Key Comparison COOMET.QM-K3.2019 – Automotive exhaust gases

Final report

A.V. Kolobova[1], B.V. Ivakhnenko[1], V.V. Pankratov[1], O.V. Efremova[1], M.P.Klunin[2], A.M. Mironchik[2], V.V. Aleksandrov[3].

[1]D.I. Mendeleyev Institute for Metrology (VNIIM), Research Department for the State Standard in the Field of Physical-Chemical Measurements; address: 198005, Russia, St.-Petersburg, Moskovsky pr. 19.
[2]Belorussian State Institute for Metrology (BelGIM), Department of Physical-Chemical and Optical Measurement, Sector of Standards and Gas Mixtures; address: 220053, Belarus, Minsk, Starovilenskiy pr. 93.
[3]RSE **"**KazStandart", Karaganda branch, Kazakhstan; address: 100009, Kazakhstan, Karaganda, Angerskayast. 22/2.

Field

Amount of substance

Subject

Comparison of amount fractions of carbon monoxide, carbon dioxide, oxygen and propane in nitrogen (track A – core competences)

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1 Introduction

COOMET key comparison COOMET.QM–K3.2019 is designed as linking to the appropriate CCQM comparison - CCQM-K3.2019 [1], which was carried out in 2019-2022.
CCQM - K3.2019 was a key comparison in the gas analysis area assessing core competences (*track A key comparisons*) [2]. Such competences include, among others, the capabilities to prepare Primary Standard gas Mixtures (PSMs), perform the necessary purity analysis on the materials used in the gas mixture preparation, the verification of the composition of newly prepared PSMs against existing ones, and the capability of calibrating a gas mixture [3].
VNIIM showed a consistent result in CCQM-K3.2019 comparison for most part of the components (carbon monoxide, carbon dioxide and propane). Therefore, the results of COOMET.QM-K3.2019 can be linked to CCQM-K3.2019 through the results of VNIIM and can be used to support CMCs of COOMET member countries NMIs.

2 Design and organisation of the comparison

2.1 Participants

Table 1 lists the participants in this key comparison.

Table 1: List of participants

Acronym	Country	Institute
VNIIM	RU	D.I. Mendeleyev Institute for Metrology
BelGIM	BY	Belorussian State Institute for Metrology
KazStandart	KZ	Kazakhstan Institute of Metrology

2.2 Measurement standards

A set of mixtures was prepared gravimetrically by VNIIM. Among them - three mixtures were prepared earlier for the CCQM-K3.2019 key comparison, another two - for the present comparison. The set of standards was verified before shipment to the participants and after their return.
Pure gases used for preparation of measurement standards were: carbon dioxide grade 5.0, nitrogen grade 6.0, oxygen grade 6.0, carbon monoxide grade 4.0 and propane grade 4.5.
Carbon dioxide, carbon monoxide and oxygen were transferred as pure gases. Propane was transferred from a premixture (1 cmol/mol) obtained by gravimetric dilution step. The mixtures were verified against a set of VNIIM PSMs. All used pure gases were subjected to a purity analysis in accordance with ISO 19229 [4] prior to use for preparation of the gas mixtures.
The filling pressure in the cylinders was approximately 10 MPa. Aluminium cylinders of 5 dm^3 water volume from Luxfer UK were used. The mixture composition and its associated uncertainty were calculated in accordance with ISO 6142-1 [3]. The amount fractions as calculated from gravimetry and purity verification of the parent gases were used as key comparison reference values (KCRVs). Each individual cylinder had its own reference values and associated expanded uncertainties. The expanded uncertainties included a contribution from the verification of the gas mixtures.

The nominal ranges of amount fractions of the targeted components in the mixtures are given in Table 2.

Table 2 Nominal composition of mixtures, given in amount fractions

Component	Amount fraction x
Carbon monoxide	(0.5 – 2) cmol mol^{-1}
Carbon dioxide	(2 – 5) cmol mol^{-1}
Oxygen	(1 – 4) cmol mol^{-1}
Propane	(100 – 300) µmol mol^{-1}
Nitrogen	Balance

2.3 Measurement protocol

The measurement protocol requested each laboratory to perform at least three measurements, with independent calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions. The protocol informed the participants about the nominal concentration ranges. The laboratories were also requested to submit a summary of their uncertainty evaluation used for estimating the uncertainty of their result.

2.4 Schedule

The schedule of this key comparison was as follows (table 3).

Table 3: Key comparison schedule

Dates	**Action**
November 2022	Agreement of protocol
January 2023	Registration of participants
July 2023 - September 2023	Preparation of mixtures and verification of their composition
October – November 2023	Dispatch of mixtures
November 2023 - March 2024	Measurements at NMIs
March 2024	Reports and cylinders arrived back at VNIIM
April 2024 – June 2024	Re-verification of the mixtures
October 2024	Draft A report available
June 2025	Draft B report available

2.5 Measurement equation

The key comparison reference values are based on the weighing data from gravimetry, and the purity verification of the parent gases. All mixtures underwent first verification before shipping them to the participants. After returning of the cylinders, they went through second verification 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 ($\Delta x_{i,nr}$).

Previous experience has indicated that there are no stability issues and no correction is needed for the partial recovery of a component. These terms are zero, and so are their associated standard uncertainties.

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

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

The equation for calculating the associated standard uncertainty reads as

$$u^2_{i,prep} = u^2\left(x_{i,grav}\right) + u^2\left(\Delta x_{i,purity}\right). \quad (2)$$

The validity of the mixtures has been demonstrated by verifying the composition as calculated from the preparation data with that obtained from (analytical chemical) measurement. In order to have a positive demonstration of the preparation data (including uncertainty), the following condition should be met

$$\left|x_{i,prep} - x_{i,ver}\right| \leq 2\sqrt{u^2_{i,prep} + u^2_{i,ver}}. \quad (3)$$

The factor 2 is a coverage factor (normal distribution, 95% level of confidence). The assumption must be made that both preparation and verification are unbiased. Such bias has never been observed. The uncertainty associated with the verification highly depends on the experimental design followed.
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 procedure and results of verification are described in more details in the next section.
The expression for the standard uncertainty of the key comparison reference value is

$$u^2_{i,ref} = u^2_{i,prep} + u^2_{i,ver}. \quad (4)$$

The values for $u_{i,prep}, u_{i,ver}$ and $u_{i,ref}$ are given in the tables containing the results of this key comparison. Here, the verification uncertainty used is the pooled uncertainty, which included measurements prior to shipping to participants and after return.

2.6 Verification – procedure and results

Verification measurements were carried out by GC-TCD for all the mixture components. The instrument used is chromatograph «Chromatec-Crystal 5000.2» (“Chromatec”, Russia). Two measuring channels were involved with TCD 1 and TCD 2. The operating mode is described in the table 4.

Table 4: Operating mode

Component	Sample loop, (cm^3)	Detector	Column/ temperature	Carrier gas /flow rate
CO, O_2	0.5, Heated valve, t=100 °C	TCD1 t=180 °C	CaA 60-80 mesh, 3 m*3 mm /100°C	He /flow rate - 15 ml/min
CO_2, C_3H_8	0.5, Heated valve, t=100 °C	TCD2 t=180 °C	HayeSep R 80-100 mesh, 3 m *3 mm/100°C	He /flow rate - 15 ml/min

Data collection: Software support “Chromatec”

The measurements for each travelling standard were repeated 3-7 times in reproducibility conditions both before shipment and after return. The measurements were performed against VNIIM PSM in the order: PSM – Travelling standard – PSM.
The link of COOMET.QM-K3.2019 and CCQM-K3.2019 results was provided through VNIIM calibration gas mixtures which were used in both comparisons (cylinders M365633 and D718476).
The gravimetric ($x_{i,prep}$) and verification values of analyte amount fraction before shipment to participants ($x_{i,ver1}$) and after return ($x_{i,ver2}$) and the appropriate uncertainties (at k=2) for the transfer standards ($u_{i,prep}$, $u_{i,ver1}$, $u_{i,ver2}$) are shown on the figures (1-4) and in the tables (5-8).
$u_{i,ver1,2}$ were calculated as standard deviation of the mean difference $|x_{i,prep} - x_{i,ver}|$ in reproducibility conditions, taking into account the number of measurements before shipment and after return.

Table 5: Preparation and verification data for carbon dioxide

Cylinder №	$x_{i,prep}$, mmol/mol	$2u_{i,prep}$, mmol/mol	$x_{i,ver1}$, mmol/mol	$2u_{i,ver1}$, mmol/mol	$x_{i,ver2}$, mmol/mol	$2u_{i,ver2}$, mmol/mol
M365633	19,966	0,0030	19,963	0,026	19,940	0,026
D997671	20,038	0,0045	20,052	0,019	20,029	0,019
D997652	20,178	0,0045	20,192	0,021	20,178	0,0017

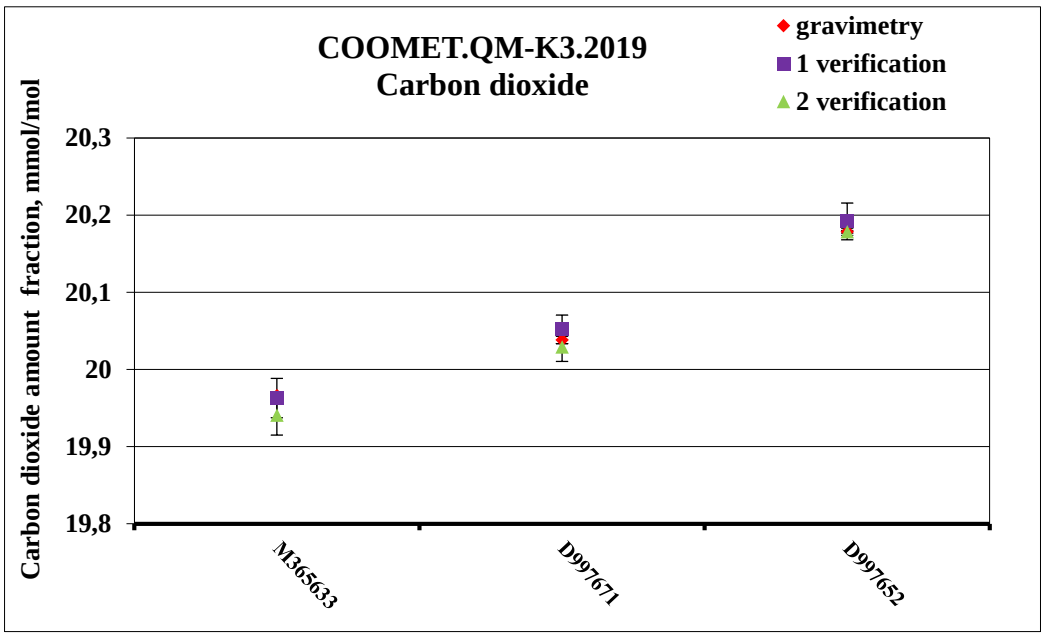

Figure 1: Preparation and verification data of the transfer standards for carbon dioxide

Table 6: Preparation and verification data for carbon monoxide

Cylinder №	*xi,prep* *mmol/mol*	*2ui,prep,* *mmol/mol*	*xi,ver1,* *mmol/mol*	*2ui,ver1,* *mmol/mol*	*xi,ver2,* *mmol/mol*	*2ui,ver2,* *mmol/mol*
M365633	9,986	0,005	9,990	0,011	9,980	0,009
D997671	10,136	0,008	10,136	0,009	10,139	0,011
D997652	10,122	0,006	10,138	0,017	10,126	0,017

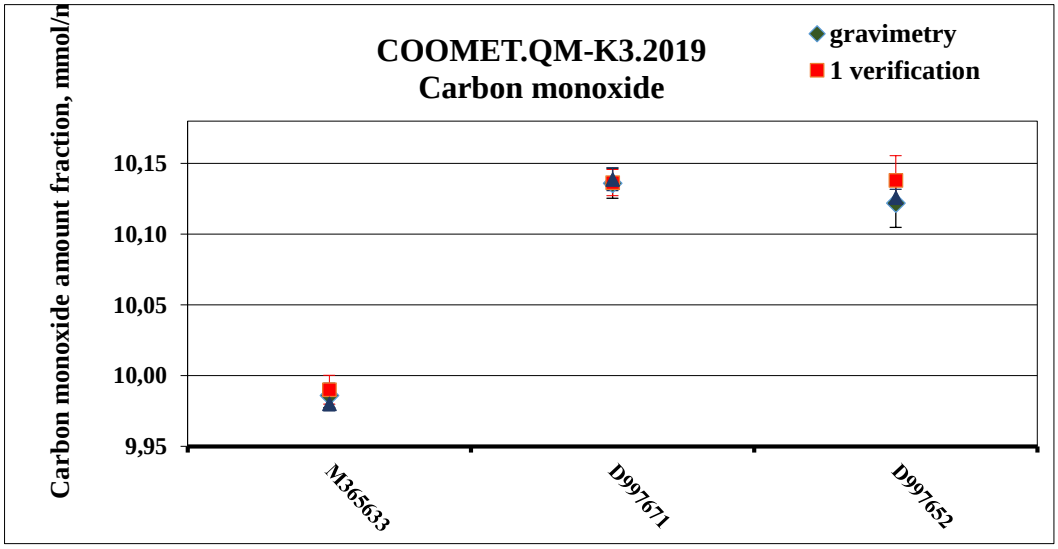

Figure 2: Preparation and verification data of the transfer standards for carbon monoxide

Table 7: Preparation and verification data for oxygen

Cylinder №	$x_{i,prep,}$ *mmol/mol*	$2u_{i,prep,}$ *mmol/mol*	$x_{i,ver1,}$ *mmol/mol*	$2u_{i,ver1,}$ *mmol/mol*	$x_{i,ver2,}$ *mmol/mol*	$2u_{i,ver2,}$ *mmol/mol*
M365633	30,068	0,006	30,074	0,072	30,087	0,061
D997671	30,024	0,006	30,039	0,027	30,022	0,032
D997652	30,003	0,012	30,026	0,04	29,979	0,052

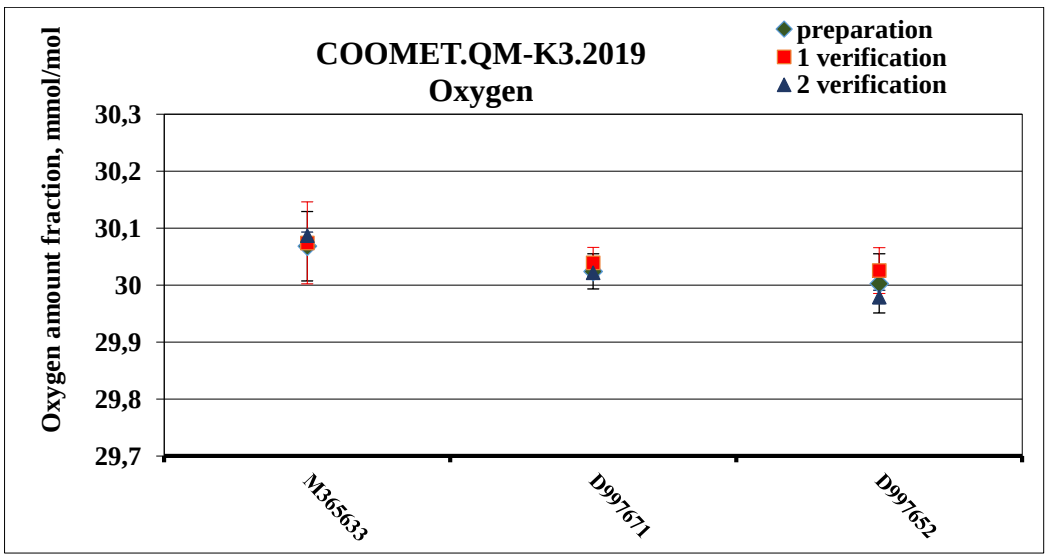

Figure 3: Preparation and verification data of the transfer standards for oxygen

Table 8: Preparation and verification data for propane

Cylinder №	*xi,prep µmol/mol*	*2ui,prep, µmol/mol*	*xi,ver1, µmol/mol*	*2ui,ver1, µmol/mol*	*xi,ver2, µmol/mol*	*2ui,ver2, µmol/mol*
M365633	199,110	0,010	198,57	0,86	198,47	0,79
D997671	201,350	0,100	200,78	0,64	200,99	0,74
D997652	199,800	0,100	199,35	0,55	199,12	0,71

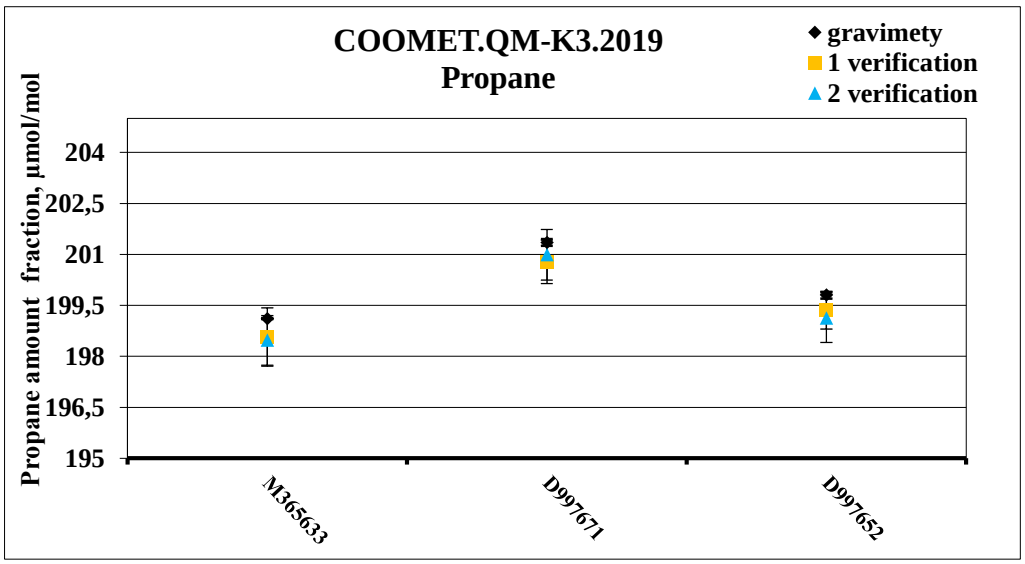

Figure 4: Preparation and verification data of the transfer standards for propane

The preparation and verification data agree quite well – differences between preparation and verification values of amount of substance fraction satisfy condition (3).

2.7 Measurement methods

The measurement methods used by the participants are described in each participant report. A summary of the calibration methods, dates of measurement and reporting, and the way, in which metrological traceability is established, is given in table 9.

Table 9: Summary of calibration methods and metrological traceability

Laboratory code	**Measurements**	**Calibration**	**Traceability**	**Matrix standards**	**Measurement technique**
BelGIM	25.04-07.05.2024	Calibration curve, 3 points	Own standards (3 mixtures)	Nitrogen	GC-TCD for O_2, CO, CO_2 GC-FID for C_3H_8
KazStandart	14-28.05.2024	Bracketing	Own standards (2 mixtures)	Nitrogen	GC-TCD for O_2, CO, CO_2 GC-FID for C_3H_8
VNIIM	12.05 -25.06.2020	One-point calibration	Own standards (3 mixtures)	Nitrogen	GC-TCD

2.8 Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as

$$\Delta x_i = d_i = x_{i,lab} - x_{i,KCRV}, \qquad (5)$$

and the uncertainty of the difference d_i at 95% level of confidence. Here $x_{i,KCRV}$ denotes the key comparison reference value ($x_{i,ref}$) , and $x_{i,lab}$ the result of laboratory i.[1] Appreciating the special conditions in gas analysis, it can be expressed as

$$\Delta x_i = d_i = x_{i,lab} - x_{i,ref}\,, \tag{6}$$

In this particular comparison $x_{i,ref}$ for each component is corrected for VNIIM's deviation from the KCRV in CCQM-K3.2019 in accordance with (7)

$$x_{i,ref} = x_{i,prep} + d_{VNIIM,CCQM\text{-}K3.2019} \tag{7}$$

The standard uncertainty of d_i can be expressed as

$$u^2(d_i) = u^2_{i,lab} + u^2_{i,prep} + u^2_{i,ver}\,, \tag{8}$$

assuming that the aggregated error terms are uncorrelated. As discussed, the combined standard uncertainty of the reference value comprises that from preparation and that from verification for the mixture involved.

Note – The uncertainty of $d_{VNIIM,CCQM\text{-}K3.2019}$ for carbon monoxide, carbon dioxide and propane is covered by verification uncertainty, for oxygen it is taken into account in the uncertainty of the reference value, see the formula (9).

3 Results

In this section, the results of the key comparison are summarised. In the tables, the following data is presented:

$x_{i,prep}$	amount fraction, from preparation (cmol/mol),
$u_{i,prep}$	standard uncertainty of x_{prep} (cmol/mol),
$u_{i,ver}$	standard uncertainty from verification (cmol/mol),
$u_{i,ref}$	standard uncertainty of reference value (cmol/mol),
$x_{i,lab}$	result of laboratory (cmol/mol),
$U_{i,lab}$	stated expanded uncertainty of laboratory, at 95 % level of confidence (cmol/mol),
$k_{i,lab}$	stated coverage factor,
d_i	difference between laboratory result and reference value (cmol/mol),
k	assigned coverage factor for degree of equivalence,
$U(d_i)$	Expanded uncertainty of difference d_i at 95 % level of confidence[2] (cmol/mol).

Tables 10-13 show the results for the components amount fraction. The degrees of equivalence are plotted in Figures 5-8.

For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor $k = 2$ was used. For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty (stated at a confidence level of 95%) from the laboratory was divided by the reported coverage factor.

[1] Each laboratory receives one cylinder, so that the same index can be used for both a laboratory and a cylinder.
[2] As defined in MRA [6] a degree of equivalence is given by d_i *and* $U(d_i)$.

Table 10: Results for the carbon dioxide amount fraction

Laboratory	Cylinder	$x_{i,prep}$	$x_{i,ref}$	$u_{i,prep}$	$u_{i,ver}$	$u_{i,ref}$	$x_{i,lab}$	$U_{i,lab}$	$k_{i,lab}$	d_i	k	$U(d_i)$
BelGIM	D997652	2.01784	2.01844	0.0002	0.00064	0.00067	2.0219	0.0027	2	0.0035	2	0.0030
KazStandart	D997671	2.00383	2.00443	0.0002	0.00061	0.00064	2.004	0.018	2	-0.0004	2	0.018
VNIIM*	8449 E	2.0025	-	0.0004	0.0006	0.0008	2.0019	0.002	2	-0.0006	2	0.0025

*VNIIM result in CCQM-K3.2019

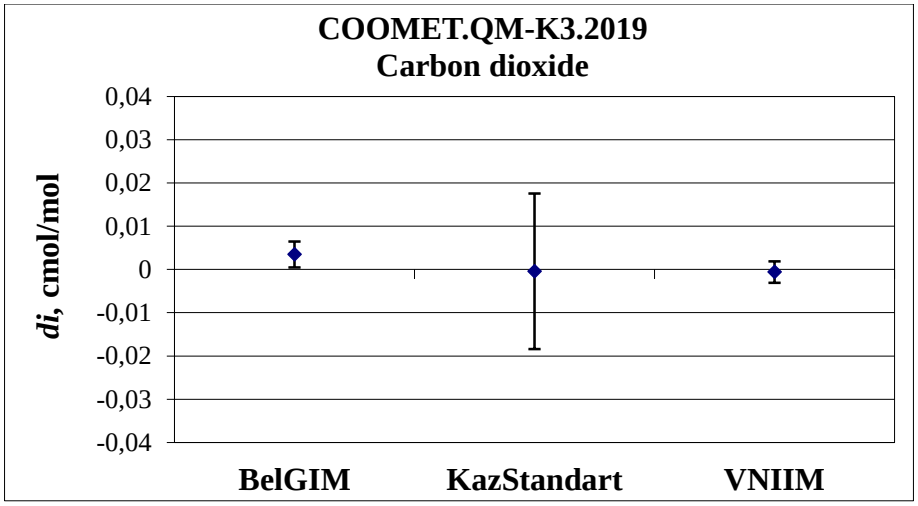

Figure 5 - The degrees of equivalence for carbon dioxide

The result for carbon dioxide of BelGIM is not consistent with the key comparison reference value.

Table 11: Results for the carbon monoxide amount fraction

Laboratory	Cylinder	$x_{i,prep}$	$x_{i,ref}$	$u_{i,prep}$	$u_{i,ver}$	$u_{i,ref}$	$x_{i,lab}$	$U_{i,lab}$	$k_{i,lab}$	d_i	k	$U(d_i)$
BelGIM	D997652	1.0122	1.0129	0.0003	0.00035	0.0005	1.0132	0.006	2	0.0003	2	0.006
KazStandart	D997671	1.0136	1.0143	0.0004	0.0006	0.0007	1.012	0.010	2	-0.0023	2	0.010
VNIIM*	8449 E	1.0007	-	0.0002	0.0004	0.00045	1.0000	0.0016	2	-0.0007	2	0.0018

*VNIIM result in CCQM-K3.2019

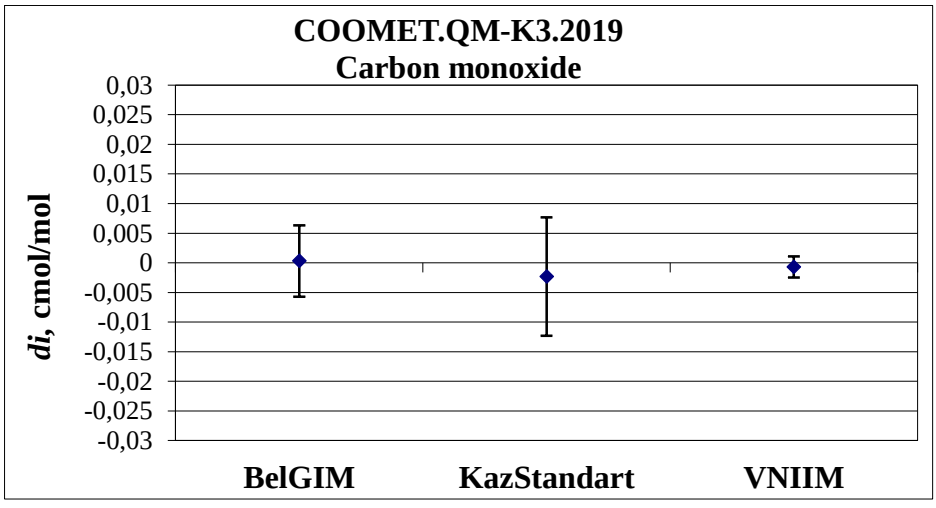

Figure 6 - The degrees of equivalence for carbon monoxide

All the results for carbon monoxide are consistent with the key comparison reference value.

Table 12: Results for the oxygen amount fraction

Laboratory	Cylinder	$x_{i,prep}$	$x_{i,ref}$	$u_{i,prep}$	$u_{i,ver}$	$u_{i,ref}$	$^{*}u'_{ref}$	x_{lab}	U_{lab}	k_{lab}	d_i	k	$U(d_i)$
BelGIM	D997652	3.0003	3.0048	0.0003	0.0016	0.0016	0.0048	3.0000	0.0034	2	-0.0048	2	0.010
KazStandart	D997671	3.0024	3.0069	0.0003	0.0011	0.0011	0.0046	2.902	0.026	2	-0.105	2	0.028
VNIIM*	8449 E	3.0116	-	0.0006	0.0008	0.0010	-	3.0071	0.0031	2	-0.0045	2	0.0037

*VNIIM result in CCQM-K3.2019

$^{*}u'_{ref}$ - is a corrected standard uncertainty of the reference value for results of the oxygen amount fraction.

u'_{ref} was calculated in accordance with equation (8)

$$u'_{ref} = \sqrt{u^2_{ref} + d^2_{i,CCQM\text{-}K3.2019}} \quad (9)$$

The correction takes into account difference between VNIIM result for O_2 amount fraction in CCQM-K3.2019 and the appropriate reference value (VNIIM d_i in CCQM-K3.2019, see Table 12).

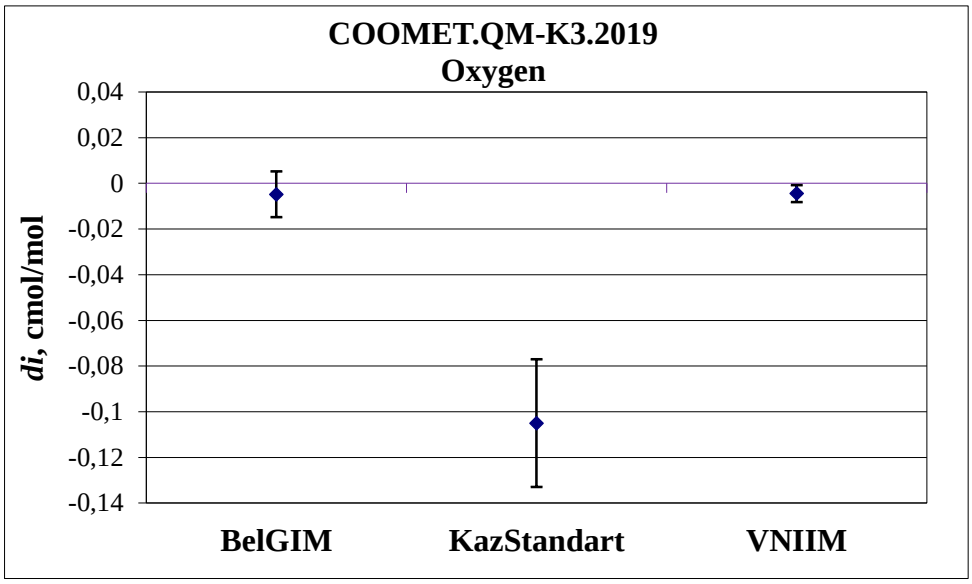

Figure 7 - The degrees of equivalence for oxygen

The result of Kazstandart is inconsistent with the key comparison reference value. The VNIIM result in CCQM-K3.2019 also did not cross the zero line with the uncertainty bars.

Table 13: Results for the propane amount fraction

Laboratory	Cylinder	$x_{i,prep}$	$x_{i,ref}$	$u_{i,prep}$	$u_{i,ver}$	$u_{i,ref}$	$x_{i,lab}$	$U_{i,lab}$	$k_{i,lab}$	d_i	k	$U(d_i)$
BelGIM	D997652	0.019980	0.019971	0.000005	0.000024	0.000025	0.019940	0.000054	2	-0.000031	2	0.000074
KazStandart	D997671	0.020135	0.020126	0.000005	0.000024	0.000025	0.02022	0.00028	2	0.000094	2	0.00028
VNIIM*	8449 E	0.019868	-	0.000005	0.000007	0.000009	0.019877	0.000038	2	0.000009	2	0.000042

*VNIIM result in CCQM-K3.2019

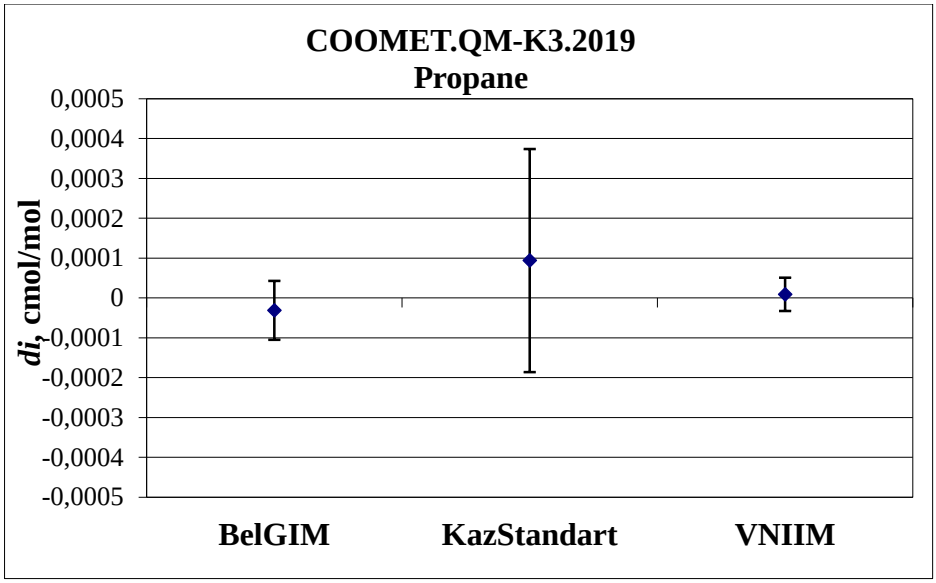

Figure 8 - The degrees of equivalence for propane

All the results for propane are consistent with the key comparison reference value.

4 Supported CMC claims

The results of this key comparison can be used to support CMC claims in two different ways:

a) For core capabilities, as track A key comparison;

b) For the components concerned (and a combination thereof) in nitrogen, as track C key comparison.

If the results are used as track A key comparison, the support is the pooled uncertainty of the four amount fractions, i.e., the mean of the four variances.

The support of CMC claims is described in more detail in the "GAWG strategy for comparisons and CMC claims" [2].

5 Discussion and conclusions

For carbon dioxide all the results are within 0.2 % relative of the key comparison reference value. The result of BelGIM is not consistent with the KCRV.
For carbon monoxide and propane all the results agree with the KCRV within 0.2 % relative (CO) and 0.4 % relative (C_3H_8).
For oxygen the result of KazStandart deviated significantly from the KCRV. The result of BelGIM agrees well with the KCRV.
BelGIM improved its performance for carbon monoxide and propane, KazStandart - for carbon dioxide, carbon monoxide and propane compared to previous COOMET comparison on automotive gas mixtures COOMET.QM-S5.

References

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Coordinators

VNIIM, Research department for the State Standards
in the field of physical-chemical measurements
A.V.Kolobova
O,V. Efremova
19 Moskovskiy pr., Saint-Petersburg, Russia, 190005
Phone: +7 812 3151145
E-mails: fhi@b10.vniim.ru; eov@b10.vniim.ru

Completion date: February 2025

Annex A

Reports submitted by participating laboratories

COOMET 864/RU/22
Key comparison "automotive exhaust 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: D997652,5 dm^3
NOMINAL COMPOSITION

- Oxygen: $1 \cdot 10^{-2}$ - $4 \cdot 10^{-2}$ mol/mol
- Carbon dioxide: $2 \cdot 10^{-2}$ - $5 \cdot 10^{-2}$ mol/mol
- Carbon oxide: $0.5 \cdot 10^{-2}$ - $2 \cdot 10^{-2}$ mol/mol
- Propane: $0.01 \cdot 10^{-2}$ – $0.03 \cdot 10^{-2}$ mol/mol
- Nitrogen: balance

Measurement No 1	Date	Result, x, mol/mol·10^{-2}	Standard deviation, % rel.	No of observations n
Oxygen	25.04.2024	3.003332	0.063	5
Carbon dioxide		2.023450	0.110	
Carbon oxide		1.012530	0.247	
Propane		0.019917	0.137	

Measurement No 2	Date	Result, x, mol/mol·10^{-2}	Standard deviation, % rel.	No of observations n
Oxygen	29.04.2024	3.000738	0.080	5
Carbon dioxide		2.023759	0.080	
Carbon oxide		1.013943	0.448	
Propane		0.019972	0.162	

Measurement No 3	Date	Result, x, mol/mol·10^{-2}	Standard deviation, % rel.	No of observations n
Oxygen	30.04.2024	2.994527	0.059	5
Carbon dioxide		2.020534	0.055	
Carbon oxide		1.014724	0.442	
Propane		0.019941	0.103	

Measurement No 4	Date	Result, x, mol/mol·10^{-2}	Standard deviation, % rel.	No of observations n
Oxygen	03.05.2024	2.998166	0.051	5
Carbon dioxide		2.021600	0.071	
Carbon oxide		1.012416	0.262	
Propane		0.019947	0.082	

Measurement No 5	Date	Result, x, mol/mol·10^{-2}	Standard deviation, % rel.	No of observations n
Oxygen	06.05.2024	3.000102	0.094	5
Carbon dioxide		2.019189	0.055	
Carbon oxide		1.013045	0.269	
Propane		0.019925	0.115	

Measurement No 6	Date	Result, x, mol/mol·10^{-2}	Standard deviation, % rel.	No of observations n
Oxygen	07.05.2024	3.002915	0.079	5
Carbon dioxide		2.022584	0.045	
Carbon oxide		1.012729	0.420	
Propane		0.019938	0.039	

Final results:

Gas mixture	Result, x, mol/mol·10^{-2}	Coverage factor	Expanded uncertainty, mol/mol·10^{-2}
Oxygen	3.0000	2	0.0034
Carbon dioxide	2.0219	2	0.0027
Carbon oxide	1.0132	2	0.0060
Propane	0.019940	2	0.000054

II. Description of study

Equipment

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

Computers and software "Chromatech Analytic", version 3.0 were used to control chromatograph and collect and process chromatographical data.

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", argon 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 6142-1-2018.

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 CCE 40K3	Sartorius, Germany	Maximum load: 41 kg; Scale division: 2 mg; Standard deviation: 6 mg for a steel cylinder with a volume of 4 dm^3; Operating temperature range: +10÷30°C; Maximum temperature change within 1 h: ±0,5 °C.

Mass-comparator type KA10-3/P	Mettler-Toledo, Switzerland	Maximum load: 15 kg; Scale division: 1 mg; Standard deviation: 6 mg for a steel cylinder with a volume of 5 dm^3; Operating temperature range: +10÷30°C; Maximum temperature change within 1 h: ±0,5 °C.
Gas mixer	BelGIM	Measurement range: 0 ÷ 20,0 MPa Accuracy class for manometers – 0,05; Device for continuous measurement and recording of dry air and nitrogen pressures in vacuum systems Meradat-VIT19IT2 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: C_3H_8-N_2		
Component	Content, ***x***, mol/mol ·10^{-2}	Standard uncertainty, ***u(x),*** mol/mol ·10^{-2}
H_2	4.95e-007	2.86e-007
N_2	99.0008	0.0013022
O_2	3.22e-005	1.86e-005
CO	4.95e-007	2.86e-007
CO_2	1.24e-006	7.14e-007
CH_4	1.49e-006	8.57e-007
C_3H_8	**0.99909**	**0.001302**
H_2O	2.48e-005	1.43e-005

Initial gas: CO		
Component	Content, ***x***, mol/mol ·10^{-2}	Standard uncertainty, ***u(x),*** mol/mol ·10^{-2}
H_2	0.00225	0.001299
N_2	0.0013	0.0003
O_2	0.0001	5.7735e-005

CO	**99.996**	**0.0013416**
CH_4	5e-005	2.8868e-005
Ar	5e-005	2.8868e-005
H_2O	0.00025	0.00014434

Initial gas: CO_2		
Component	Content, ***x***, mol/mol $\cdot 10^{-2}$	Standard uncertainty, ***u(x),*** mol/mol $\cdot 10^{-2}$
He	1e-023	1e-026
N_2	0.00015	8.6603e-005
O_2	0.0001	5.7735e-005
CO	2.5e-005	1.4434e-005
CO_2	**99.9974**	**0.00022776**
CH_4	5e-005	2.8868e-005
C_3H_8	1e-023	1e-026
Ar	1e-023	1e-026
H_2O	0.0023	0.0002

Initial gas: O_2		
Component	Content, ***x***, mol/mol $\cdot 10^{-2}$	Standard uncertainty, ***u(x),*** mol/mol $\cdot 10^{-2}$
H_2	1e-023	1e-026
He	1e-023	1e-026
N_2	2.5e-005	1.4434e-005
O_2	**99.9999**	**3.5707e-005**
CO	5e-006	2.8868e-006
CO_2	5e-006	2.8868e-006
CH_4	5e-006	2.8868e-006
C_3H_8	1e-023	1e-026
Ar	5e-005	2.8868e-005
H_2O	2.5e-005	1.4434e-005

Initial gas: N_2		
Component	Content, ***x***, mol/mol $\cdot 10^{-2}$	Standard uncertainty, ***u(x),*** mol/mol $\cdot 10^{-2}$
H_2	5e-007	2.8868e-007
He	1e-023	1e-026
N_2	**99.9999**	**6.0719e-005**
O_2	3.25e-005	1.8764e-005
CO	5e-007	2.8868e-007
CO_2	1.25e-006	7.2169e-007
CH_4	1.5e-006	8.6603e-007
C_3H_8	1e-023	1e-026
Ar	1e-023	1e-026
H_2O	0.0001	5.7735e-005

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·10^{-2}	Standard uncertainty, $u(x)$, mol/mol·10^{-2}
EEX107, 4 dm^3, aluminium, 07.02.2024.	O_2	2.770493	0.001036
	CO_2	1.842405	0.000759
	CO	0.918211	0.001203
	C_3H_8	0.018293	0.000026
	N_2	balance	
EEX051, 4 dm^3, aluminium, 07.02.2024.	O_2	3.085493	0.001034
	CO_2	2.039889	0.000758
	CO	1.018326	0.001200
	C_3H_8	0.020332	0.000029
	N_2	balance	
EEX070, 4 dm^3, aluminium, 09.02.2024.	O_2	3.334436	0.001537
	CO_2	2.234741	0.001130
	CO	1.108166	0.001793
	C_3H_8	0.022210	0.000033
	N_2	balance	

2. Number of sub-measurements for each calibration sample – 5

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

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

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:

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

(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 $n=6$ measurement series is evaluated by the formula:

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

(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	O_2	CO_2	CO	C_3H_8
1	3.003332	2.023450	1.012530	0.019917
2	3.000738	2.023759	1.013943	0.019972
3	2.994527	2.020534	1.014724	0.019941
4	2.998166	2.021600	1.012416	0.019947
5	3.000102	2.019189	1.013045	0.019925
6	3.002915	2.022584	1.012729	0.019938
Mean	2.999963	2.021853	1.013231	0.019940
u_A	5.37819E-05	0.000721532	0.000373194	7.81452E-06

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:

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

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}

	u_B, mol/mol·10^{-2}			
Component	O_2	CO_2	CO	C_3H_8
1	0.001709	0.001144	0.001670	0.000026
2	0.001459	0.000933	0.002998	0.000024
3	0.001414	0.000756	0.002285	0.000021
4	0.001391	0.000832	0.001751	0.000020
5	0.001646	0.000780	0.001642	0.000020
6	0.001590	0.000735	0.002128	0.000018
Max	0.001709	0.001144	0.002998	0.000026

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}
O_2	3.0000	0.000054	0.0017	0.0034
CO_2	2.0219	0.00072	0.0011	0.0027
CO	1.0132	0.00037	0.0030	0.0060
C_3H_8	0.019940	0.000008	0.000026	0.000054

Metrology engineer Klunin
M.P.

Head of the Production and Research
Department of Physicochemical
and Optical Measurements Mironchik
A.M.

KEY COMPARISON OF NATIONAL STANDARDS IN THE FIELD OF ANALYSIS OF A GAS MIXTURE OF CO_2, CO, O_2, C_3H_8 IN NITROGEN (AUTOMOBILE GASES)

MEASUREMENT RESULTS REPORT
KARAGANDA BRANCH OF RSE "KAZSTANDARD", REPUBLIC OF KAZAKHSTAN

I. The results of the experimental research

Cylinder number: D997671

Table 1. Measurement results №1

Measurement №1	Result, amount fraction, cmol/mol	Standard deviation, %, relative	Number of replicates, n
Carbon dioxide	2,006	0,19	5
Oxygen	2,896	0,30	5
Propane	0,02029	0,28	5
Carbon monoxide	1,011	0,34	5

Table 2. Measurement results №2

Measurement №2	Result, amount fraction, cmol/mol	Standard deviation, %, relative	Number of replicates, n
Carbon dioxide	2,003	0,17	5
Oxygen	2,905	0,23	5
Propane	0,02028	0,26	5
Carbon monoxide	1,012	0,32	5

Table 3. Measurement results №3

Measurement №3	Result, amount fraction, cmol/mol	Standard deviation, %, relative	Number of replicates, n
Carbon dioxide	2,001	0,58	5
Oxygen	2,899	0,46	5
Propane	0,02009	0,30	5
Carbon monoxide	1,010	0,46	5

Table 4. Measurement results №4

Measurement №4	Result, amount fraction, cmol/mol	Standard deviation, %, relative	Number of replicates, n
Carbon dioxide	2,006	0,21	5
Oxygen	2,902	0,08	5

Propane	0,02023	0,22	5
Carbon monoxide	1,012	0,20	5

Table 5. Measurement results №5

Measurement №4	Result, amount fraction, cmol/mol	Standard deviation, %, relative.	Number of replicates, n
Carbon dioxide	2,005	0,31	5
Oxygen	2,908	0,19	5
Propane	0,02019	0,17	5
Carbon monoxide	1,014	0,31	5

Table 6. Results

Gas mixture	**Result, amount fraction, cmol/mol**	**Coverage factor**	**Expanded uncertainty, molar fraction, %**
Carbon dioxide	2,004	2	0,018
Oxygen	2,902	2	0,026
Propane	0,02022	2	0,00028
Carbon monoxide	1,012	2	0,010

II. Calibration standards

The primary reference gas mixtures were prepared gravimetrically from pure gases in accordance with ISO 6142.

Preparation from pure substances was carried out in 2 stages. On the first stage 2 C_3H_8/N_2 gas mixtures were prepared on the concentration level of 2%. On the second stage calibration gas mixtures with amount of substance fractions very close to the comparison mixture were prepared.

The exact values of components amount fraction in gravimetric calibration gas mixtures and their standard uncertainties are shown in the table 7.

Table 7

Cylinder number	**Component**	**Amount fraction %**	**Relative standard uncertainty of preparation (weighing, purity) %, u_{cal}, %**
9251050 (k3.4)	Carbon monoxide	0,7227	0,25
	Carbon dioxide	2,1182	0,10
	Oxygen	3,1297	0,10
	Propane	0,021187	0,45
	Nitrogen	balance	
9213162 (k3.5)	Carbon monoxide	0,6888	0,25
	Carbon dioxide	1,9770	0,10
	Oxygen	2,7990	0,10

	Propane	0,020080	0,45
	Nitrogen	balance	

Calibration gas mixtures were prepared in aluminum cylinders with a capacity of 4 dm^3.

Characteristics of pure substances used for preparation of the calibration standards are shown in the tables 8 – 12.

Table 8. Purity table for carbon monoxide

Component	Amount fraction, (mol/mol)	Standard uncertainty, (mol/mol)
CO	0,99920	
N_2	0,00050	0,000150
H_2	0,00010	0,000030
O_2	0,00015	0,000045
H_2O	0,00005	0,000015

Table 9. Purity table for carbon dioxide

Component	Amount fraction, (mol/mol)	Standard uncertainty, (mol/mol)
CO_2	0,9999680	
N_2	0,0000242	0,0000073
O_2	0,0000060	0,0000030
H_2	0,0000005	0,00000025
CH_4	0,0000003	0,00000015
CO	0,0000010	0,00000050

Table 10. Purity table for oxygen

Component	Amount fraction, (mol/mol)	Standard uncertainty, (mol/mol)
O_2	0,999487	
H_2	0,000101	0,00003
Ar	0,000380	0,00019
CH_4	0,000001	0,0000005
CO	0,000001	0,0000005
CO_2	0,000001	0,0000005
N_2	0,000029	0,0000145

Table 11. Purity table for propane

Component	Amount fraction, (mol/mol)	Standard uncertainty, (mol/mol)
C_3H_8	0,999853	
C_2H_6	0,000025	0,0000125
C_3H_6	0,00003	0,000015
i-C_4H_{10}	0,000006	0,000003
n-C_4H_{10}	0,000018	0,000009
N_2	0,000056	0,000028
O_2	0,000012	0,000006

Table 12. Purity table for nitrogen

Component	Amount fraction, (mol/mol)	Standard uncertainty, (mol/mol)
N_2	0,9999508	
O_2	0,0000092	0,0000046

H_2	0,000002	0,000001
Ar	0,000035	0,0000175
CH_4	0,000001	0,0000005
CO	0,000001	0,0000005
CO_2	0,000001	0,0000005

III. Instrumentation

The instrument used for the measurements is Chromatograph «Chromatec-Crystal 5000.2» (manufacturer: Russia) with 3 detectors (3 measurement channels)/

The measurement modes are shown in Table 13.

Table 13. Measurement modes

Component	Sample loop, cm^3	Detector	Column/ Temperature	Carrier gas / flow rate
O_2	0.5, t=100°C	TCD, t=120 °C	CaA 60-80 mesh, 3 m*3 mm, t=100 °C	He / 15ml/min
CO	0.5, t=100°C	TCD, t=120 °C	CaA 60-80 mesh, 3 m*3 mm, t=100 °C	He / 15ml/min
CO_2	0.5, t=100°C	TCD, t=120 °C	Hayesep R 80-100 mesh, 3 m*3 mm, t=100 °C	He / 15ml/min
C_3H_8	0.5, t=100°C	FID, t=220 °C	CaA 60-80 mesh, 3 m*2 mm, t=100 °C	He / 15ml/min

The chromatographic data collection and processing was carried out using the “Chromatec Analytic” software, Russia.

IV. Calibration method and value assignment

Single point calibration method was used to determine components mole fraction in the comparison gas mixture. Each of the 5 measurement results was received under repeatability conditions using one calibration samples (Table 7). Each of the 5 results was calculated as the average of 6 parallel sub-measurements with alternating injection of the sample for comparisons and the calibration gas mixture.

The amount of substance fraction for a sub-measurement was calculated according to the formula:

$$X_x = X_{st}\frac{A_x}{(A'_{st} + A''_{st})},$$

where X_x and X_{st} -amount of substance fractions of component in the comparison and calibration mixtures;

A_x – analytical signal of component in the comparison gas mixture;

A'_{st} and A''_{st} - analytical signals of appropriate component in the calibration standard before and after measurement of the comparison mixture.

Relative standard deviations of sub-measurement series were from 0,08 % to 0,58 %.

V. Uncertainty evaluation

The standard uncertainty caused by temperature change in the laboratory during measurements.

The temperature change in the laboratory during the measurement period was ± 0,5 ° C. Based on the assumption of a rectangular distribution of type B, the standard uncertainty was calculated using the formula:

$$u_{temp} = \frac{0{,}5 \cdot 2}{293} \cdot \frac{1}{\sqrt{3}} \cdot 100\% = 0{,}2\ \%$$

The standard uncertainty caused by pressure change in the laboratory during measurements.

The pressure change in the laboratory during the measurement period was ± 0,4 kPa. Based on the assumption of a rectangular distribution of type B, the standard uncertainty was calculated using the formula:

$$u_p = \frac{0{,}4}{101{,}3} \cdot \frac{1}{\sqrt{3}} \cdot 100\% = 0{,}23\ \%$$

Table 14. Uncertainty budget for carbon dioxide

Uncertainty source	Designation of uncertainty	Distribution	Relative standard uncertainty, u(xi), %	Sensitivity coefficient, c_i	Contribution $u(y_i)$, %
Calibration samples	u_{cal}	Normal	0,10	1	0,10
Convergence of chromatograph readings during measurements in a series	u_{ser}	Normal	0,29	1	0,29
Temperature change	u_{temp}	Rectangular	0,20	1	0,20
Pressure change	u_P	Rectangular	0,23	1	0,23
Standard uncertainty of the measurement result	u_A	Normal	0,11	1	0,11
Combined relative standard uncertainty					**0,45**

Coverage factor: k=2

Relative extended uncertainty U: 0,9 %

Table 15. Uncertainty budget for oxygen

Uncertainty source	Designation of uncertainty	Distribution	Relative standard uncertainty, u(xi), %	Sensitivity coefficient, c_i	Contribution $u(y_i)$, %
Calibration samples	u_{cal}	Normal	0,10	1	0,10
Convergence of chromatograph readings during measurements in a series	u_{ser}	Normal	0,25	1	0,25
Temperature change	u_{temp}	Rectangular	0,20	1	0,20
Pressure change	u_P	Rectangular	0,23	1	0,23
Standard uncertainty of the measurement result	u_A	Normal	0,16	1	0,16
Combined relative standard uncertainty					**0,44**

Coverage factor: k=2

Relative extended uncertainty U: 0,9 %

Table 16. Uncertainty budget for propane

Uncertainty source	Designation of uncertainty	Distribution	Relative standard uncertainty, u(xi), %	Sensitivity coefficient, c_i	Contribution $u(y_i)$, %
Calibration samples	u_{cal}	Normal	0,45	1	0,45
Convergence of chromatograph readings during measurements in a series	u_{ser}	Normal	0,25	1	0,25
Temperature change	u_{temp}	Rectangular	0,20	1	0,20
Pressure change	u_P	Rectangular	0,23	1	0,23
Standard uncertainty of the measurement result	u_A	Normal	0,40	1	0,40
Combined relative standard uncertainty					**0,72**

Coverage factor: k=2
Relative extended uncertainty U: 1,4 %

Table 17. Uncertainty budget for carbon monoxide

Uncertainty source	Designation of uncertainty	Distribution	Relative standard uncertainty, u(xi), %	Sensitivity coefficient, c_i	Contribution $u(y_i)$, %
Calibration samples	u_{cal}	Normal	0,10	1	0,10
Convergence of chromatograph readings during measurements in a series	u_{ser}	Normal	0,33	1	0,33
Temperature change	u_{temp}	Rectangular	0,20	1	0,20
Pressure change	u_P	Rectangular	0,23	1	0,23
Standard uncertainty of the measurement result	u_A	Normal	0,25	1	0,25
Combined relative standard uncertainty					**0,53**

Coverage factor: k=2
Relative extended uncertainty U: 1,1 %

Report Form CCQM-K3.2019 “Automotive exhaust gases”

Laboratory name: D.I.Mendeleyev Institute for Metrology (VNIIM)

Cylinder number: 8449

1.1.1 Table 1: Measurement #1

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	12/05/2020	0,999124	0,22	10
Carbon dioxide	12/05/2020	2,001948	0,14	10
Oxygen	12/05/2020	3,006216	0,18	10
Propane	04/06/2020	0,019879	0,11	10
Nitrogen	-	balance	-	-

1.1.2 Table 2: Measurement #2

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	13/05/2020	0,999754	0,09	10
Carbon dioxide	13/05/2020	2,001294	0,11	10
Oxygen	13/05/2020	3,006141	0,16	10
Propane	04/06/2020	0,019899	0,15	10
Nitrogen	-	balance	-	-

1.1.3 Table 3: Measurement #3

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	14/05/2020	1,00020	0,16	10
Carbon dioxide	14/05/2020	2,00243	0,02	10
Oxygen	14/05/2020	3,008575	0,12	10
Propane	04/06/2020	0,019858	0,18	10
amNitrogen	-	balance	-	-

1.1.4 Table 4: Measurement #4

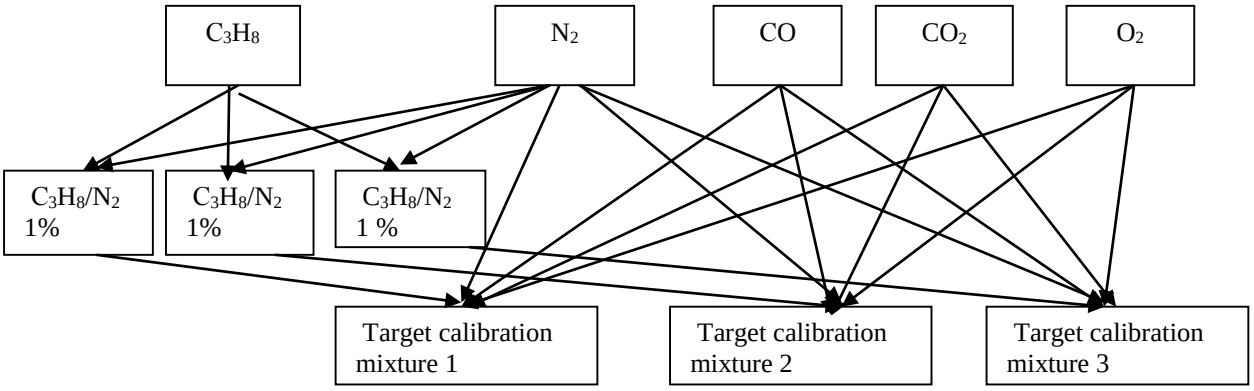
Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	25/06/2020	1,00106	0,14	7
Carbon dioxide	22/06/2020	2,00209	0,21	7
Oxygen	16/06/2020	3,00734	0,07	7
Propane	05/06/2020	0,019870	0,36	10
Nitrogen	-	balance	-	-

1.1.5 Table 5: Results

Component	Date (dd/mm/yy)	Result (cmol/mol)	Expanded uncertainty (% mol)	Coverage factor
Carbon monoxide	09/07/2020	1,0000	0,0016	2
Carbon dioxide		2,0019	0,0020	2
Oxygen		3,0071	0,0031	2
Propane		0,019877	0,000038	2
Nitrogen		-	-	-

1.1.6 Calibration standards

Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 “Gas analysis - Preparation of calibration gas mixtures - Gravimetric method” were used as calibration standards.
Preparation from pure substances was carried out in 2 stages.
On the first stage 3 C_3H_8/N_2 gas mixtures were prepared on the concentration level of 1 %.
On the second stage 3 target calibration gas mixtures with amount of substance fractions very close to the comparison mixture were prepared .Weighing data are shown in uncertainty budgets tables.
The scheme of preparation is shown below.



The exact values of components amount of substance fraction in the calibration gas mixtures and their standard uncertainties are shown in the table 6.

Table 6: Calibration gas mixtures

Cylinder number	Component	Amount fraction cmol/mol	Standard uncertainty due to weighing and purity %
D718476 (cal. mixture 1)	Carbon monoxide	1,0018	0,00035
	Carbon dioxide	1,99488	0,00022
	Oxygen	3,00646	0,00032
	Propane	0,020033	0,000008
	Nitrogen	balance	-
M365633 (cal. mixture 2)	Carbon monoxide	0,9986	0,00035
	Carbon dioxide	1,99662	0,00022
	Oxygen	3,00683	0,00032
	Propane	0,019911	0,00007
	Nitrogen	balance	-
D718479 (cal. mixture 3)	Carbon monoxide	0,9612	0,00035
	Carbon dioxide	2,00720	0,00022
	Oxygen	2,97861	0,00030
	Propane	0,019980	0,00007
	Nitrogen	balance	-

All standard gas mixtures were prepared in aluminum cylinders (Luxfer), V=5 dm^3.

Characteristics of pure substances used for preparation of the calibration standards are shown in the tables 7 - 11.

Table 7: Purity table for Carbon monoxide (cylinder № № 41850)

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
CO	998880,59	
H_2O	590	30
N_2	319	7
CO_2	114,1	2,8
H_2	89,48	0,29
O_2	5,16	0,16
CH_4	1	0,6
Ar	0,30	0,17
He	0,15	0,09
CH_3OH	0,10	0,005
C_2H_4	0,07	0,003
C_2H_6	0,035	0,020
C_3H_6	0,014	0,006
C_3H_8	0,005	0,003

Table 8: Purity table for Carbone dioxide (cylinder № 74318)

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
CO_2	999998,8	
N_2	0,45	0,26
O_2	0,30	0,17
H_2	0,15	0,09
He	0,15	0,09
CH_4	0,0574	0,0013
CO	0,0205	0,0011

1.1.7 **Table 9:** Purity table for Oxygen (cylinder № 11321)

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
O_2	999999,595	
N_2	0,315	0,007
CH_4	0,0429	0,0008
CO_2	0,0335	0,0007
Ar	0,0082	0,0005
H_2	0,0025	0,0014
Kr	0,0025	0,0014

1.1.8 Table 10: Purity table for Propane (cylinder № 312369)

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
C_3H_8	999954,2	
C_2H_6	9,7	0,5
C_3H_6	13,2	0,4
i-C_4H_{10}	2,7	0,13
n-C_4H_{10}	20,2	0,5

1.1.9 **Table 11: –** Purity table for Nitrogen (MONO 1, purification with Entegris Gas purifier “Gatekeeper-HX”)

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
N_2	999941,65	
Ar	57,3	0,37
H_2O	1,0	0,05
O_2	0,039	0,002
H_2	0,0043	0,0002
CH_4	0,0025	0,0014
CO_2	0,0025	0,0014
CO	0,0010	0,0006

Instrumentation

The instrument used for the measurements is Chromatograph «Chromatec-Crystal 5000.2» ("Chromatec", Russia) with 4 detectors (4 measurement channels).

Operating mode

Component	Sample loop, (cm^3)	Detector	Column/ Temperature	Carrier gas /flow rate
O_2	0.5, Heated valve, t=100 °C	TCD t=180 °C	CaA 60-80 mesh, 3 m*3 mm /100°C	He /flow rate - 15 ml/min
CO	0.5, Heated valve, t=100 °C	TCD t=180 °C	CaA 60-80 mesh, 3 m*3 mm /100°C	He /flow rate - 15 ml/min
CO_2	0.5, Heated valve, t=100 °C	TCD t=180 °C	HayeSep R 80-100 mesh, 3 m *3 mm/100°C	He /flow rate - 15 ml/min
C_3H_8	0.5, Heated valve, t=100 °C	FID t=220 °C	HayeSep R 80-100 mesh, 3 m *2 mm/100°C	He /flow rate - 20 ml/min

Data collection: Software support "Chromatec Analytic"(Russia

Calibration method and value assignment

Single point calibration method was used to determine components mole fraction in the comparison gas mixture.
Each of the 4 measurement results was received under repeatability conditions with the 3 different calibration standards (table 3), one of which was used for measurements twice. Each of these 4 results is the mean of 10 (7) sub-measurements with alternating injection of comparison and calibration mixtures.
The amount of substance fraction for a sub-measurement was calculated according to the formula $C_x = C_{st} \frac{A_x}{(A'_{st} + A''_{st})/2}$,
where C_x and C_{st} – amount of substance fractions of component in the comparison and calibration mixtures;
A_x – analytical signal of component in the comparison gas mixture
A'_{st} and A''_{st} analytical signals of approppriate component in the calibration standard before and after measurement of the comparison mixture.
Verification was carried out by checking consistency within the batch of newly prepared calibration mixtures.
Relative standard deviations of sub-measurement series were (0,02-0,36) %.
Temperature corrections were not applied due to use of above-mentioned measurement sequence.

Uncertainty evaluation

Table 12: Uncertainty budget for Carbon monoxide

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of CO		998880,59 µmol/mol	B	Rectangular	30,9 µmol/mol	0,00489	0,151
Purity of CO_2		999998,80 µmol/mol	B	Rectangular	0,336 µmol/mol	0,0000115	0,0000385
Purity of O_2		999999,60 µmol/mol	B	Rectangular	0,00737 µmol/mol	0,0000114	0,00000084
Purity of C_3H_8		999954.00 µmol/mol	B	Rectangular	0,809 µmol/mol	0,00000057	0,00000046
Purity of N_2		999941.65 µmol/mol	B	Rectangular	0,368 µmol/mol	0,00411	0,00152
Weighing (preparation of C_3H_8 pre-mixture)	C_3H_8	9,44587633 g	A,B	Normal	0,00201g	0,119	0,000238
	N_2	601,03724337 g	A,B	Normal	0,0120 g	0,00189	0,0000224
Weighing (preparation of final calibration mixtures)	CO	8,52386054 g	A,B	Normal	0,00201g	1160	2,33
	CO_2	26,75378719 g	A,B	Normal	0,00202 g	7,45	0,0150
	O_2	29.29573622 g	A,B	Normal	0,00204 g	10,25	0,0209
	C_3H_8 premixture	17,27869859 g	A,B	Normal	0,00202 g	11,64	0,0235
	N_2	784,59673922 g	A,B	Normal	0,0146 g	11,71	0,1706
Within and between day measurements		1,000034 %	A	Normal	7,6 µmol/mol	1	7,6
Combined standard uncertainty							7,95
Expanded uncertainty k=2							15,9

Table 13: Uncertainty budget for Carbon dioxide

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of CO		998880,59 µmol/mol	B	Rectangular	30,9 µmol/mol	0,000916	0,0283
Purity of CO_2		999998,80 µmol/mol	B	Rectangular	0,336 µmol/mol	0,0124	0,00417
Purity of O_2		999999,60 µmol/mol	B	Rectangular	0,00737 µmol/mol	0,00289	0,0000213
Purity of C_3H_8		999954.00 µmol/mol	B	Rectangular	0,809 µmol/mol	0,00000113	0,000000914
Purity of N_2		999941.65 µmol/mol	B	Rectangular	0,368 µmol/mol	0,00834	0,00307
Weighing (preparation of C_3H_8 pre-mixture)	C_3H_8	9,44587633 g	A,B	Normal	0,00201g	0,23788	0,000476
	N_2	601,03724337 g	A,B	Normal	0,0120 g	0,00374	0,0000447
Weighing (preparation of final calibration mixtures)	CO	8,52386054 g	A,B	Normal	0,00201g	23,3	0,0467
	CO_2	26,75378719 g	A,B	Normal	0,00202 g	731	1,48
	O_2	29.29573622 g	A,B	Normal	0,00204 g	20,5	0,0418
	C_3H_8 premixture	17,27869859 g	A,B	Normal	0,00202 g	23,3	0,0470
	N_2	784,59673922 g	A,B	Normal	0,0146 g	23,4	0,341
Within and between day measurements		2,00194 %	A	Normal	10,2 µmol/mol	1	10,2
Combined standard uncertainty							10,3
Expanded uncertainty k=2							20,6

Table 14: Uncertainty budget for Oxygen

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of CO		998880,59 µmol/mol	B	Rectangular	30,9 µmol/mol	0,000087	0,00269
Purity of CO_2		999998,80 µmol/mol	B	Rectangular	0,336 µmol/mol	0,010	0,00337
Purity of O_2		999999,60 µmol/mol	B	Rectangular	0,00737 µmol/mol	0,0294	0,000217
Purity of C_3H_8		999954.00 µmol/mol	B	Rectangular	0,809 µmol/mol	$1,71*10^{-6}$	0,00000138
Purity of N_2		999941.65 µmol/mol	B	Rectangular	0,368 µmol/mol	0,0125	0,00460
Weighing (preparation of C_3H_8 pre-mixture)	C_3H_8	9,44587633 g	A,B	Normal	0,00201g	0,358	0,000718
	N_2	601,03724337 g	A,B	Normal	0,0120 g	0,00563	0,0000674
Weighing (preparation of final calibration mixtures)	CO	8,52386054 g	A,B	Normal	0,00201g	35,3	0,0707
	CO_2	26,75378719 g	A,B	Normal	0,00202 g	22,4	0,04529
	O_2	29.29573622 g	A,B	Normal	0,00204 g	996	2,0328
	C_3H_8 premixture	17,27869859 g	A,B	Normal	0,00202 g	35,1	0,0708
	N_2	784,59673922 g	A,B	Normal	0,0146 g	35,3	0,514
Within and between day measurements		3,007068 %	A	Normal	15,3 µmol/mol	1	15,3
Combined standard uncertainty							15,4
Expanded uncertainty k=2							30,8

Table 14: Uncertainty budget for Propane

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of CO		998880,59 µmol/mol	B	Rectangular	30,9 µmol/mol	$1,07*10^{-6}$	0,0000332
Purity of CO_2		999998,80 µmol/mol	B	Rectangular	0,336 µmol/mol	$1,88*10^{-6}$	$6,3*10^{-7}$
Purity of O_2		999999,60 µmol/mol	B	Rectangular	0,00737 µmol/mol	$2,31*10^{-6}$	$1,7*10^{-8}$
Purity of C_3H_8		999954.00 µmol/mol	B	Rectangular	0,809 µmol/mol	0,000213	0,000172
Purity of N_2		999941.65 µmol/mol	B	Rectangular	0,368 µmol/mol	0,0000796	0,0000293
Weighing (preparation of C_3H_8 pre-mixture)	C_3H_8	9,44587633 g	A,B	Normal	0,00201g	20,8	0,0416
	N_2	601,03724337 g	A,B	Normal	0,0120 g	0,326	0,00390
Weighing (preparation of final calibration mixtures)	CO	8,52386054 g	A,B	Normal	0,00201g	0,234	0,000468
	CO_2	26,75378719 g	A,B	Normal	0,00202 g	0,149	0,000300
	O_2	29.29573622 g	A,B	Normal	0,00204 g	0,204	0,000417
	C_3H_8 premixture	17,27869859 g	A,B	Normal	0,00202 g	11,3	0,0228
	N_2	784,59673922 g	A,B	Normal	0,0146 g	0,233	0,00340
Within and between day measurements		198,77 µmol/mol	A	Normal	0,184 µmol/mol	1	0,184
Combined standard uncertainty							0,19
Expanded uncertainty k=2							0,38

Authorship: L.A. Konopelko, A.V. Kolobova, A.V. Meshkov, O.V. Efremova