International key comparison CCQM-K3.2019.1

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Table of Contents

Field

Amount of substance

Subject

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

1 Introduction

This key comparison is one of a series of key comparisons in the gas analysis area assessing core competences (track A key comparisons). Such competences include, among others, the capabilities to prepare primary standard gas mixtures (PSMs) using static gravimetry [1, 2], 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.

For this key comparison, a mixture containing carbon monoxide, carbon dioxide, oxygen, and propane in nitrogen has been chosen which is used for calibration of exhaust automotive gas analysers. This key comparison is a follow-up of CCQM-K3.2019 [3]. In the characterisation of the travelling standard, a link was created with the results of said key comparison based on the verification measurements [4]. This key comparison was organised as a 'model 1' key comparison [5].

This key comparison aims to support Calibration and Measurement Capabilities (CMCs) for the amount fractions of four components (carbon monoxide, carbon dioxide, propane and oxygen) in car exhaust gas mixtures. It is organised on behalf of the CCQM Gas Analysis Working Group (CCQM-GAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) in accordance with the provisions of the CIPM Mutual Recognition Arrangement (CIPM MRA) [6, 7] of the International Committee for Weights and Measures (CIPM).

2 Design and organisation of the key comparison

2.1 Participants

Table 1 lists the participants in this key comparison.

Table 1: Participating national metrology institutes (NMIs) in CCQM-K3.2019.1

Acronym	Country	Institute
UMTS	UA	SE "Pan-Ukrainian State Research and Production Center for Standardization, Metrology, Certification and Consumers Rights Protection" (SE "Ukrmetrteststandart"), Kyiv, Ukraine
VSL	NL	Van Swinden Laboratorium, Delft, The Netherlands

2.2 Measurement standards

A mixture was prepared gravimetrically by VSL, using carbon dioxide grade 5.5, oxygen grade 6.0, carbon monoxide grade 4.7, propane grade 3.5, and nitrogen grade 6.0 BIP+. Carbon dioxide and oxygen were transferred from the pure gas. Carbon monoxide was transferred from the pre-mixture obtained with one dilution step from the pure gas. Propane was transferred from the pre-mixture obtained with two dilution steps. The mixture was verified against a set of VSL PSMs. All pure gases were subjected to a purity analysis in accordance with ISO 19229 [8] prior to use for preparation of the gas mixture.

The filling pressure in the cylinder was approximately 11.5 MPa. An aluminium cylinder having a 5 L volume from Luxfer UK with an Aculife IV treatment was used. The mixture composition and its associated uncertainty was calculated in accordance with ISO 6142-1 [1,2]. The amount fractions as obtained from gravimetry and purity analysis of the parent gases were used as key comparison reference values (KCRVs). The expanded uncertainties include uncertainty contributions from weighing, purity analysis of the parent gases, the standard atomic weights and the verification of the gas mixture.

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 ($\mathrm{cmol\,mol^{-1}}$) [3]

Component	Amount fraction range
Carbon monoxide	0.5 – 2
Carbon dioxide	2 – 5
Oxygen	1 – 4
Propane	0.01 – 0.03
Nitrogen	Balance

2.3 Measurement protocol

The measurement protocol requested UMTS to perform at least three (3) measurements, with independent calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions. The protocol informed the participant about the nominal amount fraction ranges (see table 2). The participant was requested to submit a description of their method and a full description of their uncertainty evaluation used for evaluating the uncertainty of their result.

2.4 Schedule

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

Table 3: Schedule

Date	Event
Apr 2023	Agreement of protocol
Feb 2024	Preparation of the mixture
Mar 2024	Characterisation of mixture compositions
Jun 2024	Dispatch of the mixture
Oct 2024	Measurements by the participant
Nov 2024	Measurement report due
Feb 2025	Return of cylinder
Mar 2025	Re-characterisation of the mixture
Mar 2025	Draft A report available

2.5 Measurement equation

The KCRVs are based on the weighing data, the molar masses of the components and the purity verification of the parent gases. The mixture underwent verification prior to shipping them to UMTS. In the preparation, the following four groups of uncertainty components have been considered:

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

Previous experience has indicated that there are no stability issues and no correction is needed for the partial recovery of a component [3,9–12] These terms are set to zero, and so are their associated standard uncertainties.

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

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

Using the law of propagation of uncertainty (LPU) from the Guide to the expression of Uncertainty in Measurement (GUM) [13] for mutually independent quantities provides the equation for calculating the associated standard uncertainty which takes the form

$$u^2(x_{i,\text{prep}}) = u^2(x_{i,\text{grav}}) + u^2(\Delta x_{i,\text{purity}}) \tag{2}$$

The results of the amount fractions of the travelling standard are shown in table 4. For this key comparison, a new travelling standard was prepared with different target amount fractions than those of CCQM-K3.2019 [3]. The latter travelling standards had been used in CCQM-K3.2019 and EURAMET.QM-K3.2019 [12], so that their KCRVs were known, which makes them unfit for this follow-up key comparison.

Table 4: Composition of the travelling standard, expressed in amount fractions (cmol mol^{-1}). The standard uncertainties cover the preparation only.

Component	x_{prep}	$u(x_{\text{prep}})$
Carbon monoxide	1.117 718	0.000 055
Carbon dioxide	2.035 843	0.000 090
Propane	0.019 576 1	0.000 001 3
Oxygen	2.938 81	0.000 13

The validity of the composition of the mixture 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 [1]:

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

The factor 2 is a coverage factor (assuming a normal distribution, 95 % level of confidence). The assumption was made that both preparation and verification are unbiased. Such bias has never been observed. The uncertainty associated with the verification highly depends on the experimental design followed. In this particular key comparison, an approach has been chosen which is consistent with CCQM-K3 [10] and takes advantage of the work done in the gravimetry study CCQM-P41 [14].

The verification experiments have demonstrated that within the uncertainty of these measurements, the gravimetric values of the key comparison mixtures agreed with older measurement standards.

The expression for the standard uncertainty of the key comparison reference value is

$$u^2(x_{i,\text{KCRV}}) = u^2(x_{i,\text{prep}}) + u^2(x_{i,\text{ver}}) \tag{4}$$

2.6 Link to CCQM-K3.2019

A link with CCQM-K3.2019 [3] was established through the verification measurements of the travelling standard. In the same sequences, one of the travelling standards of CCQM-K3.2019 was included and the analytical composition was compared with the composition from preparation. The background of this way of linking key comparisons is described elsewhere [4].

The verification measurements were run on a gas chromatograph (GC) equipped with four different columns and thermal conductivity detectors (TCDs) and a flame ionisation detector (FID). The GC primarily operates with hydrogen for FID-B, argon for TCD-D, and helium for TCD-B and TCD-C. The method includes four simultaneous analyses, each with its own detector, ensuring a complete measurement in approximately 14 minutes.

Each component is analyzed using specific columns. Propane is measured on FID-B using a GS alumina plot KCl column. Oxygen is detected on TCD-D using a combination of micropacked molsieve 5A and silica gel 80/100 mesh 22" for separation. Carbon dioxide is analyzed on TCD-A using a micropacked precolumn with Hayesep A 80/100 mesh 6. Carbon monoxide is measured on TCD-C using a micropacked precolumn (Hayesep A 80/100 mesh 6) combined with a CP molsieve 5A column. A backflush mechanism optimizes separation and prevents contamination.

The new GC performs better than the GCs used in CCQM-K3.2019 and EURAMET.QM-K3 [3, 12]. The relative expanded uncertainty for the verification of the travelling standard was set at 0.10 %, which is the same as in CCQM-K3.2019 and EURAMET.QM-K3 [3, 12].

The results of the verification measurements are shown in tables 5–8. All verifications were performed against the PSMs of the coordinating laboratory. VSL428449 is one of the travelling standards from the previous key comparisons and was verified again to establish a link with CCQM-K3.2019 [4].

For carbon dioxide (table 5), the relative differences from verification are 0.02 % for the travelling standard from CCQM-K3.2019 and 0.06 % for the travelling standard used in this key comparison. The column labelled y_i shows the obtained instrument responses and the next column the associated standard uncertainty $u(y_i)$. Δx_i denotes the difference between the amount fractions from preparation and analysis. These results confirm the link between this key comparison and CCQM-K3.2019 and equivalence between the travelling standards.

For carbon monoxide (table 6), the relative differences from verification are −0.08 % for the travelling standard from CCQM-K3.2019 and −0.14 % for the travelling standard used in this key comparison. These larger differences are due to the shape of the calibration function in the neighbourhood of 1 $\mathrm{cmol\,mol^{-1}}$. A comparison using a single point calibration [15] confirmed the equivalence.

For oxygen (table 7), the relative differences from verification are −0.09 % for the travelling standard from CCQM-K3.2019 and −0.01 % for the travelling standard used in this key comparison. The equivalence was confirmed.

For propane (table 8), the relative differences from verification are 0.01 % for the travelling standard from CCQM-K3.2019 and 0.01 % for the travelling standard used in this key comparison. Equivalence was confirmed.

Table 5: Verification results for the amount fraction carbon dioxide using a multipoint calibration in accordance with ISO 6143

Mixture	y_i a.u.	$u(y_i)$ a.u.	$x_{i,\mathrm{prep}}$ $\mathrm{cmol\,mol^{-1}}$	$x_{i,\mathrm{ver}}$ $\mathrm{cmol\,mol^{-1}}$	$u(x_{i,\mathrm{ver}})$ $\mathrm{cmol\,mol^{-1}}$	$\Delta x_i/x_{i,\mathrm{prep}}$ %
VSL502704	509.66	0.04	2.035 84	2.037 09	0.000 22	0.06
VSL428449	501.09	0.08	2.002 46	2.002 78	0.000 35	0.02

Table 6: Verification results for the amount fraction carbon monoxide using a multipoint calibration in accordance with ISO 6143

Mixture	y_i a.u.	$u(y_i)$ a.u.	$x_{i,\mathrm{prep}}$ $\mathrm{cmol\,mol^{-1}}$	$x_{i,\mathrm{ver}}$ $\mathrm{cmol\,mol^{-1}}$	$u(x_{i,\mathrm{ver}})$ $\mathrm{cmol\,mol^{-1}}$	$\Delta x_i/x_{i,\mathrm{prep}}$ %
VSL502704	1115.62	0.07	1.117 72	1.116 19	0.000 09	−0.14
VSL428449	999.21	0.19	1.000 71	0.999 91	0.000 20	−0.08

Upon return, the travelling standard was checked again. This re-verification was performed on 16 June 2025. The GC was calibrated using a multipoint calibration and one of the travelling standards from CCQM-K3.2019 [3, 12] was used as reference. For the amount fraction carbon dioxide, the results differed 0.04 % (relative to the amount fraction), for propane 0.01 %, for oxygen 0.01 %

Table 7: Verification results for the amount fraction oxygen using a multipoint calibration in accordance with ISO 6143

Mixture	y a.u.	$u(y)$ a.u.	x_{prep} cmol mol^{-1}	x_{ver} cmol mol^{-1}	$u(x_{\text{ver}})$ cmol mol^{-1}	$\Delta x/x_{\text{prep}}$ %
VSL502704	2930.25	0.60	2.938 81	2.936 28	0.000 65	−0.09
VSL428449	3005.22	0.43	3.011 64	3.011 48	0.000 49	−0.01

Table 8: Verification results for the amount fraction propane using a multipoint calibration in accordance with ISO 6143

Mixture	y a.u.	$u(y)$ a.u.	x_{prep} cmol mol^{-1}	x_{ver} cmol mol^{-1}	$u(x_{\text{ver}})$ cmol mol^{-1}	$\Delta x/x_{\text{prep}}$ %
VSL502704	490.93	0.03	0.019 576 1	0.019 577 8	0.000 002 0	0.01
VSL428449	498.26	0.02	0.019 868 4	0.019 870 3	0.000 001 8	0.01

and for carbon monoxide 0.03 %. Based on these verification data, the KCRVs and their associated uncertainties were confirmed.

2.7 Measurement methods

A summary of the methods, the dates of measurement, and the way in which metrological traceability has been established is given in table 9.

Table 9: Summary of the analytical techniques, calibration approaches and measurement periods

NMI	Date	Calibration	Standards	Matrix	Technique
VSL	Mar 2024	Multipoint	Own standards (ISO 6142-1)	Nitrogen	GC/FID+GC/TCD
UMTS	Oct 2024	Multipoint	Own standards (ISO 6142-1)	Nitrogen	GC/FID+GC/TCD

2.8 Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined in the CIPM MRA as [6]

$$\Delta x_i = d_i = x_i - x_{i,\text{KCRV}}, \tag{5}$$

and the uncertainty of the difference d_i at 95 % level of confidence. Here $x_{i,\text{KCRV}}$ denotes the KCRV (the amount fraction from preparation, $x_{i,\text{prep}}$), and x_i the result of laboratory i. The standard uncertainty of d_i can be expressed as (see also equation (4))

$$u^2(d_i) = u^2(x_i) + u^2(x_{i,\text{prep}}) + u^2(x_{i,\text{ver}}) \tag{6}$$

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.

3 Results

In table 10, the KCRVs, results and degrees of equivalence are shown. The agreement is good for the amount fractions carbon dioxide, propane and oxygen. The difference for the amount fraction carbon monoxide slightly exceeds the associated expanded uncertainty.

Table 10: Key comparison reference values, results and degrees of equivalence ($\mathrm{cmol\,mol^{-1}}$). The coverage factor for all expanded uncertainties is $k = 2$.

Component	x_{KCRV}	$u(x_{\mathrm{KCRV}})$	$U(x_{\mathrm{KCRV}})$	x_{lab}	$U(x_{\mathrm{lab}})$	d	$U(d)$
Carbon monoxide	1.1177	0.0011	0.0022	1.1232	0.0033	0.0055	0.0040
Carbon dioxide	2.0358	0.0020	0.0041	2.0359	0.0056	0.0001	0.0069
Propane	0.019 576	0.000 020	0.000 039	0.019 63	0.000 10	0.000 05	0.000 11
Oxygen	2.9388	0.0029	0.0059	2.9379	0.0084	−0.001	0.010

4 Support to CMC claims

Participation in this key comparison can be used to support CMCs for core competences under the flexible regime [5] and for CMCs for the amount fractions carbon monoxide, carbon dioxide, propane and oxygen in automotive and binary mixtures in nitrogen. The full support for CMCs is described in the report of CCQM-K3.2019 [3].

5 Conclusions

Equivalence was shown for the amount fractions carbon dioxide, propane and oxygen in automotive mixtures.

This key comparison was successfully linked to CCQM-K3.2019. No additional uncertainty had to be taken into account.

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CCQM-K3.2019.1

Completion date

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A Measurement report of the participating institute

Measurement report of SE “Ukrmetrteststandart”

1. Results

Cylinder number: 2704 E.

Results are given in Tables 1 to 5.

Table 1. Measurement 1

Component	Date	Fraction (cmol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (cmol/mol)
Oxygen	18.09.2024	2.9391	0.06	4	0.0023
Carbon dioxide	18.09.2024	2.0358	0.02	4	0.0016
Propane	24.09.2024	0.019689	0.06	4	0.000018
Carbon monoxide	18.09.2024	1.1236	0.08	4	0.0014

Table 2. Measurement 2

Component	Date	Fraction (cmol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (cmol/mol)
Oxygen	19.09.2024	2.9416	0.11	3	0.0035
Carbon dioxide	19.09.2024	2.0393	0.10	3	0.002
Propane	25.09.2024	0.019574	0.13	4	0.00003
Carbon monoxide	19.09.2024	1.124	0.10	3	0.0014

Table 3. Measurement 3

Component	Date	Fraction (cmol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (cmol/mol)
Oxygen	09.10.2024	2.9321	0.03	3	0.0016
Carbon dioxide	09.10.2024	2.0328	0.02	3	0.0016
Propane	26.09.2024	0.019614	0.12	4	0.000027
Carbon monoxide	09.10.2024	1.121	0.04	3	0.0011

Table 4. Measurement 4

Component	Date	Fraction (cmol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (cmol/mol)
Oxygen	10.10.2024	2.9383	0.03	3	0.0016
Carbon dioxide	10.10.2024	2.0357	0.04	3	0.0016
Propane	10.10.2024	0.019631	0.17	4	0.000036
Carbon monoxide	10.10.2024	1.1243	0.03	3	0.0011

Table 5. Final results

Component	Fraction (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
Oxygen	2.9379	0.0084	2
Carbon dioxide	2.0359	0.0056	2
Propane	0.01963	0.00010	2
Carbon monoxide	1.1232	0.0033	2

2. Calibration standards

Three Primary Standard Gas Mixtures (PSGM) were used as calibration standards. PSGMs were prepared gravimetrically according to ISO 6142-1 [1]. Parent gases were pure nitrogen, pure oxygen, pure carbon dioxide, pure carbon monoxide and previously prepared pre-mixture with propane amount fraction of 1 % in nitrogen.

Composition of the PSGMs is given in Tables 6 to 8.

Table 6. Composition of PSGM No 1, cylinder number 81405010

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
N_2	942272	22
O_2	27424	14
CO_2	19288	10
CO	10817	16
C_3H_8	185.88	0.16
Ar	7.07	0.24
H_2O	4.06	0.19
H_2	0.328	0.009
CH_4	0.057	0.005
C_2H_6	0.0483	0.0012

Table 7. Composition of PSGM No 2, cylinder number M083222

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
N_2	939262	19
O_2	28795	11
CO_2	20232	8
CO	11501	13
C_3H_8	195.63	0.13
Ar	7.18	0.24
H_2O	4.07	0.18

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
H_2	0.349	0.009
CH_4	0.058	0.005
C_2H_6	0.0508	0.0013

Table 8. Composition of PSGM No 3, cylinder number M083217

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
N_2	935979	20
O_2	30455	13
CO_2	21362	9
CO	11986	14
C_3H_8	205.29	0.14
Ar	7.28	0.24
H_2O	4.08	0.18
H_2	0.36	0.01
CH_4	0.059	0.005
C_2H_6	0.0533	0.0013

Composition of the premixture C_3H_8 – N_2 is given in Table 9.

Table 9. Composition of the premixture C_3H_8 – N_2, cylinder number D621473

Component	Amount fraction, µmol/mol	Std. uncertainty, µmol/mol
N_2	89846	3
C_3H_8	10015.9	0.9
Ar	131	3
O_2	3.06	0.15
C_2H_6	2.60	0.06
H_2O	1.29	0.05
CO_2	0.099	0.025
CO	0.049	0.029
CH_4	0.049	0.029
H_2	0.049	0.029

Purity data are given in Tables 10 to 15.

Table 10. Purity data for nitrogen used to prepare premixture C_3H_8 – N_2

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
N_2	0.999863	0.000003
O_2	0.00000300	0.00000015
H_2O	0.00000130	0.00000005
CO_2	0.000000100	0.000000025
Ar	0.000132	0.000003
CO	0.000000050	0.000000029
CH_4	0.000000050	0.000000029
H_2	0.000000050	0.000000029

Table 11. Purity data for propane used to prepare premixture C_3H_8 – N_2

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
N_2	0.000040	0.000001
O_2	0.00000900	0.00000025
C_2H_6	0.000260	0.000006
C_3H_8	0.999691	0.000007

Table 12. Purity data for nitrogen used to prepare PSGMs

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
N_2	0.9999909	0.0000003
O_2	0.000000060	0.000000005
H_2O	0.0000039	0.0000002
CO_2	0.000000040	0.000000005
Ar	0.00000500	0.00000025
CO	0.000000005	0.000000003
CH_4	0.000000040	0.000000005
H_2	0.000000005	0.000000003

Table 13. Purity data for oxygen used to prepare PSGMs

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
N_2	0.00000050	0.00000029
O_2	0.9999975	0.0000007
H_2O	0.00000050	0.00000029
CO_2	0.000000170	0.000000017
Ar	0.0000010	0.0000006
CO	0.00000010	0.00000006
CH_4	0.00000010	0.00000006
H_2	0.00000010	0.00000006

Table 14. Purity data for carbon monoxide used to prepare PSGMs

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
N_2	0.0000466	0.0000011
O_2	0.00000290	0.00000015
CO_2	0.0000018	0.0000001
CO	0.9999191	0.0000014
H_2	0.0000296	0.0000007

Table 15. Purity data for carbon dioxide used to prepare PSGMs

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
N_2	0.00000980	0.00000025
O_2	0.0000024	0.0000001
H_2O	0.000022	0.000001
CO_2	0.999965	0.000001
CH_4	0.00000084	0.00000004

PSGMs were prepared gravimetrically according to ISO 6142-1 [1] using an automatic weighing device. PSGM composition was calculated by formula (3) from ISO 6142-1 [1].

Amount fraction of impurities was measured/calculated according to ISO 19229 [2].

Example weighing data for PSGM No 1 are given in Table 16.

Table 16. Weighing data for PSGM No 1

Parent gas	Transferred mass, g	Std. uncertainty, g
Premixture C_3H_8 – N_2	11.12800	0.00949
CO	6.44800	0.00941
CO_2	18.06400	0.00960

Parent gas	Transferred mass, g	Std. uncertainty, g
O_2	18.67400	0.00961
N_2	550.7660	0.0185

The PSGMs were verified by examining their mutual consistency according to ISO 6143 [3]. Some details are given in the *Uncertainty* section below.

3. Instrumentation

Balance used for PSGM preparation by gravimetric method: Mettler Toledo electronic balance XP26003L.

Oxygen, carbon dioxide, and carbon monoxide amount fractions were measured using gas chromatograph Agilent 6890N with a thermal conductivity detector (GC-TCD). Two columns were used: Porapak Q 9ft 80/100 mesh and Mole sieve 5A 6ft 60/80 mesh. Temperature mode – isothermal at 60 °C.

Propane amount fraction was measured using gas chromatograph Agilent 6890N with a flame ionisation detector (GC-FID) and column GS-Alumina 50 m 0,53 mm. Temperature mode – isothermal at 100 °C.

In both cases carrier gas was helium, and sample volume was 0,5 mL.

Purity analysis of parent gases was performed using Agilent 6890N gas chromatographs with helium ionization detector, flame ionization detector, thermal conductivity detector and mass spectrometry detector.

4. Calibration method and value assignment

Calibration was performed according to ISO 6143 [3] using linear model. Four measurements were made, each for one day, except for propane that was measured separately (see Tables 1 to 4). Three or four runs, each including three PSGMs and the mixture to be analysed, were performed for each measurement. For each measurement, peak areas obtained during the runs were averaged, and the averaged values were used to obtain linear function coefficients and, consequently, measured values of the component amount fraction. Calculations were performed using B_LEAST software. The values from the four measurements were pooled to give the final values (see Table 5).

5. Uncertainty evaluation

5.1 Uncertainty of PSGMs

PSGM gravimetric uncertainty was calculated by formula (4) from ISO 6142-1 [1], with no correlations taken into account. Stability term was not included into the uncertainty budget as no significant short-term drift was revealed. Also, from the long-time experience it is known that for the kind of gas mixtures concerned this term can be regarded negligible compared to the claimed uncertainty level. Thus, preparation uncertainty to be calculated by formula (7) from ISO 6142-1 [1] becomes equal to the gravimetric uncertainty.

Uncertainty term from verification, which was performed by examining PSGMs mutual consistency, was estimated for each component in each PSGM via the differences, Δ, between gravimetric values of amount fractions, y_{grav}, and those determined using linear analysis function for each component in each PSGM, y_{ver} (formula 1):

$$\Delta = y_{\text{grav}} - y_{\text{ver}} \qquad (1)$$

Value of Δ for each component was determined as an average of five measurements. In each case the compatibility criterion established by formula (8) from ISO 6142-1 [1] was met. Then the combined uncertainties in component amount fractions, $u_c(y)$, were calculated by formula (2) in accordance with formula (9) from ISO 6142-1 [1]:

$$u_c(y) = \frac{1}{2}\sqrt{u^2(y_{\text{grav}}) + u^2(\Delta) + \Delta^2} \qquad (2)$$

where $u(y_{\text{grav}})$ and $u(\Delta)$ are standard uncertainties of y_{grav} and Δ, respectively.

For all components except for CO_2 the uncertainty values calculated by formula (2) appeared to be less than gravimetric uncertainty. To be conservative, the gravimetric uncertainties for these components stated in Tables 6 to 8 were used for the subsequent uncertainty evaluation for analysis. For CO_2, increased standard uncertainty values, calculated by formula (2), were used: 20 µmol/mol for PSGM No 1, 22 µmol/mol for PSGM No 2, and 13 µmol/mol for PSGM No 3.

5.2 Uncertainty of analysis results

Uncertainty of analysis results was evaluated according to ISO 6143 [3], taking into account uncertainty of PSGMs and variability of output signal (peak areas). Calculations were performed using B_LEAST software. Standards uncertainties for each component for each measurement are given in Tables 1 to 4. Then these uncertainties were combined for each component j to obtain the standard uncertainty of a final averaged amount fraction, $u(y_j)$, by formula (3):

$$u(y_j) = \frac{\sqrt{\sum_{i=1}^{n} u_i^2(y_{j,i})}}{n} \qquad (3),$$

where $u_i(y_{j,i})$ is a standard uncertainty of an amount fraction of component j in the i-th measurement (given in Tables 1 to 4) and n is a number of measurements. In our case $n = 4$.

For each measurement, the results were obtained in repeatability conditions. To take into account the reproducibility conditions, the between-measurement (between-day) variability has to be included into the uncertainty budget. Between-day variability was evaluated as a between-day standard deviation, $s_{\text{b-d}}$, and a combined standard uncertainty, u_c, for each component was evaluated by formula (4):

$$u_c = \sqrt{u^2(y_j) + s_{\text{b-d}}^2} \qquad (4)$$

Values of $u(y_j)$, $s_{\text{b-d}}$ and u_c are given in Table 17.

Table 17. Combined standard uncertainties of final analysis results

Component	$u(y_j)$ (by formula (3)), cmol/mol	Between-day std deviation, $s_{\text{b-d}}$, cmol/mol	Combined std unc-ty, u_c, cmol/mol
O_2	0.0012	0.0040	0.0042
CO_2	0.0008	0.0027	0.0028
C_3H_8	0.000014	0.000048	0.000050
CO	0.0006	0.0015	0.0016

It can be seen from Table 17 that between-day variability was a dominating contribution to the combined uncertainty of all the components.

Combined standard uncertainties were multiplied by the coverage factor of 2 to obtain expanded uncertainties that are given in Table 5.

References

1. ISO 6142-1:2015 Gas analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures

2. ISO 19229:2019 Gas analysis – Purity analysis and the treatment of purity data

3. ISO 6143:2001 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures