$x_{i,ref}$ (10^{-2} mol/mol)	$u_{i,ref}$ (10^{-2} mol/mol)	$x_{i,lab}$ (10^{-2} mol/mol)	$u_{i,lab}$ (10^{-2} mol/mol)	D_i (10^{-2} mol/mol)	$D_{i,rel}$ %	k	$U(D_i)$ (10^{-2} mol/mol)	$U(D_i)_{rel}$ %
VNIIM	M365633	0.198767	0.000022	0.19879	0.00008	-0.000023	-0.012	2	0.000165	0.083
BAM	M365611	0.200794	0.000023	0.1999	0.0005	-0.00089	-0.44	2	0.00100	0.50
BelGIM	M365612	0.200527	0.000023	0.2000	0.0003	-0.00053	-0.25	2	0.00060	0.30
Ukrmetrteststandard	M365623	0.200630	0.000023	0.20047	0.00012	-0.00016	-0.08	2	0.00024	0.12
KazInMetr	M365622	0.200480	0.000023	0.1999	0.0016	-0.0006	-0.29	2	0.0031	1.55

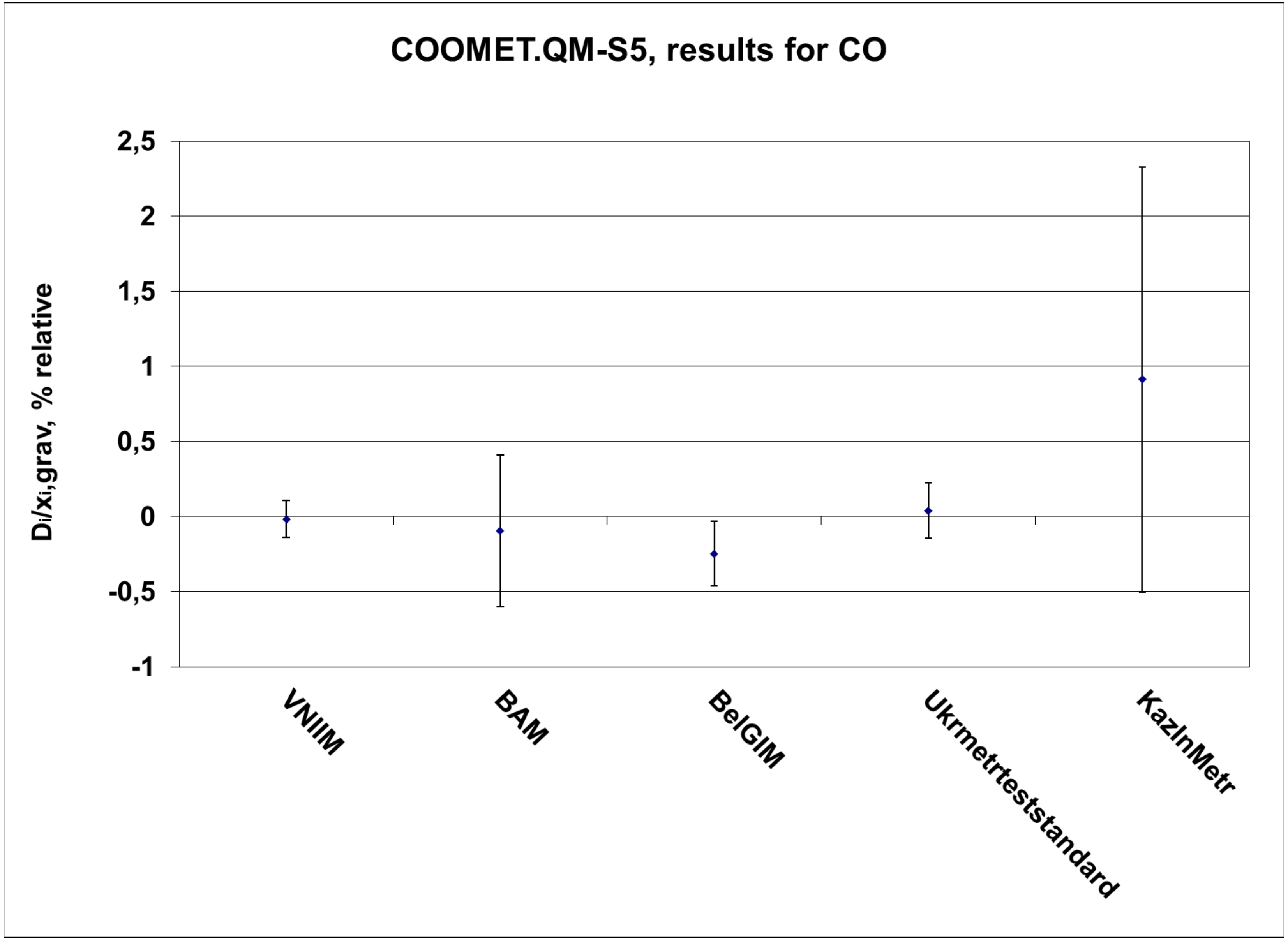

Figure 1. Degrees of equivalence for CO

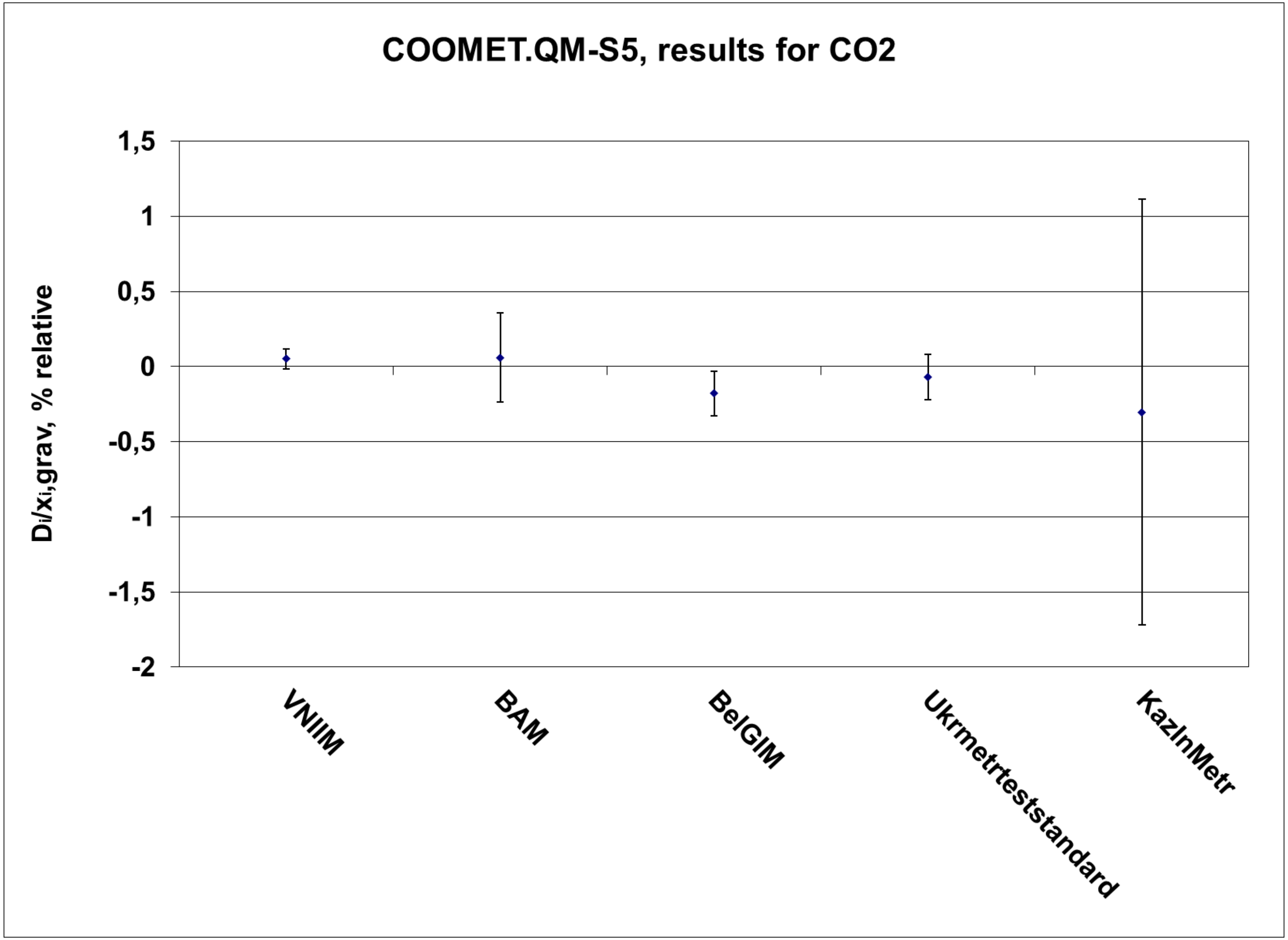

Figure 2. Degrees of equivalence for CO2

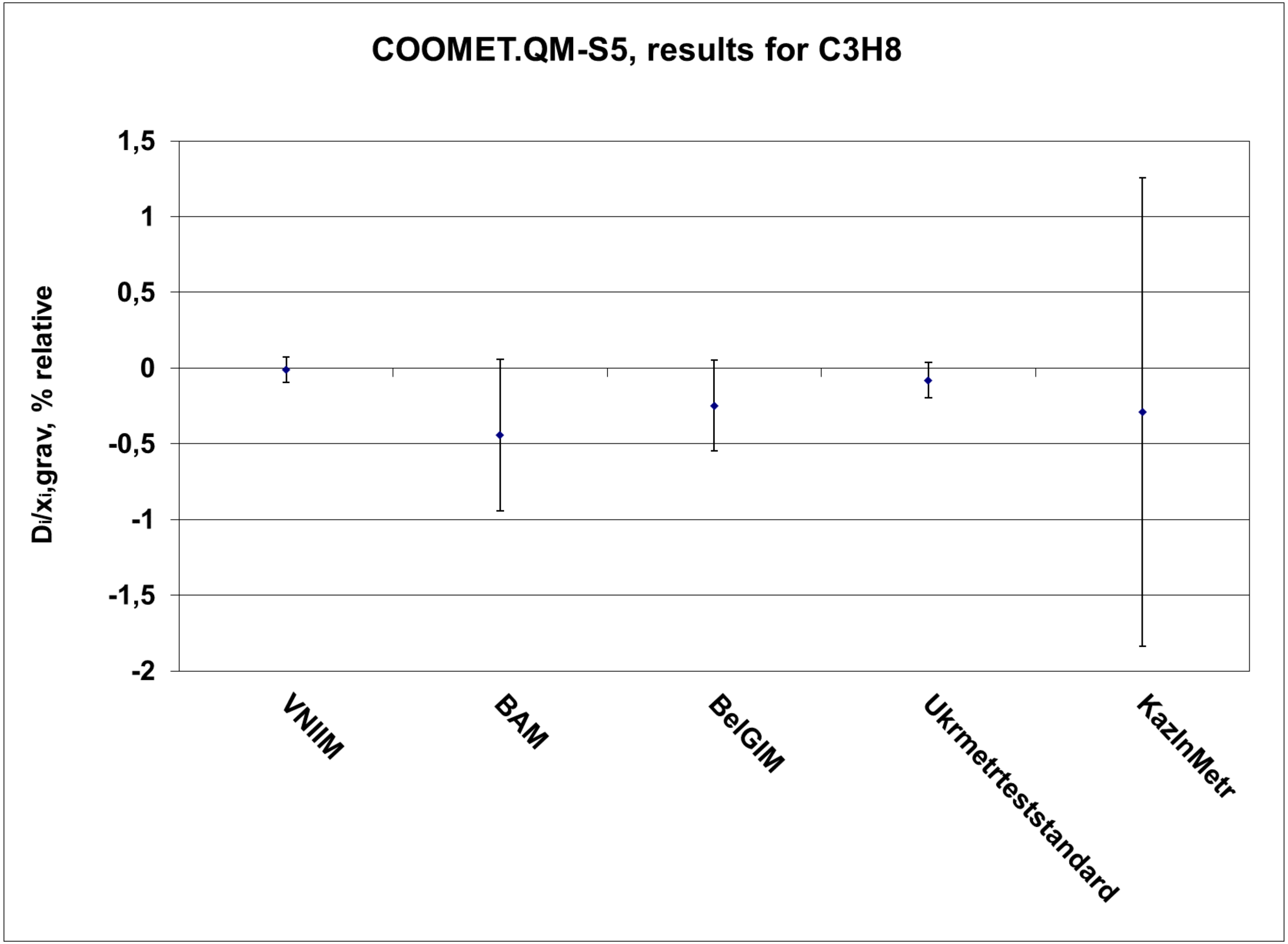

Figure 3. Degree of equivalence for C_3H_8

Discussion and Conclusions

Component CO:
All laboratories identified the values of carbon monoxide mole fraction in the gas mixture within ± 0.9134 %.

VNIIM, BAM and Ukrmetrteststandard have improved their performance compared to COOMET.QM-K3.

Component CO_2:
All laboratories identified the values of carbon dioxide mole fraction in the gas mixture within ± 0.3042%

VNIIM and Ukrmetrteststandard have improved their performance compared to COOMET.QM-K3.

Component C_3H_8:
All laboratories identified the values of propane mole fraction in the gas mixture within ± 0.443%

VNIIM and BAM have improved their performance compared to COOMET.QM-K3.

VNIIM, BAM, Ukrmetrteststandard and BelGIM previously took part in the key comparisons on automotive gas mixtures COOMET.QM-K3 (and CCQM-K3 for VNIIM and BAM), and KazInMetr took part in a comparison of such a type for the first time.

Reference

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

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

[3] International Organization for Standardization, ISO 6143:2001 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures.

Coordinator

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Annex A

Reports submitted by participating laboratories

COOMET.QM-S5

Supplementary comparisons of national standards in the field of analysis of gas mixtures containing CO_2, CO, C_3H_8 in nitrogen («automotive» gas mixtures)

MEASUREMENT REPORT

I. Results of Study

Laboratory: D.I. Mendeleyev Institute for Metrology (VNIIM), Research Department for the State Standard in the Field of Physical-Chemical Measurements

Cylinder number: M365633

NOMINAL COMPOSITION

- Carbon dioxide : $13 \cdot 10^{-2}$ - $14 \cdot 10^{-2}$mol/mol
- Carbon monoxide: $2.8 \cdot 10^{-2}$ – $3.2 \cdot 10^{-2}$ mol/mol
- Propane : 19·10-4 - $21 \cdot 10^{-4}$ mol/mol
- Nitrogen : balance

Measurement №1	Date	Result, 10^{-2} mol/mol	stand. deviation, % relative	number of sub measurements
Carbon dioxide	21.04.2014	13.6652	0.010	10
Carbon monoxide	21.04.2014	2.9932	0.018	10
Propane	21.04.2014	0.19894	0.030	10

Measurement №2	Date	Result, 10^{-2} mol/mol	stand. deviation, % relative	number of sub measurements
Carbon dioxide	28.04.2014	13.6509	0.056	10
Carbon monoxide	28.04.2014	2.9921	0.010	10
Propane	28.04.2014	0.19869	0.042	10

Measurement №3	Date	Result, 10^{-2} mol/mol	stand. deviation, % relative	number of sub measurements
Carbon dioxide	05.05.2014	13.6552	0.027	10
Carbon monoxide	05.05.2014	2.9931	0.008	10
Propane	05.05.2014	0.19874	0.042	10

Final results:

Gas mixture	Result (assigned value), 10^{-2} mol/mol	Coverage factor	Expanded uncertainty 10^{-2} mol/mol
Carbon dioxide	13.6571	2	0.0091
Carbon monoxide	2.9928	2	0.0026
Propane	0.19879	2	0.00016

II. Description of Study

Instruments

Multichannel automatic NDIR analyzer included in the set of the National Primary measurement standard of units of mole fraction and mass concentration of components in gas medium, GET 154-2011, was used for the analysis.

Calibration Standards

All calibration multicomponent gas mixtures were prepared gravimetrically according to ISO 6142.
The calibration multicomponent gas mixtures were prepared directly from pure gases for CO and CO_2 and from pre-mixtures (which were prepared from pure gases) for C_3H_8.
The content of the impurities in all pure gases was determined by GC with TCD and FID detectors, as well as standard hygrometer apparatus (condensation method of dew-point measurement).
The calibration multicomponent gas mixtures were verified with usage of newly prepared and existing gravimetric gas mixtures (there were 3 multicomponent gas mixtures with identical components content) in accordance with ISO 6143.

Composition of one of calibration standards:

Component	Cylinder № M365632	
	x, 10^{-2} mol/mol	Standard uncertainty 10^{-2} mol/mol
CO	2.9775	0.00123
CO_2	13.4135	0.0010
C_3H_8	0.19872	0.000026
N_2	Balance	

Instrument Calibration

Three independent measurements were carried out under repeatability conditions. Before each measurement an instrument calibration was made. One measurement contained 10 sub-measurements.

Sample Handling

The time of the cylinder keeping - 24 hrs.
A method of supplying the sample on the instrument - was used the automatic unit of commutation for inputting gas mixtures.

Uncertainty

Uncertainty table: CO_2

Uncertainty source ***X_i***	**Evaluation type**	**Standard uncertainty *$u(x_i)$, 10^{-2} mol/mol***	**Sensitivity coefficient *c_i, 10^{-2} mol/mol***	**Contribution to standard uncertainty *$u_i(y)$, 10^{-2} mol/mol***
Calibration gas mixture (gravimetric preparation + verification)	A, B	0.00149	1.017	0.0015
Analysis (measurements)	A	0.0043	1.00	0.0043

Coverage factor: 2
Expanded uncertainty: 0.0091 10^{-2} mol/mol

Uncertainty table: CO

Uncertainty source ***X_i***	**Evaluation type**	**Standard uncertainty *$u(x_i)$, 10^{-2} mol/mol***	**Sensitivity coefficient *c_i, 10^{-2} mol/mol***	**Contribution to standard uncertainty *$u_i(y)$, 10^{-2} mol/mol***
Calibration gas mixture (gravimetric preparation + verification)	A, B	0.00123	1.0053	0.00123
Analysis (measurements)	A	0.00036	1.00	0.00036

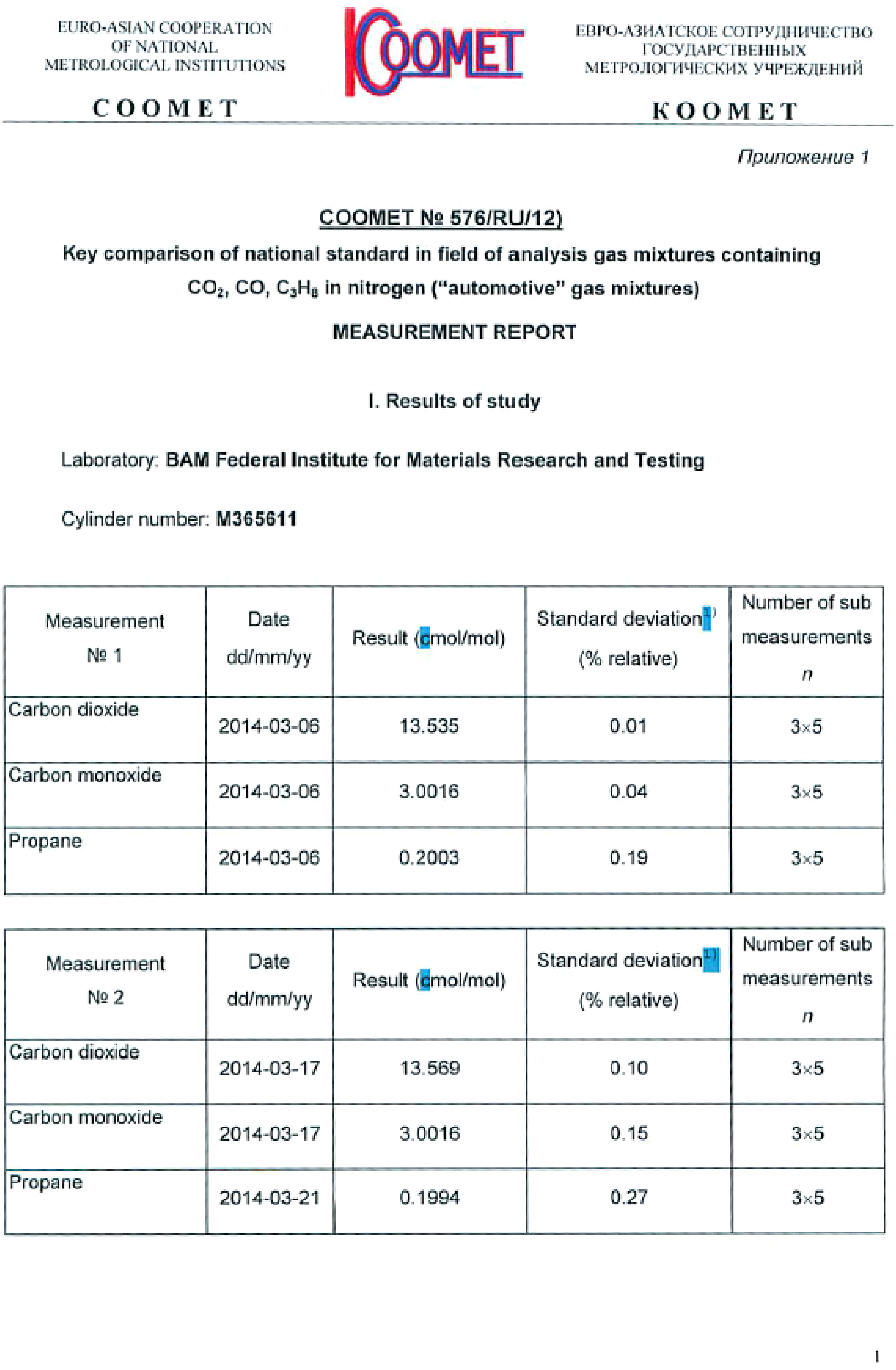
Coverage factor: 2
Expanded uncertainty: 0.0026 10^{-2} mol/mol

Uncertainty table: C_3H_8

Uncertainty source ***X_i***	**Evaluation type**	**Standard uncertainty *$u(x_i)$, 10^{-2} mol/mol***	**Sensitivity coefficient *c_i, 10^{-2} mol/mol***	**Contribution to standard uncertainty *$u_i(y)$, 10^{-2} mol/mol***
Calibration gas mixture (gravimetric preparation + verification)	A, B	0.000029	1.00023	0.000029
Analysis (measurements)	A	0.000076	1.00	0.000076

Coverage factor: 2
Expanded uncertainty: 0,00016 10^{-2} mol/mol

BAM report



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ЕВРО-АЗИАТСКОЕ СОТРУДНИЧЕСТВО
ГОСУДАРСТВЕННЫХ
МЕТРОЛОГИЧЕСКИХ УЧРЕЖДЕНИЙ
КООМЕТ

Приложение 1

COOMET № 576/RU/12)

Key comparison of national standard in field of analysis gas mixtures containing CO_2, CO, C_3H_8 in nitrogen (“automotive” gas mixtures)

MEASUREMENT REPORT

I. Results of study

Laboratory: **BAM Federal Institute for Materials Research and Testing**

Cylinder number: **M365611**

Measurement № 1	Date dd/mm/yy	Result (cmol/mol)	Standard deviation1) (% relative)	Number of sub measurements *n*
Carbon dioxide	2014-03-06	13.535	0.01	3×5
Carbon monoxide	2014-03-06	3.0016	0.04	3×5
Propane	2014-03-06	0.2003	0.19	3×5

Measurement № 2	Date dd/mm/yy	Result (cmol/mol)	Standard deviation1) (% relative)	Number of sub measurements *n*
Carbon dioxide	2014-03-17	13.569	0.10	3×5
Carbon monoxide	2014-03-17	3.0016	0.15	3×5
Propane	2014-03-21	0.1994	0.27	3×5

1

Measurement № 3	Date dd/mm/yy	Result (cmol/mol)	Standard deviation[1] (% relative)	Number of sub measurements *n*
Carbon dioxide	2014-03-19	13.553	0.06	3×3
Carbon monoxide	2014-03-19	3.0014	0.15	3×3
Propane	2014-03-25	0.1999	0.41	1×3 + 2×1

[1] Note, that the standard deviation calculated for the replicates of the sample over one measurement sequence is by no means a good estimate for the uncertainty of the measurement result of a campaign. Uncertainty of the measurement result from a campaign might be higher because other significant sources of uncertainty are ignored or might be lower taking advantage of the alternating measurement order of sample and calibration gases. For data processing, the combined uncertainty has been calculated taking its relevant sources into account.

Final results:

Gas mixture	Result (assigned value) cmol/mol	Coverage factor *k*	Assigned expanded uncertainty cmol/mol
Carbon dioxide	13.553	2	0.040
Carbon monoxide	3.002	2	0.015
Propane	0.1999	2	0.0010

II. Description of study

For more details see attached report

Instrument(s)

A specially designed Siemens Maxum process gas analyser was used applying "method 1" with 44 injections. The oven was used at 60 °C in isothermal mode. Details on Maxum operation can be found in GAS-StAA-027. For measurement campaign No. 4, different to normal operation the loop for determination of N_2 and CO was reduced from 240 µL to 120 µL. A full measurement sequence takes 4.5 h.
A Perkin Elmer PE Autosystem XL with a sample gas flow of 4 mL/min at a primary pressure of 2 bar was used. The oven was used at 80 °C in isothermic mode. A full measurement sequence takes 5 h. For FID measurements it was

equipped with a Varian capillary column containing fused silica 50 m X 0.32 mm ID with coating CP-SIL 8CB DF=5.0 and a sample loop of 100 µL. The FID was operated at 350 °C at an attenuation of "-4" using a H_2 flow of 45 mL/min and an air flow of 450 mL/min. The WLD branch of the instrument is equipped with a Porapak R column and a loop of 1 mL.

Calibration Standards

The following four calibration gases prepared at BAM by a gravimetric method according to DIN EN ISO 6142:2006 were used (u with $k = 1$):

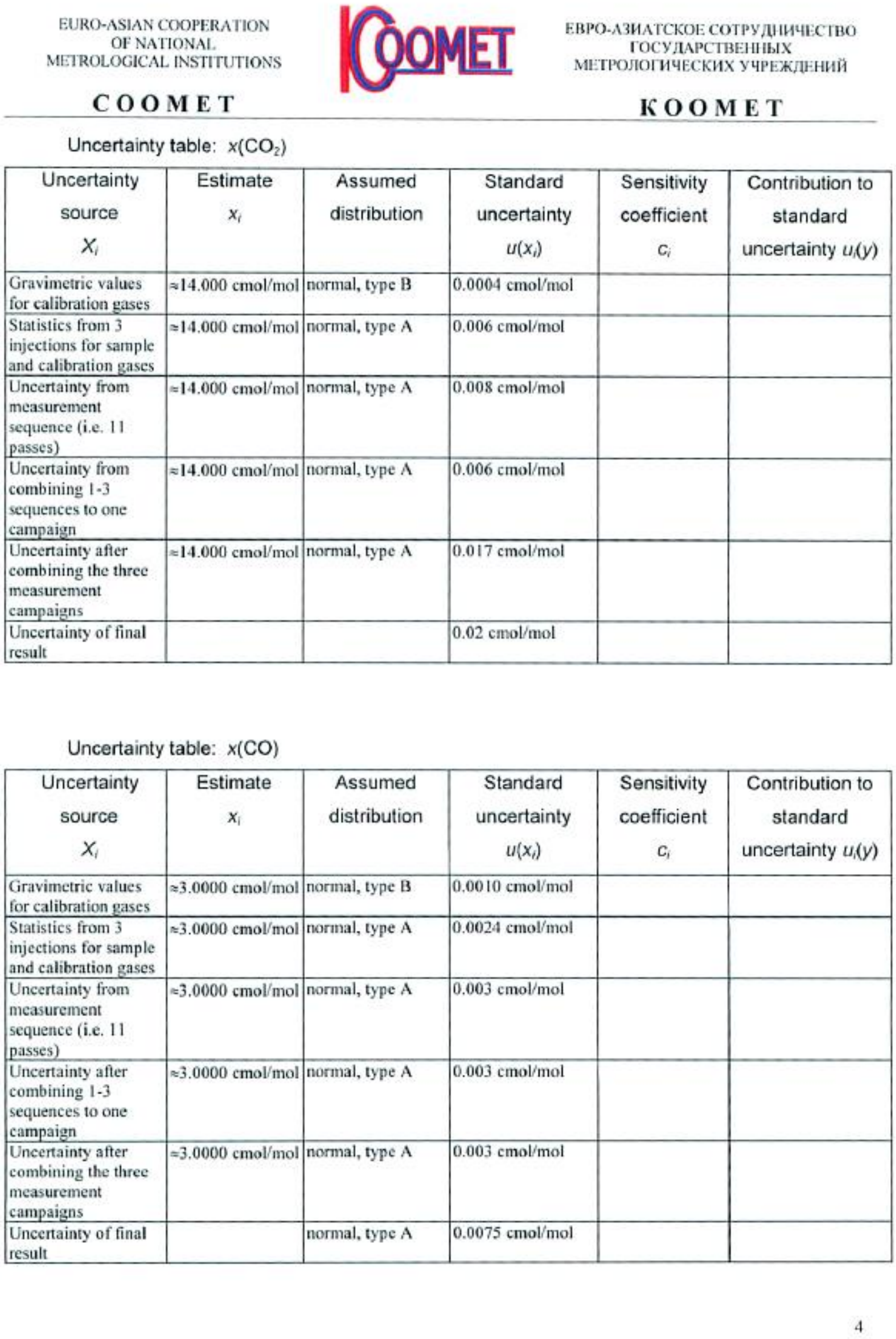
cylinder	Amount fraction Carbon dioxide / cmol/mol	Amount fraction Carbon dioxide / cmol/mol	Amount fraction Carbon monoxide / cmol/mol	Amount fraction propane / cmol/mol	Amount fraction nitrogen / cmol/mol
C49295-981022	x / %	13.31187	3.19923	0.19914	balance
	u / %	0.00359	0.00022	0.00033	
	u_{rel}	2.7E-04	7.0E-05	1.7E-03	
C49301-090922	x / %	14.57069	3.59851	0.21142	balance
	u / %	0.00364	0.00099	0.00006	
	u_{rel}	2.5E-04	2.8E-04	3.0E-04	
C49299-090609	x / %	14.70141	3.68038	0.20895	balance
	u / %	0.00074	0.00042	0.00006	
	u_{rel}	5.0E-05	1.2E-04	3.0E-04	
C49250-050722	x / %	13.67792	2.91193	0.20358	balance
	u / %	0.00075	0.00052	0.00033	
	u_{rel}	5.5E-05	1.8E-04	1.6E-03	

Instrument Calibration

For a measurement sequence the two selected calibration gases C1 & C2 and the sample S were connected to the GC. Using a stream selector valve each calibration gas was connected three times, the sample gas five times to the GC in the following order: C1/S/C2/S/C1/S/C2/S/C1/S/C2. At each connection to the GC 4 injections were made, from which only the last three were used for data evaluation. Accordingly each measurement sequence consists of 11 passes with 3 runs.
Using the Maxum two measurement campaigns with two sequences and two measurement campaigns with three sequences were conducted. In each campaign, the sequences were distributed between two different days. Additionally with the PE two measurement campaigns on different days with one sequence each was performed.
Besides the three analytes, also the matrix gas N_2 was directly determined using Maxum.
Depending on the concentration of the calibration gases vs. the sample, direct matching calibration with one calibration gas, two point bracketing or three point calibration curve (two calibration gases and zero) was applied.

Sample Handling

No heating or rolling was applied.
A DIN 477 No. 9 (oxygen)-VRC ¼" fitting was installed to the sample cylinder. A reduction valve, a needle valve for dosing and a closing valve with outlet to Swagelok 1/16" capillaries was attached. For the two at a time used calibration gases a similar assembly was used. Whereas the assembly for the sample bottle was not changed, depending on the calibration gases used, their assembly had to be changed.
A freshly installed assembly was evacuated down to 10^{-3} mbar and then filled with gas from the cylinder. The evacuating/flushing was repeated five times.

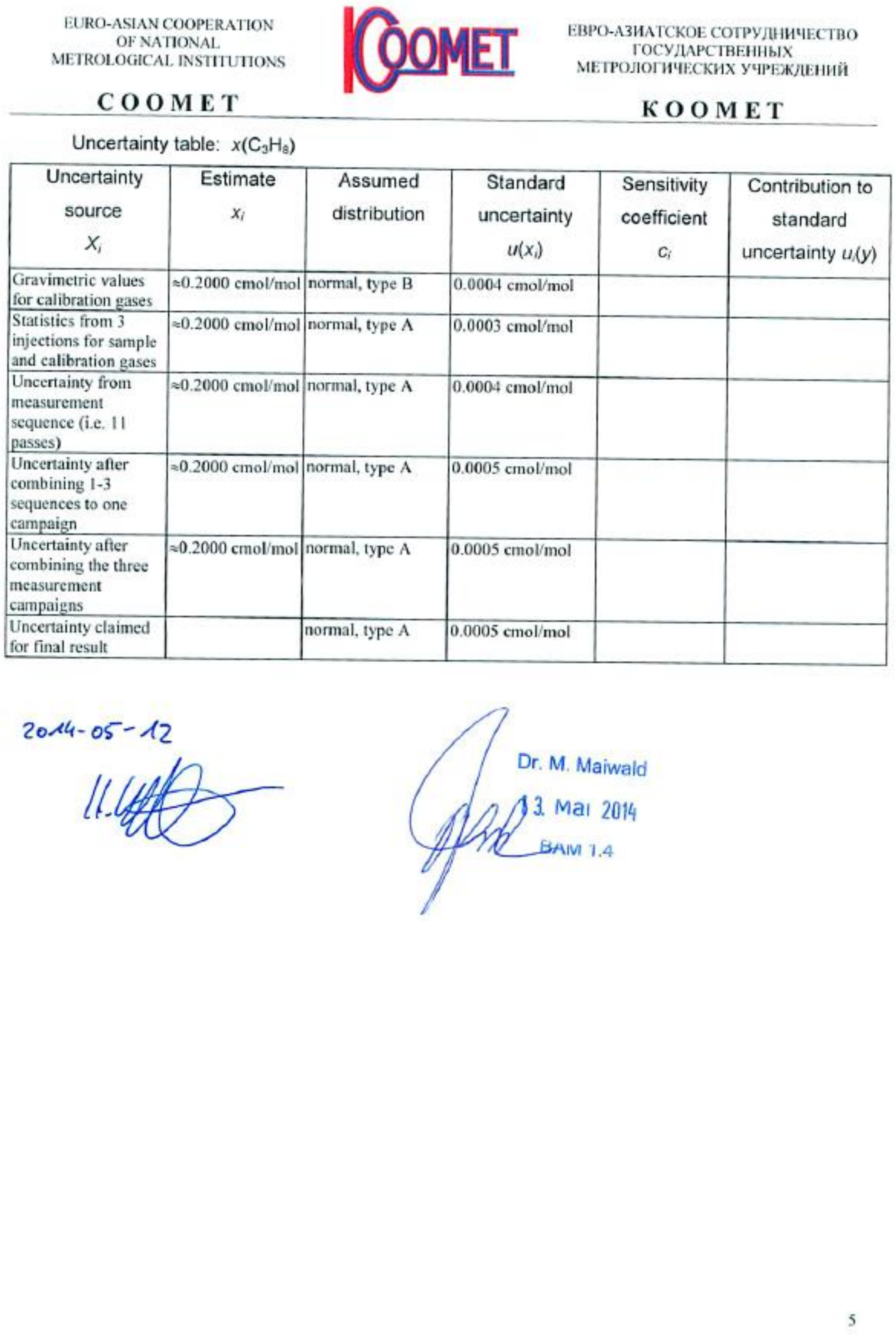


Uncertainty table: $x(CO_2)$

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Gravimetric values for calibration gases	≈14.000 cmol/mol	normal, type B	0.0004 cmol/mol		
Statistics from 3 injections for sample and calibration gases	≈14.000 cmol/mol	normal, type A	0.006 cmol/mol		
Uncertainty from measurement sequence (i.e. 11 passes)	≈14.000 cmol/mol	normal, type A	0.008 cmol/mol		
Uncertainty from combining 1-3 sequences to one campaign	≈14.000 cmol/mol	normal, type A	0.006 cmol/mol		
Uncertainty after combining the three measurement campaigns	≈14.000 cmol/mol	normal, type A	0.017 cmol/mol		
Uncertainty of final result			0.02 cmol/mol		

Uncertainty table: $x(CO)$

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Gravimetric values for calibration gases	≈3.0000 cmol/mol	normal, type B	0.0010 cmol/mol		
Statistics from 3 injections for sample and calibration gases	≈3.0000 cmol/mol	normal, type A	0.0024 cmol/mol		
Uncertainty from measurement sequence (i.e. 11 passes)	≈3.0000 cmol/mol	normal, type A	0.003 cmol/mol		
Uncertainty after combining 1-3 sequences to one campaign	≈3.0000 cmol/mol	normal, type A	0.003 cmol/mol		
Uncertainty after combining the three measurement campaigns	≈3.0000 cmol/mol	normal, type A	0.003 cmol/mol		
Uncertainty of final result		normal, type A	0.0075 cmol/mol		



EURO-ASIAN COOPERATION
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COOMET

ЕВРО-АЗИАТСКОЕ СОТРУДНИЧЕСТВО
ГОСУДАРСТВЕННЫХ
МЕТРОЛОГИЧЕСКИХ УЧРЕЖДЕНИЙ

КООМЕТ

Uncertainty table: $x(C_3H_8)$

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Gravimetric values for calibration gases	≈0.2000 cmol/mol	normal, type B	0.0004 cmol/mol		
Statistics from 3 injections for sample and calibration gases	≈0.2000 cmol/mol	normal, type A	0.0003 cmol/mol		
Uncertainty from measurement sequence (i.e. 11 passes)	≈0.2000 cmol/mol	normal, type A	0.0004 cmol/mol		
Uncertainty after combining 1-3 sequences to one campaign	≈0.2000 cmol/mol	normal, type A	0.0005 cmol/mol		
Uncertainty after combining the three measurement campaigns	≈0.2000 cmol/mol	normal, type A	0.0005 cmol/mol		
Uncertainty claimed for final result		normal, type A	0.0005 cmol/mol		

2014-05-12

Dr. M. Maiwald
13. Mai 2014
BAM 1.4

COOMET N 576/RU/12

“Additional comparisons of National Standards in field of the analysis of gas mixture with CO_2, CO, C_3H_8 in nitrogen (car gases)”

REPORT ON RESULTS OF THE STUDY

I. Results of experimental study

Laboratory: Belarus, BelGIM, Section for physicochemical and optical measurements, sector for standards and gas mixtures, 8, Serova st., Minsk.
Cylinder No: M365612, 5 dm^3
NOMINAL COMPOSITION OF GAS MIXTURE

- Carbon dioxide:	$13\cdot10^{-2}$ - $14\cdot10^{-2}$ mol/mol
- Carbon oxide:	$2,8\cdot10^{-2}$ - $3,2\cdot10^{-2}$ mol/mol
- Propane:	$0,19\cdot10^{-2}$ – $0,21\cdot10^{-2}$ mol/mol
- Nitrogen:	balance

Measurement No 1	Date	Result, x, mol/mol$\cdot10^{-2}$	Standard deviation, % rel.	No of observations n
Carbon dioxide	21.04.2014	13,490	0,12	6
Carbon oxide		3,103	0,20	6
Propane		0,19972	0,26	6

Measurement No 2	Date	Result, x. mol/mol$\cdot10^{-2}$	Standard deviation, % rel.	No of observations n
Carbon dioxide	24.04.2014	13,5026	0,05	6
Carbon oxide		3,0089	0,07	6
Propane		0,19999	0,27	6

Measurement No 3	Date	Result, x, mol/mol$\cdot10^{-2}$	Standard deviation, % rel.	No of observations n
Carbon dioxide	28.04.2014	13,504	0,05	6
Carbon oxide		3,0117	0,12	6
Propane		0.19984	0,29	6

Measurement No 4	Date	Result, x, mol/mol·10^{-2}	Standard deviation, % rel.	No of observations n
Carbon dioxide	02.05.2014	13,499	0,13	6
Carbon oxide		3,104	0,07	6
Propane		0,2002	0,2	6

Measurement No 5	Date	Result, x, mol/mol·10^{-2}	Standard deviation, % rel.	No of observations n
Carbon dioxide	05.05.2014	13,486	0,06	6
Carbon oxide		3,0069	0,07	6
Propane		0,20009	0,23	6

Final results:

Gas mixture	Result, x, mol/mol·10^{-2}	Coverage factor	Expanded uncertainty, mol/mol·10^{-2}
Carbon dioxide	13,50	2	0,02
Carbon oxide	3,010	2	0,006
Propane	0,2000	2	0,0006

II. Description of study

Equipment

Measurements were performed on a gas chromatographer "Crystal 5000" ("Chromatek Analytic", Russia) fitted with TCD1, TCD2 and FID. Gas-carrier is helium.

For the purpose of measurements the following auxiliary devices and materials were used:

1. Metallic packed column 3m x 3mm x 2mm - HayeSep N 80/100, metallic packed column 1m x 4mm x 2mm-CaA 0,16/0,25.
2. Metallic packed column 3m x 4mm x 2mm-CaA 0,16/0,25.
3. Capillary column HP PLOT/Q 30m x 0,53mm.
4. Helium gas, grade "6.0", high purity hydrogen and compressed air for FID.
5. Multicomponent calibration gas mixtures - Calibration Standards produced and certified by gravimetric method.
6. Gas flow former for creation and maintenance of constant pressure in doses.

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).

Performance and metrological characteristics of the equipment used for gravimetric preparation of mixtures are given in Table 1.

Table 1

Description of the equipment	Manufacturer	Metrological characteristics
Mass-comparator type KA10-3/P	Mettler-Toledo, Switzerland	Maximum load: 15 kg; Scale division: 1 mg; Standard deviation: 1,9 mg at load of 10 kg; Operating temperature range: +10÷30°C; Maximum temperature change within 1 h: ±0,5 °C.
Gas mixer	Belarus	Measurement range: 0 ÷ 20,0 MPa Accuracy class for manometers – 0,05; Vacuummeter with pressure sensor for measuring the residual pressure before filling; Residual pressure before filling of each component: not more than 20 Pa.

Purity analysis of initial gases

The purity analysis of initial gases is based on the information provided by the supplier or on the results of determination of impurity in pure gases using measurement procedure developed inside BelGIM.

The composition of the "pure" gases used for preparation of calibration mixtures is given in Table 2.

Table 2 - Metrological characteristics of initial gases.

Initial gas: CO		
Component	Content, ***x***, mol/mol $\cdot 10^{-2}$	Standard uncertainty, ***u(x)***, mol/mol $\cdot 10^{-2}$
N_2	0.0070	0.0005
O_2	3.00e-004	1.50e-004
CO	**99.9927**	**0.0006**

Initial gas: C_3H_8-N_2		
Component	Content, ***x***, mol/mol $\cdot 10^{-2}$	Standard uncertainty, ***u(x)***, mol/mol $\cdot 10^{-2}$
N_2	**95.0991**	**0.0004**
O_2	4.90e-004	4.80e-005
C_2H_6	1.08e-004	5.00e-006
C_3H_8	**4.8973**	**0.0004**
nC_4H_{10}	3.43e-005	2.45e-006
iC_4H_{10}	1.91e-004	2.00e-006
Ar	0.0024	0.0002
H_2O	3.14e-004	2.90e-005

Initial gas: CO_2		
Component	Content, ***x***, mol/mol $\cdot 10^{-2}$	Standard uncertainty, ***u(x)***, mol/mol $\cdot 10^{-2}$
N_2	0.0033	0.0002
O_2	3.00e-004	1.00e-004
CO_2	**99.9951**	**0.0003**
Ar	4.00e-004	2.00e-004
H_2O	9.50e-004	3.00e-005

Initial gas: N_2		
Component	Content, ***x***, mol/mol $\cdot 10^{-2}$	Standard uncertainty, ***u(x)***, mol/mol $\cdot 10^{-2}$
H2	1.00e-006	5.00e-007
N2	**99.9999**	**0.0000**
O2	6.50e-005	3.25e-005
CO	1.00e-006	5.00e-007
CO2	2.50e-006	1.25e-006
CH4	3.00e-006	1.50e-006
H2O	5.00e-005	2.50e-005

3. After preparation of mixture, the cylinder was maintained in laboratory room within 24 hours, the mixture then was homogenized on the stand by rotating on the rollers within 4-5 hours.

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 No Volume, material, preparation date	Component	Content, ***x***, mol/mol$\cdot 10^{-2}$	Standart uncertainty, ***u(x)***, mol/mol$\cdot 10^{-2}$
19994, 4 dm3,aluminum 16.04.2014	CO_2	13,718	0,001
	CO	3,111	0,001
	C_3H_8	0,2052	0,0001
	N_2	balance	
10212, 4 dm3,aluminum 15.04.2014	CO_2	13,447	0,001
	CO	2,947	0,001
	C_3H_8	0,1998	0,0001
	N_2	balance	
20002, 4 dm3,aluminum 17.04.2014	CO_2	13,319	0,001
	CO	2,880	0,001
	C_3H_8	0,1887	0,0001
	N_2	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:

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

where: x - certain content, mole/mole, %;

y - value of the chromatographer response for this component, V*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 and 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 4 individual measurements, is evaluated by following formula:

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

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:

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

where x_i - result of i measurement series;

$\bar{x}$ - arithmetic mean for five ($n=5$) measurement series.

Table 4 - A-type uncertainty evaluation results, mol/mol·10^{-2}

Component	Meas. 1	Meas. 2	Meas. 3	Meas. 4	Meas. 5	Mean	u_A
CO_2	13,490	13,5026	13,504	13,499	13,486	13,4963	0,0035
CO	3,0103	3,0089	3,0117	3,0104	3,0069	3,0096	0,0008
C_3H_8	0,19972	0,19999	0,19984	0,20020	0,20009	0,2000	0,00009

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:

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

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, mol/mol·10^{-2}

$\boldsymbol{u_B}$						
Measurement, №	1	2	3	4	5	Max
CO_2	0,0071	0,0023	0,0035	0,0092	0,0044	0,0092
CO	0,0029	0,0014	0,0025	0,0023	0,0022	0,0029
C_3H_8	0,00012	0,00009	0,00026	0,00028	0,00017	0,00028

Table 6 - Total standard uncertainty evaluation results

Component	$\boldsymbol{x}$, mol/mol·10^{-2}	$\boldsymbol{u_A}$, mol/mol·10^{-2}	$\boldsymbol{u_B}$, mol/mol·10^{-2}	$\boldsymbol{u(x)}$, mol/mol·10^{-2}
CO_2	13,4963	0,0035	0,0092	0,010
CO	3,0096	0,0008	0,0029	0,003
C_3H_8	0,2000	0,00009	0,00028	0,0003

Supplementary comparisons of national measurement standards COOMET.QM-S5 (COOMET 576/RU/12) for CO_2, CO, C_3H_8 in nitrogen (automotive gas mixtures)

MEASUREMENT REPORT

I. Results of the Study

Laboratory: Ukrmetrteststandard, Kiev, Ukraine

Cylinder number: M365623

NOMINAL COMPOSITION

- Carbon dioxide:	$14{,}0 \cdot 10^{-2}$ mol/mol
- Carbon monoxide:	$3{,}0 \cdot 10^{-2}$ mol/mol
- Propane:	$0{,}2 \cdot 10^{-2}$ mol/mol
- Nitrogen:	$82{,}8 \cdot 10^{-2}$ mol/mol

Measurement №1	Date	Results (моль/моль) $\bar{x}$	Stand. deviation $S(\bar{x})$, %	number of sub-measurements n
Carbon dioxide	28.03.14	$13{,}488 \cdot 10^{-2}$	0,114	10
Carbon monoxide	28.03.14	$3{,}007 \cdot 10^{-2}$	0,103	10
Propane	28.03.14	$20{,}070 \cdot 10^{-4}$	0,108	10

Measurement №2	Date	Results (моль/моль) $\bar{x}$	Stand. deviation $S(\bar{x})$, %	number of sub-measurements n
Carbon dioxide	02.04.14	$13{,}484 \cdot 10^{-2}$	0,126	10
Carbon monoxide	02.04.14	$3{,}005 \cdot 10^{-2}$	0,113	10
Propane	02.04.14	$20{,}033 \cdot 10^{-4}$	0,093	10

Measurement №3	Date	Results (моль/моль) $\bar{x}$	Stand. deviation $S(\bar{x})$, %	number of sub-measurements n
Carbon dioxide	04.04.14	$13{,}466 \cdot 10^{-2}$	0,146	10
Carbon monoxide	04.04.14	$2{,}999 \cdot 10^{-2}$	0,177	10
Propane	04.04.14	$20{,}037 \cdot 10^{-4}$	0,092	10

Results:

Gas mixture	Result (mol/mol)	Coverage factor	Expanded uncertainty (mol/mol)
Carbon dioxide	$13{,}479 \cdot 10^{-2}$	2	$0{,}020 \cdot 10^{-2}$
Carbon monoxide	$3{,}004 \cdot 10^{-2}$	2	$0{,}005 \cdot 10^{-2}$
Propane	$20{,}047 \cdot 10^{-4}$	2	$0{,}023 \cdot 10^{-4}$

II. Description of the Study

Instruments

Balance used for primary standard gas mixtures (PSGM) preparation by gravimetric method: Mettler Toledo XP26003L electronic balance (max. load 26,1 kg; min. 0,2 g; standard deviation 0,003 g). Measurement data were collected automatically.

Instruments for purity analysis of parent gases: Agilent 6890N gas chromatographs with helium ionization detector, flame ionization detector, thermal conductivity detector and mass spectrometric detector; GIAM-15M and Onix gas analyzers. Measurement data were collected automatically.

Gas chromatograph for analysing the mixture of CO_2, CO, C_3H_8 in nitrogen provided for comparison – Agilent 6890N:

- **for C_3H_8** - column 15FT 25# DC-200 HP19006-80105, carrier gas helium, flow rate 15 cm^3/min, detector FID, $t_{detector} = 300$ °C, $t_{oven} = 90$ °C;

- **for CO** - column 10FT HAYESEP Q 80/100 MESH HP19006-80110, carrier gas helium, flow rate 15 cm^3/min, detector TCD, $t_{detector}$ = 250 ºC, t_{oven} = 30 ºC;
- **for CO_2** - column 10FT HAYESEP Q 80/100 MESH HP19006-80110, carrier gas helium, flow rate 15 cm^3/min, detector TCD, $t_{detector}$ = 250 ºC, t_{oven} = 70 ºC.

Calibration Standards

PSGMs used in comparison were prepared by gravimetric method in aluminium cylinders according to ISO 6142.

Purity analysis of parent gases was carried out using Agilent 6890N gas chromatographs and gas analyzers specified above.

Parent gases mass was measured using Mettler Toledo XP26003L electronic balance by substitution method using weights traceable to PTB, Germany.

PSGMs were prepared in two stages using dilution method.

PSGMs gravimetric composition was verified by comparison with previously prepared PSGMs according to ISO 6143.

Uncertainty in PRGMs composition was evaluated according to ISO 6142 using GravCalc Ver. 2.3.1 software developed by NPL, UK.

Composition of the calibration standards – primary standard gas mixtures (PSGM) used for measurements by comparison method is given in the table below.

Component	PSGM-1 Cylinder №0116		PSGM-2 Cylinder №0107		PSGM-3 Cylinder №0093	
	x, %	*u*(x) , %	*x*, %	*u*(x) , %	*x*, %	*u*(x) , %
CO	2,7874	0,0015	2,9899	0,0015	3,1891	0,0015
CO_2	13,0187	0,0015	14,4456	0,0016	13,7016	0,0016
C_3H_8	0,19003	0,00008	0,20017	0,00008	0,21013	0,00008
N_2	balance		balance		balance	
Note: *x* – amount-of-substance fraction, *u(x)* – relative standard uncertainty, %						

Calibration and Measurement

Gas chromatograph was calibrated with the PSGMs. Linear analysis functions for each analyte were calculated from the calibration data using regression analysis. Calculations were made with B_LEAST software recommended in ISO 6143.

Measurement sequence:
PSGM -1 x 10;
PSGM -2 x 10;
COOMET gas mixture x 10;
PSGM -3 x 10.

Three independent measurements were performed.

Sample Handling

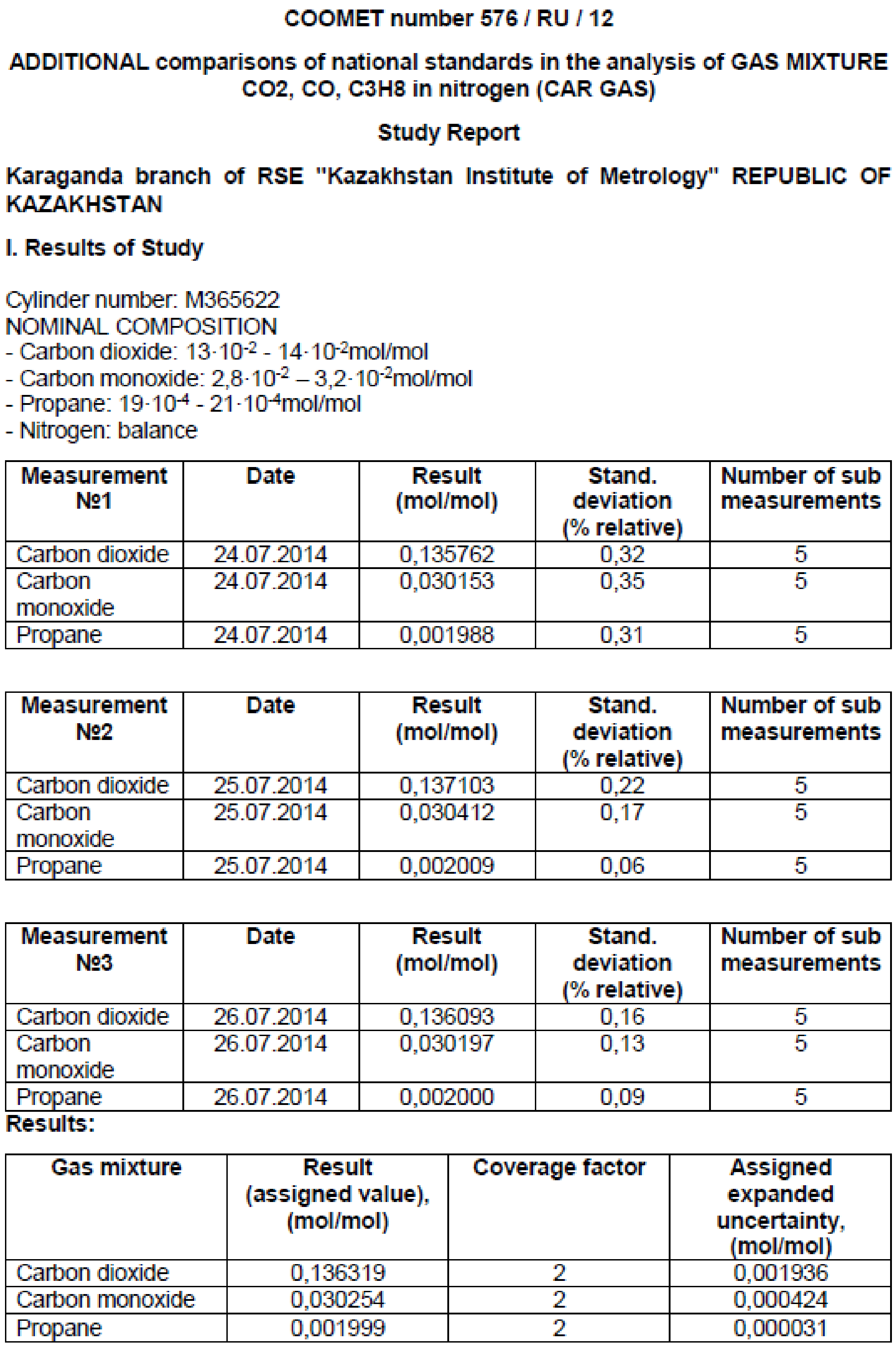
Gas mixtures were handled in accordance with ISO 16664.

The cylinders had been kept for 24 hrs at the room where the measurements were made. The room was thermostatted at $t = (20 \pm 2)$ ºC.

Uncertainty evaluation

Uncertainty evaluation was performed using B_LEAST software. The final result includes the uncertainties associated with the PSGMs composition and analysis function.

KazInMetr report



COOMET number 576 / RU / 12

ADDITIONAL comparisons of national standards in the analysis of GAS MIXTURE CO2, CO, C3H8 in nitrogen (CAR GAS)

Study Report

Karaganda branch of RSE "Kazakhstan Institute of Metrology" REPUBLIC OF KAZAKHSTAN

I. Results of Study

Cylinder number: M365622
NOMINAL COMPOSITION
- Carbon dioxide: $13 \cdot 10^{-2}$ - $14 \cdot 10^{-2}$mol/mol
- Carbon monoxide: $2{,}8 \cdot 10^{-2}$ – $3{,}2 \cdot 10^{-2}$mol/mol
- Propane: $19 \cdot 10^{-4}$ - $21 \cdot 10^{-4}$mol/mol
- Nitrogen: balance

Measurement №1	Date	Result (mol/mol)	Stand. deviation (% relative)	Number of sub measurements
Carbon dioxide	24.07.2014	0,135762	0,32	5
Carbon monoxide	24.07.2014	0,030153	0,35	5
Propane	24.07.2014	0,001988	0,31	5

Measurement №2	Date	Result (mol/mol)	Stand. deviation (% relative)	Number of sub measurements
Carbon dioxide	25.07.2014	0,137103	0,22	5
Carbon monoxide	25.07.2014	0,030412	0,17	5
Propane	25.07.2014	0,002009	0,06	5

Measurement №3	Date	Result (mol/mol)	Stand. deviation (% relative)	Number of sub measurements
Carbon dioxide	26.07.2014	0,136093	0,16	5
Carbon monoxide	26.07.2014	0,030197	0,13	5
Propane	26.07.2014	0,002000	0,09	5

Results:

Gas mixture	Result (assigned value), (mol/mol)	Coverage factor	Assigned expanded uncertainty, (mol/mol)
Carbon dioxide	0,136319	2	0,001936
Carbon monoxide	0,030254	2	0,000424
Propane	0,001999	2	0,000031

II. Description of Study

Instruments

Measurements were carried out using gas chromatograph "Crystal 5000" combined with thermal conductivity detector (CO, CO2) and flame-ionization detector (C3H8).
Computers and software "Chromatech Analytic" were used to control chromatograph and collect and process chromatographical data.

Calibration Standards

Calibration multicomponent gas mixture were prepared gravimetrically according to ISO 6142.
The calibration multicomponent gas mixture were prepared from pure gases directly on components CO, CO2 and from pre-mixtures which were prepared from pure gases on component C3H8.
The content of the impurities in all pure gases was determined by GC with flame-ionization and thermal-conductivity detectors.
Composition of calibration standards:

Component	X, mol/mol	Standard uncertainty u(x), %rel.
CO2	0,1129892	0,11
CO	0,0322053	0,24
C3H8	0,00149249	0,30
N2	balance	

Instrument Calibration

Measurement were carried out under repeatability conditions. Before measurement, an instrument calibration was made. Measurement contained 5 submeasurements.

Sample Handling

After preparation of mixture, the cylinder was maintained in laboratory room within 24 hours.
The recorded change of temperature in measurements is ± 2,0 degree.

Uncertainty

Uncertainty table: CO2

Uncertainty source X_i	Evaluation type	Standard uncertainty u(xi), %rel	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$, %rel
Calibration gas mixture	B	0,11	1	0,11
Analysis	A, B	0,70	1	0,70

Coverage factor: 2
Expanded uncertainty: 1,42

Uncertainty table: CO

Uncertainty source X_i	**Evaluation type**	**Standard uncertainty u(xi), %rel**	**Sensitivity coefficient c_i**	**Contribution to standard uncertainty $u_i(y)$, %rel**
Calibration gas mixture	B	0,24	1	0,24
Analysis	A, B	0,66	1	0,66

Coverage factor: 2
Expanded uncertainty: 1,40

Uncertainty table: C3H8

Uncertainty source X_i	**Evaluation type**	**Standard uncertainty u(xi), %rel**	**Sensitivity coefficient c_i**	**Contribution to standard uncertainty $u_i(y)$, %rel**
Calibration gas mixture	B	0,30	1	0,30
Analysis	A, B	0,71	1	0,71

Coverage factor: 2
Expanded uncertainty: 1,54