International Comparison CCQM-K3.2019 Automotive exhaust gases

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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

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) [1], 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 the first key comparison for automotive exhaust gases covering the amount fraction oxygen. The key comparison design follows that of the key comparisons CCQM-K3 [2] and CCQM-K111 [3]. This key comparison was organised as a ‘model 1’ key comparison [4].

2 Design and organisation of the key comparison

2.1 Participants

Table 1 lists the participants in this key comparison.

Table 1: List of participants

Acronym	Country	Institute
CERI	JP	Chemical Evaluation and Research Institute, Saitama, Japan
INMETRO	BR	Instituto Nacional de Metrologia, Qualidade e Technologia, Xerém RJ, Brasil
IPQ	PT	Portuguese Institute for Quality, Portugal
KRISS	KR	Korea Research Institute of Standards and Science, Deajeon, Republic of Korea
NIST	US	National Institute of Standards and Technology, Gaithersburg, United States of America
NMISA	ZA	National Metrology Institute of South Africa, Pretoria, South Africa
NPL	GB	National Physical Laboratory, Teddington, United Kingdom
VNIIM	RU	D.I. Mendeleyev Institute for Metrology, St Petersburg, Russia
VSL	NL	Van Swinden Laboratorium, Delft, the Netherlands

2.2 Measurement standards

A set of mixtures 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 premixture obtained with one dilution step from the pure gas. Propane was transferred from the premixture obtained with two dilution steps. The mixtures were verified against a set of VSL PSMs. All pure gases were subjected to a purity analysis in accordance with ISO 19229 [5] prior to use for preparation of the gas mixtures.

The filling pressure in the cylinders was approximately 11.5 MPa. Aluminium cylinders having a 5 dm^3 water volume from Luxfer UK with an Aculife IV treatment were used. The mixture composition and its associated uncertainty was calculated in accordance with ISO 6142-1 [1]. The amount fractions as obtained from gravimetry and purity verification of the parent gases were used as key comparison reference values (KCRVs). Each 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 (cmol mol^{-1})

Component	Amount fraction x (cmol mol^{-1})
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 each laboratory to perform at least 3 measurements, with independent calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions [5]. The protocol informed the participants about the nominal amount fraction ranges. The laboratories were also 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 (Table 3).

Table 3: Key comparison schedule

Date	Event
October 2018	Agreement of protocol
October 2018	Registration of participants
January 2019	Preparation of mixtures
September/October 2019	Verification of mixture compositions
February 2020	Dispatch of mixtures
December 2020 -January 2021	Reports and cylinders arrived back at VSL
February 2021	Re-verification of the mixtures
December 2021	Draft A report available

2.5 Measurement equation

The key comparison reference values are based on the weighing data, the molar masses of the components and the purity verification of the parent gases. All mixtures underwent verification prior to shipping them to the participants. After return of the cylinders, they have been verified once more to reconfirm the stability of the mixtures.

In the preparation, the following four groups of uncertainty components have been considered:

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

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

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

The equation for calculating the associated standard uncertainty reads as

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

The results of the amount fractions for one of the travelling standards are shown in

Table 4.

Table 4: Composition computed in accordance with ISO 6142-1 for mixture, expressed in amount fractions (mol mol^{-1})

Component	x	$u(x)$
Argon	$4.74 \cdot 10^{-6}$	$2.65 \cdot 10^{-6}$
Methane	$2.75 \cdot 10^{-9}$	$1.04 \cdot 10^{-9}$
Carbon monoxide	$1.013497 \cdot 10^{-2}$	$2.03 \cdot 10^{-6}$
Carbon dioxide	$1.995146 \cdot 10^{-2}$	$4.35 \cdot 10^{-6}$
Ethene	$2.498 \cdot 10^{-11}$	$1.40 \cdot 10^{-12}$
Ethane	$2.698 \cdot 10^{-9}$	$1.60 \cdot 10^{-10}$
Propene	$1.4508 \cdot 10^{-8}$	$3.80 \cdot 10^{-10}$
Propane	$1.99808 \cdot 10^{-4}$	$5.07 \cdot 10^{-8}$
n-butane	$5.395 \cdot 10^{-11}$	$9.99 \cdot 10^{-12}$
iso-butane	$3.997 \cdot 10^{-11}$	$5.99 \cdot 10^{-12}$
Hydrogen	$2.86 \cdot 10^{-8}$	$1.36 \cdot 10^{-8}$
Water	$4.11 \cdot 10^{-8}$	$1.23 \cdot 10^{-8}$
Nitrogen	$9.400113 \cdot 10^{-1}$	$8.92 \cdot 10^{-6}$
Oxygen	$2.969767 \cdot 10^{-2}$	$5.92 \cdot 10^{-6}$

The validity of the composition 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 [1]:

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

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. In this particular key comparison, an approach has been chosen which is consistent with CCQM-K3 [2] and takes advantage of the work done in the gravimetry study CCQM-P41 [7].

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

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

The values for $u\left(x_{i,\text{ver}}\right)$ are given in Tables 10-13.

The relative difference from verification is defined as

$$e_{ij} = \frac{x_{\text{ver},ij} - x_{\text{prep},ij}}{x_{\text{prep},ij}}$$

and expressed as percentage. $x_{\text{prep},ij}$ denotes the amount fraction as calculated from static gravimetric preparation for mixture i and verification j, and $x_{\text{ver},ij}$ the amount fraction obtained from the analytical verification. The results of the verification of the mixtures are summarised in Tables 5-8.

The uncertainty of the differences is dominated by the precision of the measurements, both within a run as well as between runs. Hence, the differences have been treated as uncorrelated. For each of the components and each of the mixtures, a difference has been calculated from the verification data before shipment and after return of the mixtures. The differences e_{ij} have been modelled using a random effects model

$$e_{ij} = \mu_i + B_{ij} + \varepsilon_{ij}$$

where μ_i denotes the mean relative difference for mixture *i*, B_{ij} a reproducibility effect in the verification measurements *j*, and ε_{ij} a random measurement error term. Both B_{ij} and ε_{ij} are assumed to be normally distributed with zero mean and variances τ_i^2 and σ_i^2, respectively.

The mean difference was formed by using restricted maximum likelihood estimation (REML) to the observed differences. Under the assumptions of the random effects model, the log likelihood function takes the form [8]

$$\log L(\mu, \tau^2) = -\frac{1}{2}\sum_j \log\left(2\pi\left(\sigma_j^2 + \tau^2\right)\right) - \frac{1}{2}\sum_j \log\frac{\left(e_j - \mu\right)^2}{\left(\sigma_j^2 + \tau^2\right)}$$

where the index *i* has been dropped. To obtain the estimates for the model parameters, the log likelihood function is maximised. The restricted maximum likelihood (REML) estimator is used, as this estimator is generally preferred over the maximum likelihood estimator in case of small data sets (thus, a small number of degrees of freedom). In Tables 5-8, the mean computed using REML is denoted by $\bar{e}$ and the associated standard uncertainty by $u(\bar{e})$.

The calculations have been performed using the metafor package [9] and R [10]. The standard uncertainty of the difference was calculated using the procedures of ISO 6143 [11] (in the case of a multipoint calibration) and ISO 12963 [12] (in the case of a single point calibration), followed by applying the law of propagation of uncertainty from the GUM (Guide to the expression of uncertainty in measurement) [13] to obtain the standard uncertainty associated with the relative difference.

Table 5 shows the verification results of the mixtures for carbon dioxide. The values for the excess standard deviation (τ) vary appreciably which is partly due to the low number of degrees of freedom on which they are based. The within-group standard uncertainty (σ) is very similar for each of the mixtures. All mixtures save D340045[1] pass on the basis of this calculation the verification criterion of ISO 6143 (see equation (3)). For the verification uncertainty in this key comparison, the pooled standard uncertainty of all verifications is used, which is 0.031 %. With this standard uncertainty, also D340045 meets the criterion of ISO 6143.

Table 6 summarises the verification results of the mixtures for carbon monoxide. All mixtures save 8451 E pass, based on the same calculations as used for carbon dioxide, the verification criterion of ISO 6143. As in the case of carbon dioxide, the values of the between-group standard deviation τ are appreciably different. For the verification uncertainty, the pooled standard uncertainty of all verifications is used, which is 0.038 %. With this standard uncertainty, all mixtures pass the criterion of ISO 6143.

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[1] For brevity, the same identifiers are used for the cylinder and the gas mixture.

Table 7 summarises the verification results of the mixtures for propane. All mixtures save MR8468 and 8457 E pass, based on the same calculations as used for carbon dioxide, the verification criterion of ISO 6143. As in the case of carbon dioxide, the values of the between-group standard deviation τ are appreciably different. For the verification uncertainty, the pooled standard uncertainty of all verifications is used, which is 0.035 %. With this standard uncertainty, all mixtures pass the criterion of ISO 6143.

Table 8 summarises the verification results of the mixtures for oxygen. All mixtures save D751979 and 8449 E pass, based on the same calculations as used for carbon dioxide, the verification criterion of ISO 6143. As in the case of carbon dioxide, the values of the between-group standard deviation τ are appreciably different. For the verification uncertainty, the pooled standard uncertainty of all verifications is used, which is 0.026 %. With this standard uncertainty, all mixtures pass the criterion of ISO 6143.

Table 5: Verification results for carbon dioxide, expressed as relative differences with respect to the amount fractions as calculated from preparation (%)

Cylinder	e_1	$u(e_1)$	e_2	$u(e_2)$	e_3	$u(e_3)$	e_4	$u(e_4)$	τ	σ	$\bar{e}$	$u(\bar{e})$
ML 6817	0.00	0.03	0.00	0.05	0.02	0.01	-0.04	0.02	0.02	0.03	-0.003	0.017
8500 E	-0.06	0.03	-0.10	0.04	0.00	0.01	0.08	0.01	0.07	0.03	-0.014	0.039
MR8468	0.09	0.02	-0.06	0.06	-0.08	0.01	-0.03	0.01	0.07	0.03	-0.018	0.040
D751979	0.03	0.03	0.07	0.05	-0.07	0.02	-0.02	0.02	0.05	0.03	-0.008	0.028
ML 6812	-0.03	0.04	-0.18	0.06	0.01	0.01	0.00	0.03	0.06	0.04	-0.033	0.035
9373 E	-0.06	0.03							0.00	0.03	-0.060	0.033
D340045	0.05	0.03	0.10	0.04	0.09	0.02	-0.01	0.02	0.05	0.03	0.054	0.026
8449 E	-0.05	0.04	-0.05	0.04	0.04	0.02	-0.02	0.01	0.03	0.03	-0.013	0.021
8451 E	-0.07	0.04	0.03	0.05	0.05	0.01	0.02	0.01	0.03	0.03	0.019	0.021
8457 E	0.11	0.03	-0.10	0.05	-0.04	0.01	-0.04	0.03	0.08	0.03	-0.015	0.044

Table 6: Verification results for carbon monoxide, expressed as relative differences with respect to the amount fractions as calculated from preparation (%)

Cylinder	e_1	$u(e_1)$	e_2	$u(e_2)$	e_3	$u(e_3)$	τ	σ	$\bar{e}$	$u(\bar{e})$
ML 6817	0.02	0.02	0.00	0.03	0.01	0.01	0.00	0.02	0.011	0.008
8500 E	-0.12	0.02	-0.16	0.02	0.03	0.01	0.10	0.02	-0.082	0.058
MR8468	0.01	0.02	-0.07	0.03	-0.04	0.01	0.03	0.02	-0.031	0.021
D751979	-0.03	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.003	0.010
ML 6812	-0.02	0.03	-0.18	0.02	0.01	0.03	0.10	0.02	-0.065	0.060
9373 E	0.04	0.02					0.03	0.01	0.016	0.020
D340045	-0.11	0.02	-0.07	0.02	0.02	0.01	0.07	0.02	-0.052	0.039
8449 E	-0.12	0.02	-0.11	0.03	0.03	0.02	0.08	0.02	-0.065	0.049
8451 E	-0.10	0.02	-0.06	0.02	-0.05	0.01	0.02	0.02	-0.067	0.016
8457 E	-0.02	0.03	-0.15	0.02	0.01	0.02	0.08	0.02	-0.054	0.050

Table 7: Verification results for propane, expressed as relative differences with respect to the amount fractions as calculated from preparation (%)

Cylinder	e_1	$u(e_1)$	e_2	$u(e_2)$	e_3	$u(e_3)$	τ	σ	$\bar{e}$	$u(\bar{e})$
ML 6817	-0.06	0.03	0.06	0.02			0.08	0.03	0.003	0.060
8500 E	-0.01	0.02	0.02	0.02			0.00	0.02	0.003	0.016
MR8468	-0.04	0.02	-0.04	0.02	-0.05	-0.01	0.00	0.02	-0.045	0.009
D751979	0.01	0.02	-0.02	0.02	-0.04	-0.01	0.02	0.01	-0.019	0.014
ML 6812	-0.07	0.02	0.14	0.02	0.03	0.01	0.10	0.02	0.034	0.060
9373 E	0.02	0.02					0.00	0.02	0.020	0.019
D340045	-0.04	0.02	0.01	0.02			0.03	0.02	-0.014	0.025
8449 E	-0.03	0.03	0.02	0.02			0.03	0.02	-0.004	0.025
8451 E	-0.08	0.02	0.03	0.02			0.07	0.02	-0.025	0.055
8457 E	-0.05	0.02	-0.02	0.02			0.00	0.02	-0.032	0.015

Table 8: Verification results for oxygen, expressed as relative differences with respect to the amount fractions as calculated from preparation (%)

Cylinder	e_1	$u(e_1)$	e_2	$u(e_2)$	τ	σ	$\bar{e}$	$u(\bar{e})$
ML 6817	0.01	0.02	-0.04	0.02	0.03	0.02	-0.014	0.025
8500 E	-0.03	0.02	-0.02	0.03	0.00	0.03	-0.026	0.017
MR8468	-0.05	0.03	-0.01	0.02	0.01	0.02	-0.029	0.020
D751979	-0.04	0.02	-0.02	0.02	0.00	0.02	-0.029	0.014
ML 6812	0.04	0.03	-0.02	0.02	0.03	0.02	0.004	0.029
9373 E	0.01	0.02			0.00	0.02	0.010	0.025
D340045	-0.01	0.02	0.02	0.02	0.00	0.02	0.005	0.016
8449 E	0.03	0.02	0.05	0.02	0.00	0.02	0.038	0.014
8451 E	0.05	0.02	0.00	0.02	0.03	0.02	0.022	0.025
8457 E	0.03	0.02	-0.07	0.02	0.07	0.02	-0.021	0.050

2.6 Measurement methods

The measurement methods used by the participants are described in annexes A-I of this 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.

2.7 Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as [13]

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

and the uncertainty of the difference d_i at 95 % level of confidence. Here $x_{i,\mathrm{KCRV}}$ denotes the key comparison reference value (the amount fraction from preparation, $x_{i,\mathrm{prep}}$), and x_i the result of laboratory i.[2] Appreciating the special conditions in gas analysis, it can be expressed as

$$\Delta x_i = d_i = x_i - x_{i,\mathrm{KCRV}}. \tag{6}$$

The standard uncertainty of d_i can be expressed as

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

$$u^2(d_i) = u^2(x_i) + u^2(x_{i,\mathrm{prep}}) + u^2(\Delta x_{i,\mathrm{ver}}), \tag{7}$$

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.

Table 9: Summary of calibration methods and metrological traceability

Laboratory	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
CERI	1-4 June, 7-11 June, 16-17 June and 19 June 2020	Bracketing	Own standards	Nitrogen	GC-FID and GC-TCD
INMETRO	13-15 May, 17-18 June, 01-02 July, 07 July and 16 July 2020	ISO 6143	Own standards (ISO 6142)	Nitrogen	GC-FID and GC-TCD
IPQ	14, 20, 21, 28 January; 11-13 and 26 February; 05, 09, and 10 March 2020	ISO 6143	Own standards (ISO 6142) and NPL and VSL standards	Nitrogen	GC-TCD, NDIR and Paramagnetism
KRISS	23-25 and 27 August, 01-02 September 2020	Single point calibration	Own standards (ISO 6142)	Nitrogen	GC-FID and GC-TCD
NIST	06-08, 14, 27 January, 04-05, 10-11, 26 February, 03 and 05 March 2020	ISO 6143	Own standards (ISO 6142)	Nitrogen	GC- FID and GC-TCD, Paramagnetism
NMISA	11, 18, 20 May, 03, 05-06 June and 02 September 2020	Single point calibration and multipoint calibration	Own standards (ISO 6142)	Nitrogen	GC- FID and GC-TCD, GC- μ-ECD
NPL	12, 16-17 March, 8,17,25 September, 02 October 2020	Bracketing	Own standards (ISO 6142)	Nitrogen	GC- FID and GC-TCD Paramagnetism
VNIIM	12-14 May, 04-05, 16,22 and 25 June 2020	Single point calibration	Own standards (ISO 6142)	Nitrogen	GC- FID and GC-TCD
VSL	21, 25, 28 February, 06, 10, 12, 16, 18, 31 March. 02,06 April and 18 May	ISO 6143	Own standards (ISO 6142)	Nitrogen	GC- FID and GC-TCD

3 Results

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

x_prep	amount fraction, from preparation (cmol mol^{-1})
u_prep	standard uncertainty of x_{prep} (cmol mol^{-1})
u_ver	standard uncertainty from verification (cmol mol^{-1})
u_KCRV	standard uncertainty of key comparison reference value (cmol mol^{-1})
x_lab	result of laboratory (cmol mol^{-1})
U_lab	stated uncertainty of laboratory, at 95 % level of confidence (cmol mol^{-1})
k_lab	stated coverage factor

d	difference between laboratory result and reference value (cmol mol^{-1})
k	assigned coverage factor for degree of equivalence
$U(d)$	Expanded uncertainty of difference d_i, at 95 % level of confidence[3] (cmol mol^{-1})

Table 10 shows the results for the amount fraction carbon dioxide. All results are consistent with the key comparison reference value. The degrees of equivalence are plotted in Figure 1.

Table 11 shows the results for the amount fraction carbon monoxide. All results, save those of INEMTRO are consistent with the key comparison reference value. The degrees of equivalence are plotted in Figure 2.

Table 10: Results for the amount fraction carbon dioxide

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{KCRV}	x_{lab}	U_{lab}	k_{lab}	d	k	$U(d)$
VSL	8457 E	2.0138	0.0004	0.0006	0.0008	2.0153	0.0020	2	0.0015	2	0.0025
CERI	8451 E	1.9846	0.0004	0.0006	0.0008	1.983	0.005	2	-0.0016	2	0.0052
INMETRO	ML 6812	1.9993	0.0004	0.0006	0.0008	1.9930	0.010	2	-0.0063	2	0.0101
IPQ	ML 6817	1.9951	0.0004	0.0006	0.0008	1.9937	0.004	2	-0.0014	2	0.0043
KRISS	D751979	1.9731	0.0004	0.0006	0.0008	1.9726	0.0048	2	-0.0005	2	0.0050
NIST	MR8468	2.0018	0.0004	0.0006	0.0008	2.0001	0.0037	2	-0.0017	2	0.0040
NMISA	D340045	1.9965	0.0004	0.0006	0.0008	1.9945	0.0085	2	-0.0020	2	0.0086
NPL	8500 E	1.9998	0.0004	0.0006	0.0008	2.0024	0.0031	2	0.0026	2	0.0035
VNIIM	8449 E	2.0025	0.0004	0.0006	0.0008	2.0019	0.002	2	-0.0006	2	0.0025

Table 11: Results for the amount fraction carbon monoxide

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{KCRV}	x_{lab}	U_{lab}	k_{lab}	d	k	$U(d)$
VSL	8457 E	1.0162	0.0002	0.0004	0.0004	1.0155	0.0012	2	-0.0007	2	0.0015
CERI	8451 E	1.0026	0.0002	0.0004	0.0004	1.0021	0.0029	2	-0.0005	2	0.0030
INMETRO	ML 6812	1.0052	0.0002	0.0004	0.0004	0.999	0.004	2	-0.0062	2	0.0041
IPQ	ML 6817	1.0135	0.0002	0.0004	0.0004	1.0130	0.0038	2	-0.0005	2	0.0039
KRISS	D751979	1.0100	0.0002	0.0004	0.0004	1.0106	0.0032	2	0.0006	2	0.0033
NIST	MR8468	1.0033	0.0002	0.0004	0.0004	1.0030	0.0040	2	-0.0003	2	0.0041
NMISA	D340045	1.0010	0.0002	0.0004	0.0004	1.0012	0.0029	2	0.0002	2	0.0030
NPL	8500 E	0.9939	0.0002	0.0004	0.0004	0.9946	0.0019	2	0.0007	2	0.0020
VNIIM	8449 E	1.0007	0.0002	0.0004	0.0004	1.0000	0.0016	2	-0.0007	2	0.0018

---

[3] As defined in the MRA [14], a degree of equivalence is given by d and $U(d)$.

Table 12 the results for the amount fraction propane are shown. All results, save those from INMETRO and IPQ are consistent with the key comparison reference value. The degrees of equivalence are plotted in Figure 3.

Table 13 shows the results for the amount fraction oxygen. Two results are discrepant with respect to the key comparison reference value: those from INMETRO and VNIIM. The degrees of equivalence are plotted in Figure 4.

Table 12: Results for the amount fraction propane

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{KCRV}	x_{lab}	U_{lab}	k_{lab}	d	k	$U(d)$
VSL	8457 E	0.020327	0.000005	0.000007	0.000009	0.020310	0.000020	2	-0.000017	2	0.000027
CERI	8451 E	0.020017	0.000005	0.000007	0.000009	0.02000	0.00004	2	-0.000017	2	0.000044
INMETRO	ML 6812	0.020163	0.000005	0.000007	0.000009	0.02002	0.00011	2	-0.000143	2	0.000111
IPQ	ML 6817	0.019981	0.000005	0.000007	0.000009	0.02060	0.00014	2	0.000619	2	0.000141
KRISS	D751979	0.019665	0.000005	0.000007	0.000009	0.01967	0.00004	2	0.000002	2	0.000043
NIST	MR8468	0.019954	0.000005	0.000007	0.000009	0.019962	0.000028	2	0.000008	2	0.000033
NMISA	D340045	0.019986	0.000005	0.000007	0.000009	0.02003	0.00013	2	0.000044	2	0.000131
NPL	8500 E	0.020116	0.000005	0.000007	0.000009	0.02010	0.00002	2	-0.000016	2	0.000026
VNIIM	8449 E	0.019868	0.000005	0.000007	0.000009	0.019877	0.000038	2	0.000009	2	0.000042

Table 13: Results for the amount fraction oxygen

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{KCRV}	x_{lab}	U_{lab}	k_{lab}	d	k	$U(d)$
VSL	8457 E	2.8924	0.0006	0.0008	0.0010	2.8938	0.0023	2	0.0014	2	0.0030
CERI	8451 E	3.0080	0.0006	0.0008	0.0010	3.006	0.004	2	-0.0020	2	0.0045
INMETRO	ML 6812	2.9606	0.0006	0.0008	0.0010	2.923	0.016	2	-0.0376	2	0.0161
IPQ	ML 6817	2.9698	0.0006	0.0008	0.0010	2.971	0.013	2	0.0012	2	0.0131
KRISS	D751979	3.0649	0.0006	0.0008	0.0010	3.0687	0.0100	2	0.0038	2	0.0102
NIST	MR8468	2.9833	0.0006	0.0008	0.0010	2.9783	0.0048	2	-0.0050	2	0.0052
NMISA	D340045	3.0016	0.0006	0.0008	0.0010	3.001	0.012	2	-0.0006	2	0.0122
NPL	8500 E	3.0137	0.0006	0.0008	0.0010	3.0136	0.0043	2	-0.0001	2	0.0048
VNIIM	8449 E	3.0116	0.0006	0.0008	0.0010	3.0071	0.0031	2	-0.0045	2	0.0037

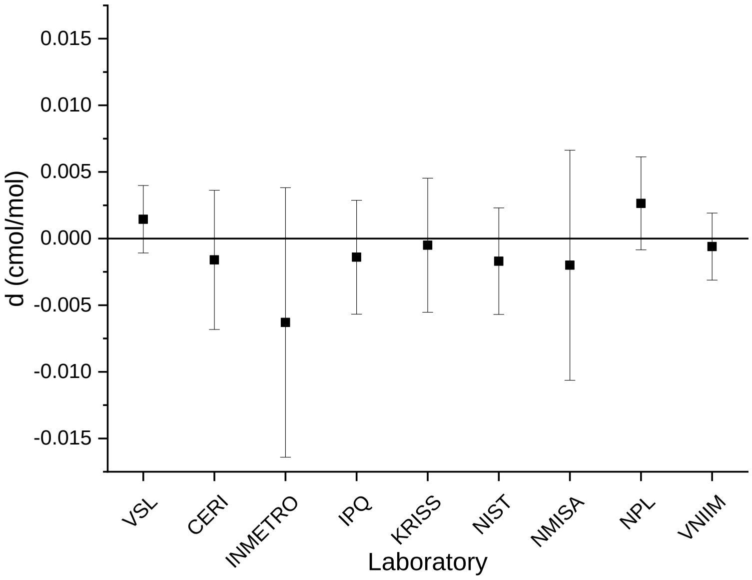

Figure 1: Degrees of equivalence for the amount fraction carbon dioxide at 2 cmol mol^{-1}

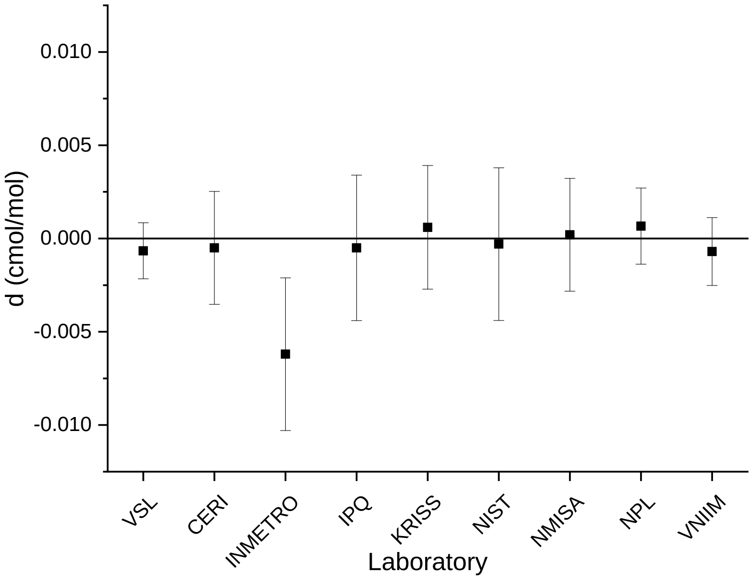

Figure 2: Degrees of equivalence for the amount fraction carbon monoxide at 1 cmol mol^{-1}

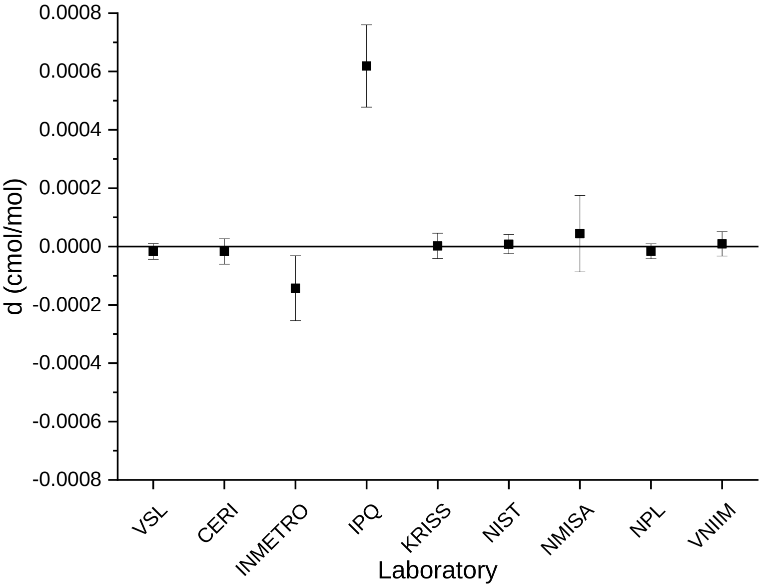

Figure 3: Degrees of equivalence for the amount fraction propane at 0.02 cmol mol^{-1}

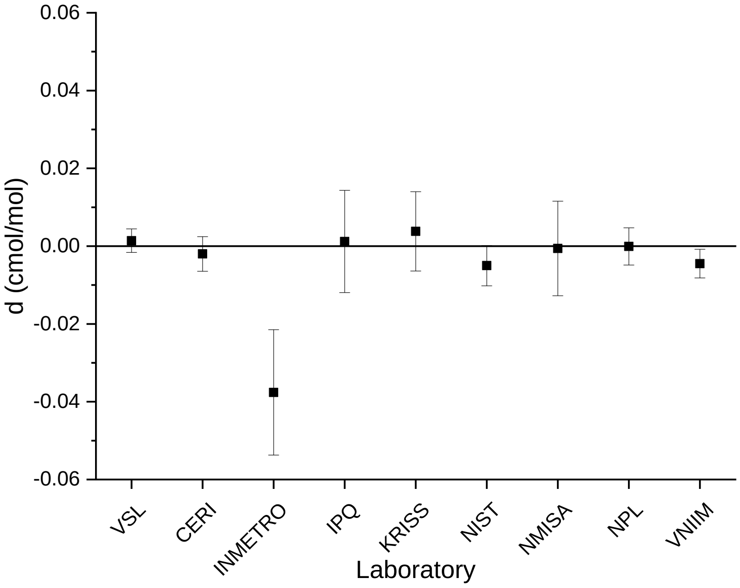

Figure 4: Degrees of equivalence for the amount fraction oxygen at 3 cmol mol^{-1}

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”.

5 Discussion and conclusions

The results in this key comparison show generally good agreement. Most results agree within 0.2 % relative of the key comparison reference value. The deviations and the stated expanded uncertainties are generally larger than for the corresponding binary mixtures in previous track A key comparisons (e.g., CCQM-K120 Carbon dioxide, CCQM-K111 Propane, CCQM-K51 Carbon monoxide).

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Project reference

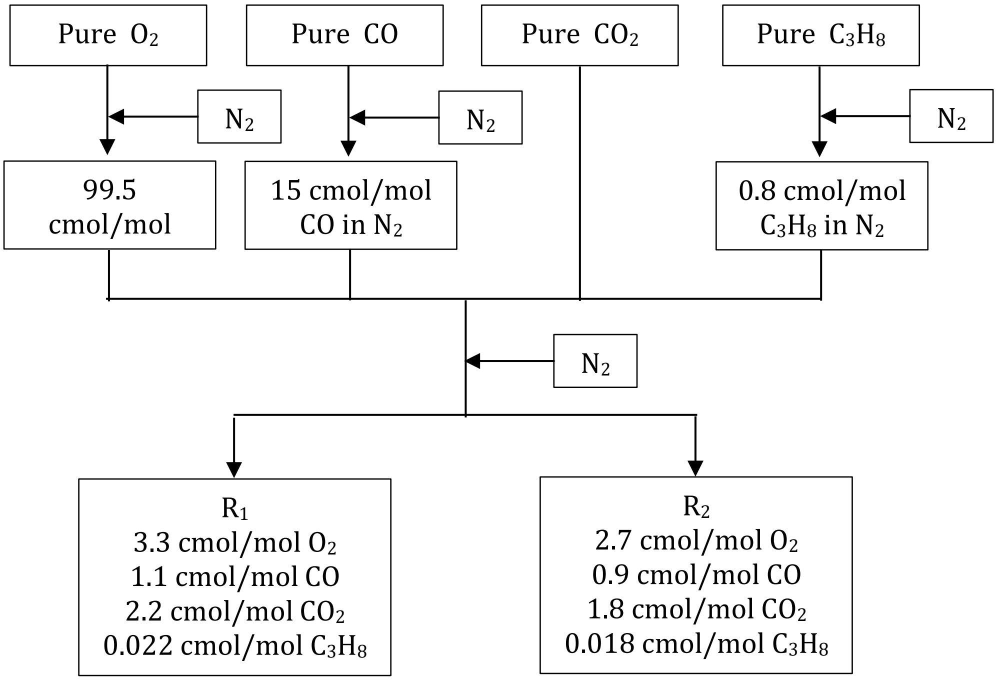
CCQM-K3.2019

Completion date

December 2021

Annex A Measurement report of CERI

A.1 Calibration standards



R_1

1) Evacuated cylinder - Tare cylinder : 3.796 g
2) Cylinder filled with pure CO_2 - Tare cylinder : 22.421 g
3) Cylinder filled with 99.5 cmol/mol O_2 in N_2 - Tare cylinder : 42.298 g
4) Cylinder filled with 0.8 cmol/mol C_3H_8 in N_2 - Tare cylinder : 56.938 g
5) Cylinder filled with 15 cmol/mol CO in N_2 - Tare cylinder : 95.357 g
6) Cylinder filled with nitrogen - Tare cylinder : 545.918 g

R_2

1) Evacuated cylinder - Tare cylinder : 3.884 g
2) Cylinder filled with pure CO_2 - Tare cylinder : 21.053 g
3) Cylinder filled with 99.5 cmol/mol O_2 in N_2 - Tare cylinder : 39.125 g
4) Cylinder filled with 0.8 cmol/mol C_3H_8 in N_2 - Tare cylinder : 53.459 g
5) Cylinder filled with 15 cmol/mol CO in N_2 - Tare cylinder : 88.536 g
6) Cylinder filled with nitrogen - Tare cylinder : 629.866 g

Purity table of oxygen

Analyte	Mole fraction	Standard uncertainty

i	µmol/mol	µmol/mol
N_2	6	1.73
Ar	3	0.866
CO	0.1	0.0289
CO_2	0.1	0.0289
Total hydro carbon (THC)	0.1	0.0289
O_2	999990.7	1.94

Purity table of carbon monoxide

Analyte *i*	Mole fraction µmol/mol	Standard uncertainty µmol/mol
H_2	2.69	0.20
He	27.5	1.58
N_2	1.52	0.88
O_2	0.52	0.30
CO_2	0.42	0.24
H_2O	1.47	0.85
CO	999965.9	2.05

Purity table of carbon dioxide

Analyte *i*	Mole fraction µmol/mol	Standard uncertainty µmol/mol
N_2	0.87	0.50
O_2	0.43	0.25
CH_4	0.0048	0.0028
H_2	0.89	0.51
H_2O	4.5	2.6
CO_2	999993.3	2.7

Purity table of propane

Analyte *i*	Mole fraction µmol/mol	Standard uncertainty µmol/mol

N_2	2.3	1.3
O_2	1.8	1.0
Ar	2.8	1.6
CO_2	2.8	1.6
ethane	3.8	2.2
propylene	30.6	0.2
cyclopropane	2.5	1.4
butane	1.9	1.1
isobutane	1.9	1.1
H_2O	66.2	18
C_3H_8	999883.4	18.5

Purity table of N_2

Analyte *i*	Mole fraction μmol/mol	Standard uncertainty μmol/mol
O_2	0.05	0.02890
Ar	0.5	0.2890
CO	0.005	0.002890
CO_2	0.005	0.002890
Total hydro carbon (THC)	0.005	0.002890
SO_2	0.0025	0.001443
NOx	0.0025	0.001443
N_2	999999.43	0.2905

We prepared gas standards for verification. Theirs concentrations were intermediate between R_1 and R_2. The gas standards were evaluated by GC-TCD and GC-FID. Deviation of gravimetric value and measured value is one of the uncertainty sources.

A.2 Instrumentation

Instruments for O_2 and CO measurement

GC-TCD (Type: GC-2014, Make: Shimadzu corporation)
Column: Molecular Sieve 5A in stainless column (3m, 3 mm i.d)
+ Porapak Q in stainless column (1m, 3 mm i.d)

Instruments for CO_2 measurement

GC-TCD (Type: 7890B, Make: Agilent Technologies)
Column: Porapak N in stainless column (5m, 3 mm i.d)

Instruments for C_3H_8 measurement

GC-FID (Type: 7890A, Make: Agilent Technologies)
Column: Porapak Q in stainless column (3m, 3 mm i.d)

A.3 Calibration method and value assignment

The instruments were calibrated using two gravimetrically prepared standards. Analytical scheme was, R_1 – CCQM sample – R_2 or R_2 – CCQM sample – R_1. This scheme was repeated 3-times in a day and iterated for 5 days.

Concentrations of standards:

Component	Concentration (cmol/mol)	
	R_1	R_2
O_2	3.252	2.551
CO	1.0975	0.8647
CO_2	2.225	1.770
C_3H_8	0.02185	0.01846

The concentrations of CCQM sample were calculated using the formula below.

$$Y = \frac{A(E-D)+B(C-E)}{(C-D)}$$

where *Y*: Concentration of sample
A: Concentration of standard (R_1)
B: Concentration of standard (R_2)

C: Standard (R_1) peak area
D: Standard (R_2) peak area
E: Sample peak area

A.4 Uncertainty evaluation

Oxygen

Uncertainty source	Estimate $u(x_i)$	Assumed distribution	Standard uncertainty $U(x_i)$
Gas standards	0.0003725	Normal	0.0003725
Verification	0.0004	Normal	0.0004
Measurement	0.0002009	Normal	0.0002009

Combined uncertainty	0.0005824	(rel.)
Expanded uncertainty (*k*=2)	0.001165	(rel.)
Expanded uncertainty (*k*=2)	0.004	cmol mol^{-1}

Carbon monoxide

Uncertainty source	Estimate $u(x_i)$	Assumed distribution	Standard uncertainty $U(x_i)$
Gas standards	0.001009	Normal	0.001009
Verification	0.0009	Normal	0.0009
Measurement	0.0004810	Normal	0.0004810

Combined uncertainty	0.001435	(rel.)
Expanded uncertainty (*k*=2)	0.002870	(rel.)
Expanded uncertainty (*k*=2)	0.0029	cmol mol^{-1}

Carbon dioxide

Uncertainty source	Estimate $u(x_i)$	Assumed distribution	Standard uncertainty $U(x_i)$
Gas standards	0.0003306	Normal	0.0003306
Verification	0.001	Normal	0.001
Measurement	0.0004703	Normal	0.0004703

Combined uncertainty	0.001153	(rel.)
Expanded uncertainty (*k*=2)	0.002307	(rel.)
Expanded uncertainty (*k*=2)	0.005	cmol mol^{-1}

Propane

Uncertainty source	Estimate $u(x_i)$	Assumed distribution	Standard uncertainty $U(x_i)$
Gas standards	0.0007623	Normal	0.0007623
Verification	0.0005	Normal	0.0005
Measurement	0.0001072	Normal	0.0001072

Combined uncertainty	0.0009179	(rel.)
Expanded uncertainty (*k*=2)	0.001836	(rel.)
Expanded uncertainty (*k*=2)	0.00004	cmol mol^{-1}

Annex B Measurement report of INMETRO

B.1 Results

Cylinder number: ML6812

Measurement #1

Component	**Date (dd/mm/yy)**	**Result (cmol/mol)**	**Standard deviation (%relative)**	**Number of replicates**
Carbon monoxide	13/05/2020	0.997	0.15	5
Carbon dioxide	13/05/2020	1.987	0.19	5
Propane	13/05/2020	0.01982	0.10	5
Oxygen	01/07/2020	2.939	0.12	8

Measurement #2

Component	**Date (dd/mm/yy)**	**Result (cmol/mol)**	**Standard deviation (%relative)**	**Number of replicates**
Carbon monoxide	14/05/2020	0.999	0.14	5
Carbon dioxide	14/05/2020	1.996	0.22	5
Propane	14/05/2020	0.02007	0.10	5
Oxygen	02/07/2020	2.912	0.14	8

Measurement #3

Component	**Date (dd/mm/yy)**	**Result (cmol/mol)**	**Standard deviation (%relative)**	**Number of replicates**
Carbon monoxide	15/05/2020	1.000	0.14	5
Carbon dioxide	15/05/2020	1.996	0.19	5
Propane	15/05/2020	0.02011	0.10	5
Oxygen	07/07/2020	2.906	0.15	8

Measurement #4

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (%relative)	Number of replicates
Carbon monoxide	-----	-----	-----	-----
Carbon dioxide	-----	-----	-----	-----
Propane	17/06/2020	0.02003	0.13	5
Oxygen	16/07/2020	2.934	0.11	8

Measurement #5

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (%relative)	Number of replicates
Carbon monoxide	-----	-----	-----	-----
Carbon dioxide	-----	-----	-----	-----
Propane	18/06/2020	0.02005	0.08	6
Oxygen	-----	-----	-----	-----

Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
Carbon monoxide	0.999	0.004	2
Carbon dioxide	1.993	0.010	2
Propane	0.02002	0.00011	2
Oxygen	2.923	0.016	2

B.2 Calibration standards

Inmetro used maximum 8 own certified mixtures (table 1) for the calibration curve for automotive emissions except for the component oxygen. It was also prepared and used 5 new binary mixtures of oxygen in nitrogen specific for the comparison concentration range (table 2). All standards were prepared individually according to ISO 6142 “Gas analysis - Preparation of calibration gases - Gravimetric Method”.

Table 14. Calibration standards prepared by Inmetro

Cylinder number	PSM116123		PSM126797		PSM102259	
Component	**Certified value (x) cmol/mol**	**Standard uncertainty (u(x)) cmol/mol**	**Certified value (x) cmol/mol**	**Certified uncertainty (u(x)) cmol/mol**	**Certified value (x) cmol/mol**	**Certified uncertainty (u(x)) cmol/mol**
Carbon monoxide	0.10	0.0005	0.3920	0.0015	0.5850	0.0025

Carbon dioxide	9.98	0.06	13.83	0.08	3.52	0.02
Propane	0.010	000005	0,024455	0,000423	0.019608	0.000065
Cylinder number	**PSM117524**		**PSM102247**		**PSM113670**	
Component	**Certified value (x) cmol/mol**	**Certified uncertainty (u(x)) cmol/mol**	**Certified value (x) cmol/mol**	**Certified uncertainty (u(x)) cmol/mol**	**Certified value (x) cmol/mol**	**Certified uncertainty (u(x)) cmol/mol**
Carbon monoxide	1.9970	0.0055	2.462	0.006	4.986	0.017
Carbon dioxide	12.01	0.05	7.39	0.03	15.0	0.085
Propane	0.100130	0.000288	0.073902	0.000276	0.050077	0.000244
Cylinder number	**PSM102273**		**PSM102267**			
Component	**Certified value (x) cmol/mol**	**Certified uncertainty (u(x)) cmol/mol**	**Certified value (x) cmol/mol**	**Certified uncertainty (u(x)) cmol/mol**		
Carbon monoxide	0.2601	0.0005	1.0015	0.0020		
Carbon dioxide	1.536	0.008	2.001	0.046		
Propane	0.007970	0.000053	0.029175	0.000136		

Table 2. Calibration standards of Oxygen prepared by Inmetro

Cylinder number	**PSM153638**		**PSM113644**		**PSM117586**	
Component	**Gravimetric value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**	**Gravimetric value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**	**Gravimetric value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**
Oxygen	1.9995	0.0001	2.5078	0.0002	2.9999	0.0002
Cylinder number	**PSM113807**		**PSM117509**			
Component	**Gravimetric value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**	**Gravimetric value (x) cmol/mol**	**Gravimetric uncertainty (u(x)) cmol/mol**		
Oxygen	4.0008	0.0002	4.9876	0.0002		

B.3 Instrumentation

For the measurement of the automotive emissions mixture 2 equipment’s where used:

1) Micro GC (Agilent) for the binary oxygen mixtures

Model: 4900

Channel 1. 10m MS5A Heated Injector, Backflush

Carrier: Argon

2) GC CP-3800sp (Varian) for the multicomponent certified mixtures

The GC-NGA is equipped with a 12 ports Multi Position Valve (MPV). The system is divided in 2 channels: the Flame Ionization Detector (FID) channel and the Thermal Conductivity Detector (TCD) channel. Injections on both channels are done via a Gas Sampling Valve (GSV). The carrier is Helium.

TCD Channel:

10 port switching valve, 6 Port switching valve, Hayesep T column. Mesh 80-100, l: 0.5m, id: 2 mm; Hayesep Q column. Mesh 80-100, l: 0.5m, id: 2mm; Molsieve 13x column, Mesh 80-1000l: 1.5m, id: 2mm;

FID Channel:

CP-1177 Split/split less injector, CP-Sil 5CB column, WCOT silica, l: 60 m, id: 0.25 mm.

B.4 Calibration method and value assignment

The sample and calibration standards were connected to a reducer and after flushing connected to the multi position valve. Every line was flushed separately and the flow for each mixture was set equally. For all the measurements the reducers were disconnected and connected to a different cylinder. Also a different position on the multiposition valve was used to connect the cylinder. The flushing and setting of the flow was done equal to the first measurement. Every mixture was injected 7 times and the first 2 injections was dictated for the GC CP-3800sp. For the micro-GC every mixture was injected 10 times and the first 2 injections was dictated.

The calibration of the instrument was done according to ISO 6143. The calibration curve was made using the software XLgenline and Curve Fit. The goodness of fit for all measurements was lower than 2. A 2nd order model was used for all the components as calibration function.

B.5 Uncertainty evaluation

The uncertainty was calculated according to ISO 6143 using the software XLgenline and Curve Fit. Three sources of uncertainty were considered:

- Uncertainty of the standards (certificate – type B)
- Uncertainty of the area (analysis – type A)
- Uncertainty of the reproducibility (analysis – type A)

The associated uncertainty is obtained using the law of propagation of uncertainty. To arrive at the final result, the results of all measurements done were averaged. The standard error of the mean was combined with the pooled uncertainty from evaluating the data.

The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95%.

References

[1] International Organization for Standardization, "ISO 6142-1:2015(E) – Gas analysis -- Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures", ISO Geneva, 2015

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Annex C Measurement report of IPQ

C.1 Results

Cylinder code: 6817

Measurement	**1**				
Component	Date	Fraction (cmol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (cmol/mol)
Oxygen	2020-01-14	2.973	0.20%	3	0.011
Carbon dioxide	2020-02-11	1.9934	0.01%	3	0.0034
Propane	2020-03-05	0.02064	0.60%	3	0.00013
Carbon monoxide	2020-01-28	1.0131	0.30%	3	0.0026

Measurement	**2**				
Component	Date	Fraction (cmol/mol)	Rel. std. deviation	Number of replicates	Standard uncertainty (cmol/mol)
Oxygen	2020-01-20	2.973	0.01%	3	0.012
Carbon dioxide	2020-02-12	1.9934	0.01%	3	0.0034
Propane	2020-03-09	0.02059	0.20%	3	0.00010
Carbon monoxide	2020-02-10	1.0124	0.20%	3	0.0019

Measurement	**3**				
Component	Date	Fraction (cmol/mol)	Rel. std. deviation	Number of replicates	Standard uncertainty (cmol/mol)
Oxygen	2020-01-21	2.968	0.05%	3	0.011
Carbon dioxide	2020-02-13	1.9943	0.01%	3	0.0035
Propane	2020-03-10	0.02057	0.20%	3	0.00010
Carbon monoxide	2020-02-26	1.0135	0.20%	3	0.0016

Results			
Component	Fraction (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
Oxygen	2.971	0.013	2.0
Carbon dioxide	1.9937	0.004	2.0
Propane	0.0206	0.00014	2.0
Carbon monoxide	1.013	0.0038	2.0

C.2 Calibration standards

Method of preparation and Weighing data

The Calibration Standards were prepared according to ISO 6142-1:2015 – Gravimetric Method and certified according to ISO 6143:2001.

The measurement uncertainty evaluation was done according to GUM: 1995 “Guide to the Expression of Uncertainty in Measurement”.

Purity tables (composition) of the parent gases

Purity Table for nominally pure N_2

Component	Method	Mole Fraction (mol/mol)
N_2	specification	> 99,9999 x10^{-2}
H_2O	specification	< 0,5 x10^{-6}
O_2	specification	< 0,1 x10^{-6}
C_nH_m	specification	< 0,1 x10^{-6}
CO	specification	< 0,1 x10^{-6}
CO_2	specification	< 0,1 x10^{-6}
H_2	specification	< 0,1 x10^{-6}

Purity Table for nominally pure CO

Component	Method	Mole Fraction (mol/mol)
CO	specification	> 99,9971 x10^{-2}
N_2	specification	< 10,0 x10^{-6}
Ar	specification	< 7,00 x10^{-6}
CO_2	specification	< 1,00 x10^{-6}
H_2O	specification	< 3,00 x10^{-6}
H_2	specification	< 1,00 x10^{-6}
O_2	specification	< 5,00 x10^{-6}
C_nH_m	specification	< 2,00 x10^{-6}

Purity Table for nominally pure CO_2

Component	Method	Mole Fraction (mol/mol)
CO_2	specification	> 99,9987 x10^{-2}
N_2	specification	< 5,0 x10^{-6}
CO	specification	< 1,0 x10^{-6}
H_2O	specification	< 3,0 x10^{-6}
O_2	specification	< 3,0 x10^{-6}
C_nH_m	specification	< 1,0 x10^{-6}

Purity Table for nominally pure C_3H_8

Component	**Method**	**Mole Fraction (mol/mol)**
C_3H_8	specification	> 99,9500 x10^{-2}
N_2	specification	< 40 x10^{-6}
CO_2	specification	< 5,0 x10^{-6}
H_2O	specification	< 5,0 x10^{-6}
H_2	specification	< 40 x10^{-6}
O_2	specification	< 10 x10^{-6}
C_3H_6	specification	< 200 x10^{-6}
C_nH_m	specification	< 200 x10^{-6}

Purity Table for nominally pure O_2

Component	**Method**	**Mole Fraction (mol/mol)**
O_2	specification	> 99,9997 x10^{-2}
H_2O	specification	< 3,0 x10^{-6}
C_nH_m	specification	< 0,5 x10^{-6}

Verification measures

Cylinder	Component	Assigned value (x) (mol/mol)	Expanded Uncertainty (U(x)) (mol/mol)
VSL6189	CO	1,001 x10^{-3}	2,0 x10^{-6}
PSM105403	CO	5,014 x10^{-3}	2,6 x10^{-5}
PSM108952	CO	6,998 x10^{-3}	2,4 x10^{-5}
VSL4802	CO	1,0003 x10^{-2}	1,0 x10^{-5}
VSL4690	C_3H_8	5,000 x10^{-5}	1,5 x10^{-7}
PSM403404	C_3H_8	5,005 x10^{-5}	2,7 x10^{-7}
PSM202513	C_3H_8	1,0189 x10^{-4}	7,0 x10^{-7}
PSM308339	C_3H_8	6,145 x10^{-4}	3,2 x10^{-6}
NPL1804	CO_2	1,0000 x10^{-2}	4,1 x10^{-5}
NMI2689	CO_2	1,7510 x10^{-2}	7,1 x10^{-5}
PSM503640	CO_2	2,0011 x10^{-2}	8,2 x10^{-5}

NMI3638	CO_2	2,499 x10^{-2}	1,1 x10^{-4}
NPL5901	CO_2	3,000 x10^{-2}	1,3 x10^{-4}
VSL3704	O_2	4,998 x10^{-3}	1,0 x10^{-5}
VSL8612	O_2	1,003 x10^{-2}	1,9 x10^{-4}
PSM308345	O_2	2,999 x10^{-2}	3,0 x10^{-4}
PRM012763	O_2	9,939 x10^{-2}	2,5 x10^{-4}
PSM205429	O_2	9,996 x10^{-2}	7,1 x10^{-4}

C.3 Instrumentation

A Gas Chromatograph was used for carbon monoxide and propane analyses.

GC: HP 5890

Columns: Porapak Q, 80/100 Mesh, 10 ft, 0,125 inch OD Stainless

Molecular Sieve 5A, 45/60 Mesh, 10 ft, 0,125 inch OD Stainless

Detector: 1 Thermal Conductivity Detector (TCD)

Valves: System of two valves

Sample introduction: Multi position gas sampling valves.

Oven Temperature: 160 ºC (propane) and 150 ºC (carbon monoxide)

Carrier: He

Data Collection: Agilent Chemstation Plus program.

A Non Dispersive Infrared Analyser (NDIR - Uras 26) was used for carbon dioxide analyses.

Sample introduction: Multi position gas sampling valves.

Data Collection: Software Sira version 1.0.

A Paramagnetic Analyser (Magnos 16) was used for oxygen analyses.

Sample introduction: Multi position gas sampling valves.

Data Collection: Software Sira version 2.0.

C.4 Calibration method and value assignment

The certification was done according to ISO 6143:2001 through a calibration curve. We used the XGenline V8.1 program (NPL) to fit the best model for data handling. All components of mixture have a goodness of fit less than 2 using a linear or quadratic function.

For Carbon Monoxide (CO) was used a set of four PSM (from IPQ and VSL).

For Propane (C_3H_8) was used a set of four PSM (from IPQ and VSL).

For Carbon Dioxide (CO_2) was used a set of five PSM (from IPQ and NPL).

For Oxygen (O_2) was used a set of five PSM (from IPQ and VSL).

C.5 Uncertainty evaluation

The measurement uncertainty evaluation was done according to GUM: 1995 "Guide to the Expression of Uncertainty in Measurement".

The uncertainty of each run was obtained according to ISO 6143 (XGenline V8.1 (NPL)).

The potential sources that influence the uncertainty of the final measurement result:

a. Uncertainty related to the repeatability
b. Uncertainties related to the Reproducibility
c. Uncertainties related to the Calibration

These standard uncertainties were combined and then the combined uncertainty was multiplied by the Coverage factor for a confidence interval of 95 %, to calculate the expanded uncertainty.

References

[1] ISO 6142-1:2015 – "Gas Analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures";

[2] ISO 6143:2001 – "Gas Analysis – Comparison methods for determination and checking the composition of calibration gas mixtures";

[3] ISO 17034:2016 - General requirements for the competence of reference material producers;

[4] D. C. Montgomery, Introduction to Statistical Quality Control, Singapore: John Wiley & Sons, 3rd ed., ISBN 0-471-51988-X, 485-524 (1996);

[6] ISO 11095:1996, Linear calibration using reference materials. Switzerland: ISO. 29 p.;

[7] Guide to the expression of uncertainty in measurement. ISO, Geneva (1993). (Reprinted 1995: Reissued as ISO Guide 98-3 (2008), JCGM 100:2008;

[8] ISO Guide 35:2017 – Reference materials – General and statistical principles for certification.

Annex D Measurement report of KRISS

D.1 Results

VSL Cylinder: #D751979

Pressure: 65 Bar

Results:

Component	Results (x) cmol/mol	expanded unc. (U) cmol/cmol, k = 2	Coverage factor
C_3H_8	0.019667	0.000040	2
CO	1.0106	0.0032	2
CO_2	1.9726	0.0048	2
O_2	3.0687	0.0100	2

D.2 Calibration standards

Method of preparation: Gravimetry by ISO 6142[1]

We prepared our own standards for calibration. The details of the calibration standards (primary reference material) used for this comparison are described followings;

Table 1: uncertainty budget for reference values of gravimetric standards: D769658 (A-4)

Cylinder Identification Number	Manufactured value	component	prep. Value [cmol/mol]	Preparation Uprep [µmol/mol]	Verification Uver [µmol/mol]	Combined Ucomb [µmol/mol]	Coverage Factor
D769658 (A-4)	Jul. 25, 2019	C_3H_8	0.020633	0.04	0.21	0.20	k = 2
		CO	1.23515	1.1	12.4	12.4	k = 2
		CO_2	3.51890	1.7	35.2	35.2	k = 2
		O_2	2.33699	2.4	35.1	35.2	k = 2

Table 2: uncertainty budget for reference values of gravimetric standards: D769672 (A-3)

Cylinder Identification Number	Manufactured value	component	prep. Value [cmol/mol]	Preparation Uprep [µmol/mol]	Verification Uver [µmol/mol]	Combined Ucomb [µmol/mol]	Coverage Factor
D769672 (A-3)	Jul. 25, 2019	C_3H_8	0.020515	0.04	0.21	0.21	k = 2
		CO	1.25354	1.2	12.5	12.6	k = 2
		CO_2	3.50564	2.1	35.1	35.2	k = 2
		O_2	2.49531	2.7	37.4	37.5	k = 2

Table 3: uncertainty budget for reference values of gravimetric standards: D769664 (C-3)

Cylinder Identification Number	Manufactured value	component	prep. Value [cmol/mol]	Uncertainty of Preparation Uprep [µmol/mol]	Uncertainty of verification Uver [µmol/mol]	Combined Ucomb [µmol/mol]	Coverage Factor
D769664 (C-3)	Jul. 25, 2019	C_3H_8	0.030308	0.05	0.30	0.30	k = 2
		CO	0.49159	0.8	4.9	5.0	k = 2
		CO_2	2.01146	1.5	20.1	20.2	k = 2
		O_2	3.98530	2.0	59.9	59.9	k = 2

Weighing data (cylinder tree)

A set of primary standard gas mixtures (PSMs) was gravimetrically prepared for this comparison. All source reagents were analyzed to determine their purities. The PSMs were prepared by 1-3 times dilution with nitrogen from cmol/mol to several hundred µmol/mol (Figure 1). The PSMs at each stage were analyzed against each other for verification.

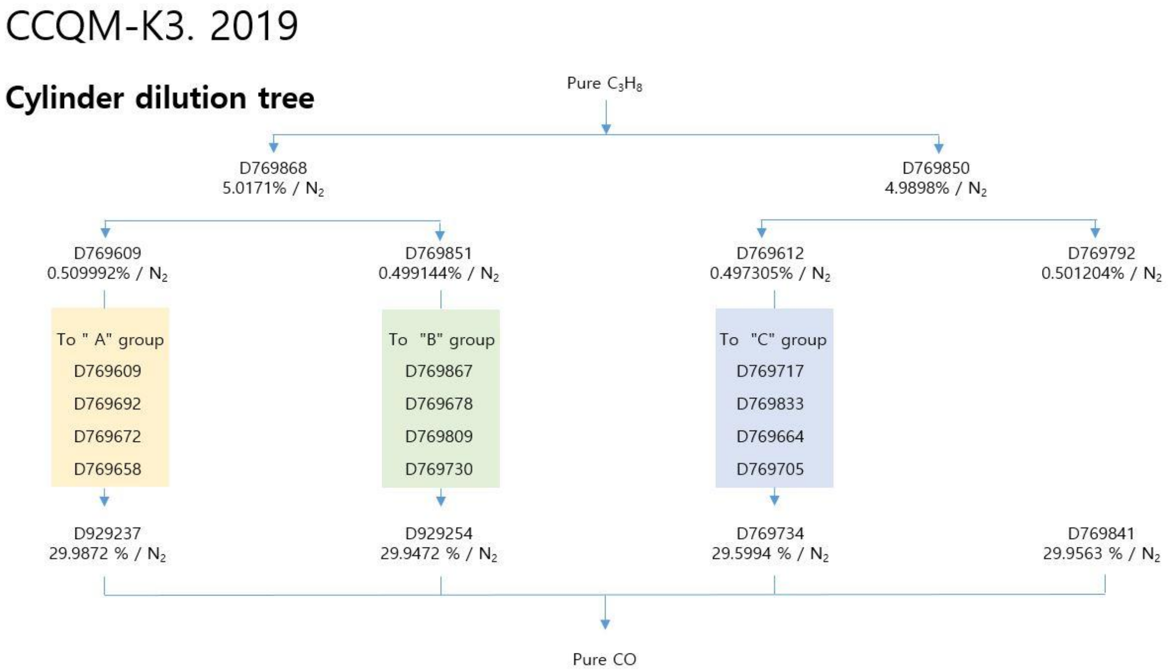


Figure 5. Brief outline of the dilution series for this comparison.

Purity tables (composition) of the parent gases:

a purity table of raw CO_2 gas;

cylinder number : ENKB 12781

component	value (cmol/mol)	detector	Distribution	Amount of mole fraction (cmol/mol)	Standard uncertainty (cmol/mol, *k* = 1)
H_2	0.000026	GC/TCD	Rectangular	1.31E-05	7.55E-06
O_2	0.0000257	Galvanic Sensor oxygen analyzer	Normal	2.57E-05	2.57E-06
Ar	0.000081	GC/TCD	Normal	8.06E-05	8.06E-06
CO	0.000175	GC/FID	Normal	1.75E-04	1.75E-05
N_2	0.000487	GC/TCD	Normal	4.87E-04	4.87E-05
CH_4	0.0000001	GC/FID	Rectangular	4.65E-08	2.68E-08
H_2O	0.000364	dew point meter	Normal	3.64E-04	3.64E-05
C_3H_8	0.00000007	GC/FID	Rectangular	3.62E-08	2.09E-08
THC	0.000050	GC/FID	Rectangular	2.50E-05	1.44E-05
			impurities	1.31E-05	7.55E-06
			CO_2 purity	**99.99883**	0.00013 *k*=2

a purity table of raw N_2 gas;

cylinder number : NK 05541 (DukYang)

component	value (cmol/mol)	detector	Distribution	Amount of mole fraction (cmol/mol)	Standard uncertainty (cmol/mol, *k* = 1)
H_2	0.000026	GC/TCD	Rectangular	1.28E-05	7.41E-06
O_2	0.000013	Galvanic Sensor oxygen analyzer	Normal	1.34E-05	1.34E-06
Ar	0.004237	GC/TCD	Normal	4.2366E-03	4.2366E-04
CO	0.0000002	GC/FID	Rectangular	1.10E-07	6.35E-08
CO_2	0.0000002	GC/FID	Rectangular	1.35E-07	7.77E-08
CH_4	0.0000002	GC/FID	Rectangular	1.09E-07	6.26E-08
H_2O	0.0000641	dew point meter	Normal	6.41E-05	6.41E-06
C_3H_8	0.000001	GC/FID	Rectangular	3.62E-08	2.09E-08
THC	0.00005	GC/FID	Rectangular	2.50E-05	1.44E-05
			impurities	0.004352	0.000420
			N_2 purity	**99.99565**	0.00085 (*k* = 2)

a purity table of raw O_2 gas;

cylinder number : NK04387 (Daesung gas)

component	value (cmol/mol)	detector	Distribution	Amount of mole fraction (cmol/mol)	Standard uncertainty (cmol/mol, k = 1)
H_2	0.000026	GC/TCD	Rectangular	1.31E-05	7.55E-06
N_2	0.000055	GC/TCD	Rectangular	2.77E-05	1.60E-05
CO	0.0000002	GC/FID	Rectangular	1.10E-07	6.35E-08
CO_2	0.0000081	GC/FID	Normal	8.10E-06	8.10E-07
CH_4	0.0000002	GC/FID	Rectangular	1.09E-07	6.26E-08
H_2O	0.0000294	dew point meter	Normal	2.94E-05	2.94E-06
C_3H_8	0.00000007	GC/FID	Rectangular	3.62E-08	2.09E-08
THC	0.00005	GC/FID	Rectangular	2.50E-05	1.44E-05
			impurities	0.000104	0.000023
			O_2 purity	**99.999896**	0.000046 k=2

a purity table of raw CO gas;

cylinder number : RF 00096

component	value (cmol/mol)	detector	Distribution	Amount of mole fraction (cmol/mol)	Standard uncertainty (cmol/mol, k = 1)
H_2	0.000026	GC/TCD	Rectangular	1.31E-05	7.55E-06
Ar	0.00000763	GC/TCD	Normal	7.63E-06	7.63E-07
O_2	0.000005	GC/TCD	Rectangular	2.50E-06	1.44E-06
N_2	0.000499	GC/TCD	Normal	4.99E-04	4.99E-05
CO_2	0.007348	GC/TCD	Normal	7.35E-03	7.35E-04
CH_4	0.0000002	GC/FID	Rectangular	1.08E-07	6.24E-08
H_2O	0.002407	dew point meter	Normal	2.41E-03	2.41E-04
C_3H_8	0.00000007	GC/FID	Rectangular	3.62E-08	2.09E-08
THC	0.00005	GC/FID	Rectangular	2.50E-05	1.44E-05
			impurities	0.0103	0.0008
			CO purity	99.9897	0.0015 k=2

a purity table of raw C_3H_8 gas

cylinder number : VC1389

component	value (cmol/mol)	detector	Distribution	Amount of mole fraction (cmol/mol)	Standard uncertainty (cmol/mol, *k* = 1
H_2	0.000005	GC/TCD	Rectangular	2.50E-06	1.44E-06
O_2+Ar	0.000073	Galvanic Sensor oxygen analyzer	Normal	7.30E-05	7.30E-06
CO2	0.000065		Normal	6.50E-05	6.50E-06
i-C4H10	0.000973	GC/TCD	Normal	9.73E-04	9.73E-05
CO	0.000003	GC/FID	Rectangular	1.50E-06	8.66E-07
N_2	0.000153	GC/TCD	Normal	1.53E-04	1.53E-05
CH_4	0.00001	GC/FID	Rectangular	5.00E-06	2.89E-06
H_2O	0.00003	dew point meter	Normal	3.00E-05	3.00E-06
n-C4H10	0.000437	GC/FID	Normal	4.37E-04	4.37E-05
THC	0.00006	GC/FID	Rectangular	5.00E-05	2.89E-05
			impurities	0.00179	0.00011
			C3H8 purity	**99.99821**	0.00022

Verification

Mixtures prepared were then verified using a GC/FID or GC/TCD analyzer by evaluating sensitivity ratio against one of them. Verification uncertainties were within a maximum of 0.1~0.15 %rel, which were given from the half of scattering of sensitivities. Their values are bigger than the preparation uncertainties (~ 0.01% rel. in table 1-3).

Verification test was conducted with all gravimetric standards of the compounds. Verification tests were repeated by 2-3 times during a period of 8 months. Every mixtures were in a verification criteria of $\left|\chi_{grav} - \chi_{ver}\right| \leq 2 \cdot \sqrt{u_{grav}^2 + u_{ver}^2}$. Measured responses of GC-TCD and GC-FID were considered to be linear within the range. In this regard, verification uncertainty was composed of measurement repeatability of each standard and deviation between verified vale and gravimetric value. Their values were taken to give total verification uncertainty and listed in tables 1-3.

D.3 Instrumentation

Separation column was Molsieve (5A, 80/100, 9 ft*2, 1/8 inch) for O_2 and CO and Parapak Q (80/100, 9 ft*2, 1/8 inch) for CO, CO_2, and C_3H_8. Oven temperature was set at 40-100°C. Strong nitrogen peak and possible CO_2 peak in molsieve column-GC/TCD combination which exhibited long tail was sufficiently separated from oxygen peak and removed by backflush through 1S uni-beads column. Samples and standards were injected via mass flow controller at a 50 mL/min and loaded to sample loops of sub mL (0.01 and 1) size. Carrier gas was a purified He. Detector temperature was around 250°C for TCD and 300°C for FID. During measurement, instrumental drift was corrected by monitoring response variation of working standard taken by bracketing measurement in sequence of R-S-R.... Every measurement was repeated by a set of 5-6 injections. First two injected measurements among them were discarded because of memory of previous measurement.

Configuration of analysis system: gas cylinder → regulator →MPV → MFC → GC-TDC or GC-FID-Methanizer → response comparison → results

D.4 Calibration method and value assignment

Samples parallel connected 3 mixtures (in table 1 to 3) and one KC cylinder(#D2792) through MPV were sequently introduced to the sample loop then analyzed by means of a GC/FID-metanizer or GC/TCD analyser. The instrument was calibrated using the three gravimetrically prepared standards.

C_3H_8

	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (%relative)	Number of replicates	Reference
1	23/08/20	0.019661	0.038	3	D769672
2	23/08/20	0.019666	0.022	3	D769672
3	24/08/20	0.019671	0.018	3	D769658
4	25/08/20	0.019668	0.050	4	D769664

CO

	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (%relative)	Number of replicates	Reference
1	23/08/20	1.01012	0.084	3	D769672 & D769658
2	23/08/20	1.00934	0.025	3	D769672 & D769658
3	27/09/20	1.0096	0.044	4	D769664 & D769658
4	01/09/20	1.01224	0.051	4	D769664 & D769658
5	02/09/20	1.01190	0.11	4	D769867 & D769658

CO_2

	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (%relative)	Number of replicates	Reference
1	25/08/20	1.97366	0.054	4	D769664
2	26/08/20	1.97322	0.099	4	D769664
3	27/08/20	1.97204	0.020	4	D769664
4	01/09/20	1.97197	0.023	4	D769664
5	01/09/20	1.97206	0.003	4	D769664

O_2

	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation	Number of replicates	Reference

			(%relative)		
1	25/08/20	3.07049	0.122	3	D769664 & D769658
2	27/08/20	3.0696	0.069	4	D769664 & D769658
3	24/08/20	3.06746	0.066	4	D769664 & D769658
4	01/09/20	3.06710	0.103	4	D769664 & D769658

D.5 Uncertainty evaluation

- (PRM) Uncertainty components through gravimetric preparation have been considered [1,2]:

1. gravimetric preparation (weighing process) ($x_{i,grav}$)
2. purity of the parent gases ($\Delta x_{i,purity}$)
3. stability of the gas mixture ($\Delta x_{i,stab}$)

The amount of substance fraction *x*i,prep of a particular component in mixture i, as it appears during use of the cylinder, can now be expressed as

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

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

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} + \Delta x_{i,stab} \qquad (2)$$

For the mixtures used in this key comparison, the preparation method has been designed in such a way that long-term stability has been regarded as;

$$\Delta x_{i,stab} = 0 \qquad (3)$$

as well as their standard uncertainty. Accordingly, Eq. (1 to 3) reduce to

$$\Delta x_{i,stab} = 0 \qquad (4)$$

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2 \ . \qquad (5)$$

Uncertainties of their preparation were computed by way of GUM (Guide to the Expression of Uncertainty in Measurement).

ISO 6143[3] describes the general procedure for verification of prepared mixtures. For the purpose of assigning values to a gas mixture the verification procedure requires the validity of $x_{i,prep}$and its uncertainty such that

$$\left| x_{i,prep} - x_{i,ver} \right| \leq 2\sqrt{u_{i,prep}^2 + u_{i,ver}^2} \qquad (6)$$

The factor 2 is a coverage factor, which is corresponding to a 95% coverage interval.

As far as 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 reference value in Eq. (7) comes to the preparation value. As a result, the standard uncertainty of a reference value is expressed as

$u_{i,ref}^2 = u_{i,prep}^2 + u_{i,ver}^2$ (7)

In this comparison, the verification uncertainty (k = 2) was set as 0.10 % based on the uncertainties of repeatability, and reproducibility during the measurement and whose drift was additionally and separately treated.

- (key comparison sample: #D751979)

The mole fraction and associated uncertainty of each component in this mixture were calculated as follows:

- Each calibration curve was assumed to be linear so values of the comparison cylinder were calculated from 1-point neighbour bracket measurement for CO_2 and C_3H_8 to get sensitivity.

$x_s = \frac{A_s}{A_r} x_r$ (8)

Where, x_s: key comparison sample amount, A_s: analyser response of key comparison sample, A_r: analyser response of reference (PRM), x_r: reference(PRM) amount of prepared cylinder. In the equation, A_r was given $\frac{A_{r1}+A_{r2}}{2}$ to compensate drift by instrument, where A_{r1} and A_{r2} are response values before and after sample measurement.

- for CO and O_2 we had no references similar to the comparison sample. Therefore two adjacent references were used to determine the sample (comparison) amount.

$x_s = x_{r1} + \frac{x_{r2}-x_{r1}}{A_{r2}-A_{r1}} \cdot (A_s - A_{r1})$ (9)

Where, x_s: key comparison sample amount, A_s: analyser response of key comparison sample, A_{ri}: analyser responses of references (PRM), x_{ri}: references (PRM) amounts of prepared cylinder.

Their uncertainties were calculated by uncertainty propagation.

- Instrument drifts worked as one factor of uncertainty.

Key-comparison mixture analysis Results (cylinder number: #D751979)

Component	Results (x) cmol/mol	u_{sd} %	$u(x)$ %	combined. unc.(u) cmol/mol	exp. Unc. (U) %, k = 2
C_3H_8	0.019667	0.012	0.10	2.0E-05	0.20
CO	1.0106	0.078	0.14	1.6E-03	0.32
CO_2	1.9726	0.023	0.12	2.4E-03	0.24
O_2	3.0687	0.031	0.16	5.0E-03	0.32

References

[1] Lee et al. International comparison CCQM-K84: Carbon monoxide in synthetic air at ambient level, Metrologia 54 08016

[2] International organization for standardization, ISO 6142-1:2015. “Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures, ISO, 2015 (E)

[3] International organization for standardization, ISO 6143:2001. “Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures”, ISO, 2001(E).

Annex E Measurement report of NIST

E.1 Results

Cylinder number: MR8468

Measurement 1

Component	Date (mm/dd/yyyy)	Fraction (cmol/mol)	Std deviation (% relative)	Number of replicates	Standard uncertainty (cmol/mol)
Oxygen	01/06/2020	2.9793	0.066	5	0.0024
Carbon dioxide	02/04/2020	2.0019	0.067	3	0.0016
Propane	01/14/2020	0.019961	0.033	3	0.000008
Carbon monoxide	02/26/2020	1.0035	0.189	3	0.0021

Measurement 2

Component	Date (mm/dd/yyyy)	Fraction (cmol/mol)	Std deviation (% relative)	Number of replicates	Standard uncertainty (cmol/mol)
Oxygen	01/07/2020	2.9780	0.034	5	0.0024
Carbon dioxide	02/10/2020	1.9979	0.095	3	0.0021
Propane	01/27/2020	0.019964	0.049	3	0.000010
Carbon monoxide	03/03/2020	1.0030	0.098	3	0.0012

Measurement 3

Component	Date (mm/dd/yyyy)	Fraction (cmol/mol)	Std deviation (% relative)	Number of replicates	Standard uncertainty (cmol/mol)
Oxygen	01/08/2020	2.9775	0.072	5	0.0024
Carbon dioxide	02/11/2020	2.0005	0.061	3	0.0017
Propane	02/05/2020	0.019962	0.032	3	0.000007
Carbon monoxide	03/05/2020	1.0024	0.224	3	0.0024

Results

Component	Fraction (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
Oxygen	2.9783	0.0048	2
Carbon dioxide	2.0001	0.0037	2
Propane	0.019962	0.000028	2
Carbon monoxide	1.0030	0.0040	2

E.2 Oxygen (O_2)

E.2.1 Calibration standards

The CCQM-K3.2019 sample (cylinder # MR8468) was analyzed against five NIST primary standard mixtures (PSMs) ranging from nominal (1 to 5) cmol mol^{-1} oxygen in nitrogen (O_2/N_2). The PSMs and their respective expanded uncertainties are listed in Table 1.

Table 1. Primary standard mixtures used in the O_2 value assignment of CCQM-K3.2019 sample MR8468.

Cylinder Number	Amount fraction (cmol mol^{-1})*	Year Prepared
CAL1013	1.02126 ± 0.00012	2013
CAL3252	2.02573 ± 0.00019	2013
CAL7538	3.22046 ± 0.00025	2013
FF19043	3.97198 ± 0.00031	2013
CAL1210	4.99673 ± 0.00041	2013

* Uncertainties are expressed at approximately 95 % confidence (k = 2).

The PSMs were prepared gravimetrically by dilution of aliquots of independently prepared parent mixtures (Table 2), in accordance with ISO 6142-1:2015 [1]. A predetermined amount of the respective parent mixture was transferred into the PSM cylinder. The cylinders were weighed a minimum of ten times before and after the addition of the parent mixture. The difference in these two measurements was calculated to determine the total mass of the parent mixture added. The PSM cylinders were then filled with a balance of built-in-purifier (BIP) N_2 (Table 3), and again weighed a minimum of ten times.

Utilizing the gravimetric additions of both the parent mixture and balance N_2 a total amount fraction and uncertainty were calculated. Samples of the weighing data and corresponding determination of the final amount fraction are included in Figures 1 and 2, respectively. A purity assay of the research grade (99.999 %) O_2 used to prepare the parent mixtures is listed in Table 4.

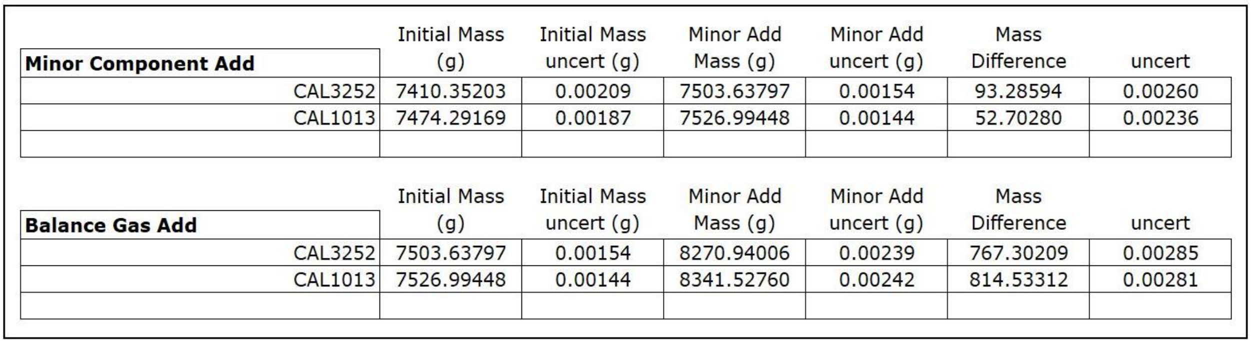
Table 2. Composition of parent mixtures used to prepare NIST O_2/N_2 PSMs. Amount fractions are expressed as µmol mol^{-1}, with associated expanded uncertainties (k = 2).

Parent Mixture	CAL7564	CAL7351	CAL7610	CAL7347	CAL7549
O_2	171907 ± 11	191414 ± 11	212295 ± 11	231563 ± 12	257305 ± 15
Argon	38 ± 5	38 ± 5	37 ± 5	36 ± 5	35 ± 5
N_2	828054 ± 41	808548 ± 40	787668 ± 38	768401 ± 37	742660 ± 36
PSM prepared	*CAL1013*	*CAL3252*	*CAL7538*	*FF19043*	*CAL1210*

Table 3. Assay of balance nitrogen (cylinder # TW06-115304) used to prepare NIST O_2/N_2 PSMs.

Component	Amount fraction (µmol mol^{-1})*
O_2 (Analyzed)	0.004 ± 0.002
Argon (Analyzed)	81 ± 10
N_2 (Difference)	999919 ± 10

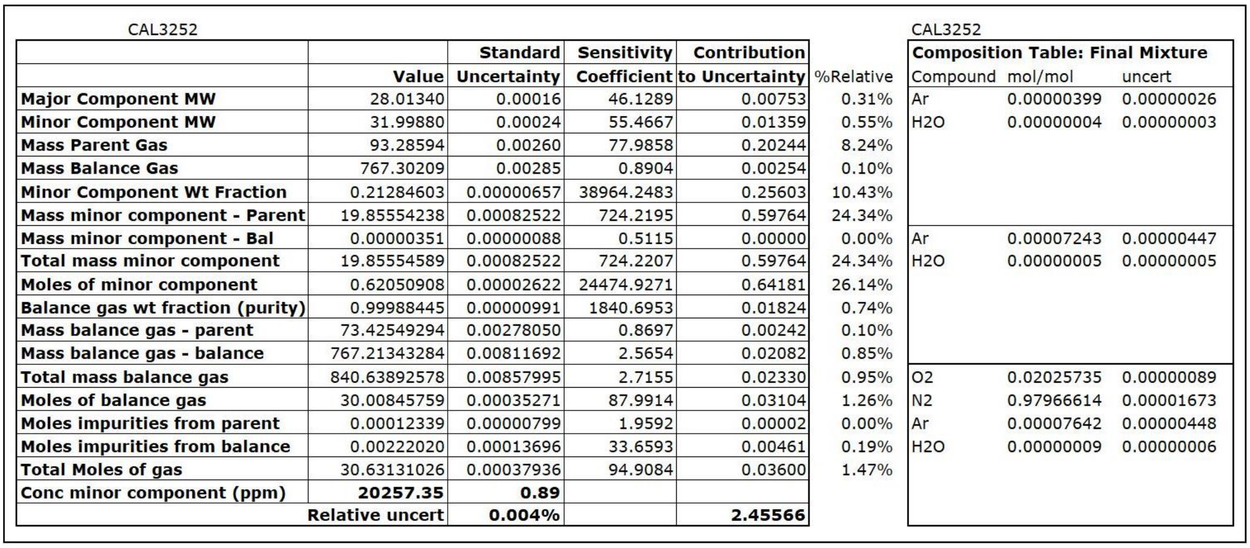
* Uncertainties listed are expanded, k = 2.



Minor Component Add	Initial Mass (g)	Initial Mass uncert (g)	Minor Add Mass (g)	Minor Add uncert (g)	Mass Difference	uncert
CAL3252	7410.35203	0.00209	7503.63797	0.00154	93.28594	0.00260
CAL1013	7474.29169	0.00187	7526.99448	0.00144	52.70280	0.00236

Balance Gas Add	Initial Mass (g)	Initial Mass uncert (g)	Minor Add Mass (g)	Minor Add uncert (g)	Mass Difference	uncert
CAL3252	7503.63797	0.00154	8270.94006	0.00239	767.30209	0.00285
CAL1013	7526.99448	0.00144	8341.52760	0.00242	814.53312	0.00281

Figure 1. Cylinder weighing data for PSMs CAL3252 and CAL1013, nominal (2 and 1) cmol mol^{-1}, respectively. Uncertainties listed are standard combined uncertainties, *k* = 1.



CAL3252

	Value	Standard Uncertainty	Sensitivity Coefficient	Contribution to Uncertainty	%Relative
Major Component MW	28.01340	0.00016	46.1289	0.00753	0.31%
Minor Component MW	31.99880	0.00024	55.4667	0.01359	0.55%
Mass Parent Gas	93.28594	0.00260	77.9858	0.20244	8.24%
Mass Balance Gas	767.30209	0.00285	0.8904	0.00254	0.10%
Minor Component Wt Fraction	0.21284603	0.00000657	38964.2483	0.25603	10.43%
Mass minor component - Parent	19.85554238	0.00082522	724.2195	0.59764	24.34%
Mass minor component - Bal	0.00000351	0.00000088	0.5115	0.00000	0.00%
Total mass minor component	19.85554589	0.00082522	724.2207	0.59764	24.34%
Moles of minor component	0.62050908	0.00002622	24474.9271	0.64181	26.14%
Balance gas wt fraction (purity)	0.99988445	0.00000991	1840.6953	0.01824	0.74%
Mass balance gas - parent	73.42549294	0.00278050	0.8697	0.00242	0.10%
Mass balance gas - balance	767.21343284	0.00811692	2.5654	0.02082	0.85%
Total mass balance gas	840.63892578	0.00857995	2.7155	0.02330	0.95%
Moles of balance gas	30.00845759	0.00035271	87.9914	0.03104	1.26%
Moles impurities from parent	0.00012339	0.00000799	1.9592	0.00002	0.00%
Moles impurities from balance	0.00222020	0.00013696	33.6593	0.00461	0.19%
Total Moles of gas	30.63131026	0.00037936	94.9084	0.03600	1.47%
Conc minor component (ppm)	**20257.35**	**0.89**			
	Relative uncert	**0.004%**		**2.45566**	

CAL3252

Composition Table: Final Mixture

Compound	mol/mol	uncert
Ar	0.00000399	0.00000026
H2O	0.00000004	0.00000003
Ar	0.00007243	0.00000447
H2O	0.00000005	0.00000005
O2	0.02025735	0.00000089
N2	0.97966614	0.00001673
Ar	0.00007642	0.00000448
H2O	0.00000009	0.00000006

Figure 2. Value assignment and uncertainty budget for PSM CAL3252, nominal 2 cmol mol^{-1}. Uncertainties listed are standard combined uncertainties, *k* = 1.

Table 4. Assay of research grade oxygen (cylinder # T227483) used to prepare O_2/N_2 parent mixtures.

Component	Amount fraction (µmol mol^{-1})*
O_2 (Difference)	999990
Argon (Analyzed)	7.0 ± 1.9
N_2 (Analyzed)	2.5 ± 2.0
Water (Analyzed)	0.5 ± 0.3

* Uncertainties are expressed as standard uncertainties (*k* = 1).

The PSMs were verified by comparison to previously prepared O_2/N_2 standards. The PSMs were also compared to a NIST Standard Reference Material (SRM) lot standard, 73-EL-01 (cylinder # CC508716), to ensure consistency within the NIST O_2 standards and measurement program. The lot standard served as the analytical control cylinder for this comparison. A ratio of the response for each of the five PSMs was calculated to that of the control. The gravimetric values of the PSMs and corresponding response ratios were then evaluated using a linear generalized least-squares regression [2,3], from which the amount fraction of the control was predicted. The PSMs were considered stable because the predicted value for the control cylinder agreed with its original certified value within the associated expanded uncertainty.

E.2.2 Instrumentation

The oxygen analysis of this sample was carried out using a Siemens Oxymat 6 paramagnetic analyzer. An automated gas sampling system (COGAS # 7) was used to deliver a sample flow of 300 mL min^{-1} to the instrument. As described above, NIST lot standard 73-EL-01 was used as the control for this analysis. The control cylinder was analyzed repeatedly throughout the analysis to monitor instrument performance and compensate for any instrument drift. A minimum of five repetitions of the sampling sequence (control, sample, control) for each of the PSMs and the CCQM sample constituted one analytical sequence. This analytical sequence was repeated three times over three days to produce three sets of measurement results.

E.2.3 Calibration method and value assignment

The CCQM sample and PSMs were compared to the control cylinder a minimum of five times per analytical day. Instrument response ratios (R) were determined as:

$$R = \frac{r_S}{r_C} \tag{1}$$

where r_S is the instrument response of the sample cylinder, and r_C is the drift-corrected response of the control, calculated as:

$$r_C = r_{C1} + \frac{r_{C2} - r_{C1}}{N-1} \cdot (n-1) \tag{2}$$

In Equation 2, r_{C1} and r_{C2} are the instrument responses of the control taken before and after the sample measurements; N is the total number of measurements in the sampling sequence; and n is the order number of the sample measurement within the sequence.

An ISO 6143 compliant generalized least-squares regression program (GenLine) [2,3] was used to assign a first-order regression to the gravimetric values and response ratios of the PSMs. This regression equation was then used to predict the amount fraction of the CCQM sample from its response ratio. The regression equations determined for each of the three analytical sets, along with their predicted values for the CCQM sample are listed in Table 5. The three individual values were then averaged to determine a final amount fraction for the CCQM sample, as listed in Table 6.

Table 5. Oxygen regression coefficients (b) and predicted amount fractions (y) for the CCQM-K3.2019 sample, with associated standard uncertainties.

Measurement	$y = b_0 + b_1 x$		y (cmol mol^{-1})
	b_0	b_1	
1	−0.0480 ± 0.0012	2.0144 ± 0.0012	2.9793 ± 0.0024
2	−0.0461 ± 0.0012	2.0132 ± 0.0012	2.9780 ± 0.0024
3	−0.0454 ± 0.0012	2.0116 ± 0.0012	2.9775 ± 0.0024

Table 6. Final oxygen value assignment for the CCQM-K3.2019 sample, with associated uncertainty for 95 % confidence (k = 2).

Sample Number	Amount fraction (cmol mol^{-1})
MR8468	2.9783 ± 0.0048

E.2.4 Uncertainty evaluation

The calculations for the O_2 amount fraction in the CCQM sample were reviewed for sources of systematic and random error. The review identified two sources of uncertainty whose importance required quantification: (i) the gravimetric determinations of the PSMs, and (ii) the measured O_2 response ratios. The gravimetric uncertainties were assigned during the blending process, as shown in Figures 1 and 2. The uncertainties of all response ratios were assumed to be equal to the largest relative standard deviation determined from the replicated response ratios of each PSM and the CCQM sample.

The combined uncertainty assigned to the CCQM sample (u_c) was determined by pooling the three individual uncertainties from Table 5 (u_N), using Equation 3.

$$u_c = \sqrt{\frac{u_1^2+u_2^2+u_3^2}{3}} \tag{3}$$

The final uncertainty is expressed as:

$$U = ku_c$$

where the coverage factor k is equal to 2. The true value is therefore asserted to lie in the interval defined by the assigned amount fraction ± U, with a confidence of approximately 95 % [4].

E.3 Carbon monoxide (CO)

E.3.1 Calibration standards

Six NIST gravimetrically prepared PSMs, ranging from nominal (0.6 to 2.5) cmol mol^{-1} carbon monoxide in nitrogen (CO/N_2), were utilized in the analysis of the CCQM-K3.2019 sample. The PSMs and their respective expanded uncertainties are listed Table 7.

Table 7. Primary standard mixtures used in the CO value assignment of the CCQM-K3.2019 sample.

Cylinder Number	Amount fraction (cmol mol^{-1})*	Year Prepared
X139406	0.6119 ± 0.0012	1979
CAL7262	0.8123 ± 0.0016	2011
FF23069	0.9856 ± 0.0020	2007
CAL7553	1.5002 ± 0.0030	2011
X302473	2.0200 ± 0.0040	1997
X302511	2.4660 ± 0.0049	1997

* Uncertainties represent k = 2 expanded uncertainties, set to 0.2 % of the gravimetric values.

The PSMs were prepared gravimetrically using a multiple step dilution starting from pure materials, in a similar manner as described in Section E.2.1. PSMs X139406, CAL7262, FF23069 and CAL7553 were blended from existing CO/N_2 parent mixtures, and PSMs X302473 and X302511 were blended directly from pure carbon monoxide. Assays of the pure CO and N_2 starting materials used to prepare the PSMs are included in Tables 8 and 9, respectively. The compositions of the PSMs were verified by comparison to previously prepared PSMs.

For this analysis, one SRM lot standard at nominal 1 cmol mol^{-1} CO/N_2 was used as the analytical control. The lot standard (sample # 54-FL-01, cylinder # CC339398) was originally certified in 2012. Its predicted amount fraction during the analysis of the CCQM sample agreed with its 2012 certified value within the associated standard uncertainty, indicating stability in both the PSMs and the lot standard.

Table 8. Assay of pure CO used in the preparation of NIST CO/N_2 PSMs. All amount fractions are expressed as µmol mol^{-1}, with associated standard uncertainties (k = 1).

Cylinder Number	46975	CC199977	FF25980
CO (Difference)	998400 ± 998	999989 ± 5	999954 ± 15
Argon	30.00 ± 0.03	0.63 ± 0.04	20 ± 6
CO_2	280.00 ± 0.28	NA*	2.3 ± 2.3
Water	NA*	NA*	8 ± 2
Methane	10.00 ± 0.01	1.06 ± 1.06	2 ± 2
O_2	380.00 ± 0.38	0.68 ± 0.68	1.5 ± 1.5
N_2	900.0 ± 0.9	8.15 ± 0.46	12.7 ± 12.7
PSM(s) Prepared	*X139406, X302473, X302511*	*CAL7262, CAL7553*	*FF23069*

* Not analyzed.

Table 9. Assay of nitrogen balance gases used to prepare CO/N_2 PSMs. All values are expressed as µmol mol^{-1}, with associated expanded uncertainties (k = 2). Purity information is not available for the balance N_2 used in PSMs X139406, X302473 and X302511.

Cylinder Number	AIRPRO-319532	TW05-866031	SG9904839A	TWO5-867552
CO	0.123 ± 0.010	0.015 ± 0.004	0.010 ± 0.003	0.004 ± 0.010
Argon	75 ± 7	73 ± 7	68 ± 7	14 ± 4
CO_2	0.12 ± 0.12	0.24 ± 0.03	0.77 ± 0.19	0.14 ± 0.28
Water	0.4 ± 0.4	0.2 ± 0.2	0.8 ± 0.8	0.3 ± 0.6
Methane	0.01 ± 0.01	0.03 ± 0.03	0.01 ± 0.01	0.01 ± 0.02
O_2	NA*	NA*	NA*	0.002 ± 0.002
N_2 (Difference)	999924.3 ± 2.8	999926.2 ± 4.0	999936.6 ± 3.0	999985 ± 4
PSM(s) Prepared	*CAL7262*	*CAL7262, CAL7553*	*CAL7553*	*FF23069*

* Not analyzed.

E.3.2 Instrumentation

The CO content of the CCQM sample was analyzed using an Agilent 6890 gas chromatograph equipped with a thermal conductivity detector (GC-TCD), along with a computer operated gas sampling system (COGAS # 10).

The components in the sample were separated using a 4.52 m × 3.18 mm stainless steel column packed with Molesieve 5A. The column was operated isothermally at 130 °C with a carrier gas flow of 30 mL min^{-1} ultra high purity helium (UHP He). The TCD was set to 150 °C with a reference flow of 45 mL min^{-1} UHP He. The GC sampling valve was equipped with a 3 mL sample loop, which was flushed with a sample flow of 40 mL min^{-1} for a period of 90 s. At 0.1 min prior to injection on the column, the sample flow was directed to vent to bring the sample loop to ambient pressure, ensuring a consistent amount of sample for every injection.

The COGAS unit was used to randomize the sampling of the cylinders to be tested each analytical day. It was programmed to inject each sample three times before moving to the next cylinder in the sequence, and to compare each sample to the control three time.

E.3.3 Calibration method and value assignment

The GC-TCD was calibrated with the six PSMs listed in Table 7. NIST SRM lot standard 54-FL-01 was used as the analytical control. It was periodically sampled throughout the analytical sequence to monitor the TCD performance and allow response correction due to detector drift. Each cylinder was injected three times and the responses were averaged. Response ratios were calculated by dividing the average cylinder response by the drift-corrected response of the control, using Equations 1 and 2. On each analytical day, the cylinders were compared to the control three times, yielding a total of nine ratios for each PSM and the CCQM sample. The collected data were divided into three analytical sets containing three ratios for each PSM and the CCQM sample. Each analytical set was evaluated using a second-order generalized least-squares regression (GenLine) compliant with ISO 6143 [2,3]. The regression equations and predicted values of the CCQM sample are listed in Table 10. The final reported value, listed in Table 11, was calculated as the mean of the three individual measurement results.

Table 10. Carbon monoxide regression coefficients (b) and predicted amount fractions (y) for the CCQM-K3.2019 sample, with associated standard uncertainties.

Measurement	$y = b_0 + b_1x + b_2x^2$			y (cmol mol^{-1})
	b_0	b_1	b_2	
1	0.0004 ± 0.0041	0.9867 ± 0.0073	0.0020 ± 0.0025	1.0035 ± 0.0021
2	0.0010 ± 0.0033	0.9864 ± 0.0057	0.0019 ± 0.0020	1.0030 ± 0.0012
3	−0.0034 ± 0.0037	0.9931 ± 0.0067	−0.0003 ± 0.0023	1.0024 ± 0.0024

Table 11. Final CO value assignment for the CCQM-K3.2019 sample and associated uncertainty for 95 % confidence (k = 2).

Sample Number	Amount fraction (cmol mol^{-1})
MR8468	1.0030 ± 0.0040

Uncertainty evaluation

The uncertainties calculated by GenLine for each measurement result were based upon the gravimetric uncertainties of the NIST PSMs, as well as the analytical uncertainties of the cylinder response ratios. All uncertainties in the gravimetric values were assumed to be 0.1 %. The uncertainty for each response ratio, $u(R)$, was determined from the uncertainties in the replicated GC injections for both the sample, $u(r_S)$, and the control, $u(r_{C1})$ and $u(r_{C2})$, using Equation 4.

$$u(R) = \sqrt{u^2(r_{C1}) + u^2(r_S) + u^2(r_{C2})} \quad (4)$$

The final uncertainty assigned to the CCQM sample, u_c, was calculated by combining the three individual uncertainties determined by GenLine (as shown in Table 10), using Equation 3.

The expanded uncertainty is expressed as:

$$U = ku_c$$

where the coverage factor k is equal to 2. The true value for the CO amount fraction is therefore asserted to lie in the interval defined by the assigned amount fraction ± U, with a confidence of approximately 95 % [4].

E.4 Carbon dioxide (CO_2)

E.4.1 Calibration standards

Three PSMs at nominal (1.2 to 2.1) cmol mol^{-1} carbon dioxide (CO_2) in nitrogen and one PSM at nominal 2 cmol mol^{-1} CO_2 in air were utilized in the analysis of the CCQM-K3.2019 sample. The gravimetric values and associated expanded uncertainties of the PSMs are listed Table 12.

Table 12. Primary standard mixtures used in the CO_2 value assignment of the CCQM-K3.2019 sample.

Cylinder Number	Balance Gas	Amount fraction (cmol mol^{-1})*	Year Prepared
CAL016496	N_2	1.2119 ± 0.0008	2009
CAL014149	N_2	1.57227 ± 0.00052	2017
FB03277	Air	2.05399 ± 0.00031	2011
CAL017277	N_2	2.06307 ± 0.00154	2017

* Uncertainties are expressed at approximately 95 % confidence (k = 2).

Each of the NIST PSMs was prepared by gravimetric dilution of an existing parent mixture, in a similar manner as described in Section E.2.1. The compositions of the parent mixtures used are listed in Table 13. The N_2 and air balance gases were analyzed for impurities and (based on the mass fraction of each balance gas used) the contribution of those impurities was incorporated into the final composition of the PSM. Assays of the balance gases used are shown in Table 14. Purity assays of the CO_2 used to prepare the parent mixtures are listed in Table 15.

The PSMs were verified against other previously prepared PSMs. The PSMs were also compared to a NIST SRM lot standard, 33-DL-01 (cylinder # ALM045210), which was used as the analytical control for this analysis. The predicted amount fraction of the lot standard during the analysis of the CCQM sample agreed with its 1995 certified value within the associated expanded uncertainty, indicating stability of both the PSMs and the lot standard.

Table 13. Composition of parent mixtures used to prepare NIST CO_2 PSMs. Amount fractions are expressed as µmol mol^{-1}, with associated expanded (k = 2) uncertainties.

Cylinder Number	FF19100	FF19031	CAL016406	CAL5918
CO_2	122806.8 ± 42.9	151512.4 ± 7.6	143504.7 ± 13.9	136969.7 ±7.1
Argon	49.7 ± 8.8	68.9 ± 1.9	8009.7 ± 21.0	70.0 ± 1.9
CO*	1.0 ± 1.8	NA	NA	NA
Water*	0.9 ± 0.6	NA	NA	NA
Methane*	1.0 ± 1.8	NA	NA	NA
O_2*	NA	NA	179305.6 ± 58.4	NA
N_2 (Difference)	877140.6 ± 204.8	848418.8 ± 25.0	669180.0 ± 85.1	862960.3 ± 24.9
PSM prepared	*CAL016496*	*CAL014149*	*FB03277*	*CAL017277*

* NA – not analyzed.

Table 14. Assay of balance gases used in the preparation of NIST CO_2 PSMs. All amount fractions are expressed as µmol mol^{-1}, with associated expanded (k = 2) uncertainties.

Cylinder Number(s)	TWO6-999303 and AIRPRO-357074	TWO5-86618	CA06680 and CA02774
CO_2	0.20 ± 0.02	0.07 ± 0.02	0.098 ± 0.004
Argon	18.6 ± 0.6	80.3 ± 2.0	9342.6 ± 26.2
CO*	0.003 ± 0.002	NA	NA
Water*	0.4 ± 2.6	NA	NA
Methane*	0.007 ± 0.004	NA	NA
O_2*	NA	NA	209367.6 ± 75.1
N_2 (Difference)	999980.8 ± 2.6	999919.6 ± 2.0	781289.7 ± 79.6
PSM(s) prepared	*CAL016496*	*CAL014149, CAL017277*	*FB03277*

* NA – not analyzed.

Table 15. Assay of pure carbon dioxide used in the preparation of NIST CO_2 PSMs. All amount fractions are expressed as µmol mol^{-1}, with associated standard (k = 1) uncertainties.

Cylinder Number	A-7656	CC343037	CC282116
CO_2 (Difference)	999994 ± 2	999892 ± 4	999994 ± 2
Argon*	NA	3.0 ± 3.0	2.0 ± 1.2
N_2*	NA	105.0 ± 2.5	2.0 ± 1.2
O_2*	NA	NA	2.0 ± 1.2
Methane*	0.6 ± 0.1	NA	NA
Ethane*	0.2 ± 0.5	NA	NA
Ethylene*	0.2 ± 0.5	NA	NA
CO*	0.9 ± 0.5	NA	NA
Water*	4 ± 2	NA	NA
PSM(s) prepared	*CAL016496*	*CAL014149, CAL017277*	*FB03277*

* NA – not analyzed.

E.4.2 Instrumentation

The CO_2 content of the CCQM sample was measured using an Agilent 6890N gas chromatograph equipped with a thermal conductivity detector (GC-TCD), along with a computer operated gas sampling system (COGAS # 12).

The components in the sample were separated using a 3.66 m × 3.18 mm stainless steel column packed with Porapak Q. The column was operated isothermally at 40 °C with a carrier gas flow of 30 mL min^{-1} UHP He. The TCD was set to 150 °C with a reference gas flow of 45 mL min^{-1} UHP He. The GC sampling valve was equipped with a 2 mL sample loop. For a period of 90 s, the sample loop was flushed with a sample flow of 40 mL min^{-1}. At 0.1 min prior to injection, the sample flow was then directed to vent, to allow the contents of the sample loop to come to ambient pressure.

COGAS # 12 was used to randomize the sampling of the cylinders to be tested each analytical day. The control cylinder was tested repeatedly throughout the analysis in order to monitor the detector performance. For each analysis, the COGAS unit was programmed to inject each sample three times before moving to the next cylinder in the sequence, and to compare each sample to the control three times.

E.4.3 Calibration method and value assignment

The GC-TCD was calibrated with the 4 PSMs listed in Table 12. NIST SRM lot standard 33-DL-01 was used as the analytical control. The control cylinder was periodically sampled throughout the analytical sequence to monitor the TCD performance and allow for correction due to detector drift. Each cylinder was injected three times before the sequence switched to the next cylinder. The cylinder responses were averaged, and a response ratio to the control was calculated using Equations 1 and 2. On each analytical day, the cylinders were compared to the control three times. The collected data were divided into three analytical sets containing three ratios for each PSM and the CCQM sample. Each analytical set was evaluated using a first-order generalized least-squares regression (GenLine) compliant with ISO 6143 [2,3]. The regression analysis was then used to assign an amount fraction to the CCQM sample. The regression equations and associated predicted values of the CCQM sample are listed in Table 16. The final reported value, given in Table 17, is the mean of the three individual measurement results.

Table 16. Carbon dioxide regression coefficients (b) and predicted amount fractions (y) for the CCQM-K3.2019 sample, with associated standard uncertainties.

Measurement	$y = b_0 + b_1x$		y (cmol mol^{-1})
	b_0	b_1	
1	−0.0094 ± 0.0026	1.9682 ± 0.0032	2.0019 ± 0.0016
2	−0.0079 ± 0.0025	1.9669 ± 0.0032	1.9979 ± 0.0021
3	−0.0071 ± 0.0027	1.9660 ± 0.0035	2.0005 ± 0.0017

Table 17. Final CO_2 value assignment for the CCQM-K3.2019 sample and associated uncertainty for 95 % confidence (k = 2).

Sample Number	Amount fraction (cmol mol^{-1})
MR8468	2.0001 ± 0.0037

E.4.4 Uncertainty evaluation

The uncertainties calculated by GenLine for each analytical set were based upon the uncertainties in the gravimetric determinations of the PSMs (Table 12), as well as the uncertainties in the analytical response ratios (calculated using Equation 4).

The final uncertainty assigned to the CCQM sample, u_c, was determined by combining the three individual GenLine uncertainties (as shown in Table 16), using Equation 3.

The expanded uncertainty is expressed as:

$$U = ku_c$$

where the coverage factor k is equal to 2. The true value is therefore asserted to lie in the interval defined by the assigned amount fraction ± U, with a confidence of approximately 95 % [4].

E.5 Propane (C_3H_8)

E.5.1 Calibration standards

The CCQM-K3.2019 sample was analyzed against five NIST PSMs ranging from nominal (150 to 250) µmol mol^{-1} propane (C_3H_8) in nitrogen (Table 18). The PSMs were prepared gravimetrically using a multiple step dilution starting from pure materials, in a similar manner as described in Section E.2.1. Assays of the pure propane and balance nitrogen used to prepare the PSMs are listed in Tables 19 and 20, respectively. In addition to the PSMs, one NIST SRM lot standard, 101-CL-01 (cylinder # XC021159B), was included in the analysis to ensure consistency within the NIST C_3H_8 standards and measurement program. The lot standard was originally certified in 2000. The amount fraction assigned to the lot standard during this analysis agreed with its original certified value within the associated standard uncertainty, indicating stability of the PSMs over time.

Table 18. Primary standard mixtures used in the C_3H_8 value assignment of the CCQM-K3.2019 sample.

Cylinder Number	Amount fraction (µmol mol^{-1})*	Year Prepared
X40563	153.57 ± 0.31	2000
CAL8347	201.697 ± 0.036	2018
X40548	206.98 ± 0.41	2000
CAL8210	224.872 ± 0.038	2018
CAL11313	250.706 ± 0.042	2018

* Uncertainties are expressed at approximately 95 % confidence (k = 2).

Table 19. Assay of pure propane (cylinder # 6722213) used to prepare NIST C_3H_8/N_2 **PSMs.**

Component	Amount fraction (µmol mol^{-1})*
Ethane	2.7 ± 0.4
Argon	0.44 ± 0.04
Oxygen	2.5 ± 0.2
Nitrogen	12.6 ± 1.3
Propane	999981.8 ± 1.4

* Uncertainties are expressed as standard (k = 1) uncertainties.

Table 20. Assay of nitrogen balance gases used to prepare NIST C_3H_8/N_2 **PSMs.** Amount fractions are listed as **µmol mol**$^{-1}$, with associated standard (k = 1) uncertainties.

Cylinder Number	AIRPRO-320714	K-013668
Propane	0.002 ± 0.002	< 0.03 (minimum detection limit)
Argon	17.0 ± 2.0	NA
Methane	0.001 ± 0.001	NA
PSM(s) Prepared	*CAL8347, CAL8210, CAL11313*	*X40563, X40548*

E.5.2 Instrumentation

The propane analysis of this sample was performed using an Agilent 6890N gas chromatograph with flame ionization detection (GC-FID). The GC was fitted with a 2.5 m × 3.18 mm × 2 mm ID stainless steel column packed with Porapak Q 80/100. The column was operated isothermally at 120 °C with a UHP He carrier gas flow rate of 43 mL min^{-1}. The FID was set to 250 °C, with a fuel gas mixture of 40 mL min^{-1} hydrogen and 320 mL min^{-1} air.

Gas samples were delivered to the GC using a computer operated gas analysis system (COGAS # 11) and injected onto the head of the column via a 1 mL stainless steel sample loop connected to a 6-port stainless steel gas sampling valve. This automated sampling system randomized the cylinder samples such that detector performance could be monitored for stability through use of an analytical control (101-CL-01). Each sample in the measurement sequence was injected a minimum of three times and the responses were averaged.

E.5.3 Calibration method and value assignment

The GC-FID was calibrated using the five PSMs listed in Table 18. SRM lot standard 101-CL-01 was used as the analytical control, and was sampled throughout the measurement sequence to account for instrument drift. The PSMs and the CCQM sample were each compared to the control a minimum of three times. Response ratios were determined by dividing the average C_3H_8 response of each measurement sample by the drift-corrected C_3H_8 response of the control, using Equations 1 and 2. The response ratios for the PSMs and their corresponding amount fractions were evaluated using a first-order, generalized least-squares regression (GenLine) compliant with ISO 6143 [2,3]. This regression was then used to predict the amount fraction of the CCQM sample from its response ratio. This process was repeated for each of three analytical periods; the resulting regression equations and predicted values of the CCQM sample are listed in Table 21. The final reported value was calculated as the mean of the three individual measurement results, and is listed in Table 22.

Table 21. Propane regression coefficients (b) and predicted amount fractions (y) for the CCQM-K3.2019 sample, with associated standard uncertainties.

Measurement	$y = b_0 + b_1x$		y (µmol mol^{-1})
	b_0	b_1	
1	−0.7073 ± 0.2765	247.2850 ± 0.3052	199.61 ± 0.08
2	−0.6128 ± 0.2198	247.2050 ± 0.2499	199.64 ± 0.10
3	−0.7546 ± 0.3163	247.3448 ± 0.3559	199.62 ± 0.07

Table 22. Final propane value assignment for the CCQM-K3.2019 sample, with associated uncertainty for 95 % confidence (k = 2).

Sample Number	Amount fraction (µmol mol^{-1})
MR8468	199.62 ± 0.28

E.5.4 Uncertainty evaluation

The uncertainties assigned to the CCQM sample were calculated independently for each analytical period from the gravimetric uncertainties of the PSMs (as listed in Table 18) and the analytical uncertainties of the C_3H_8 response ratios (as determined using Equation 4). The combined uncertainty, u_c, was determined by pooling the individual uncertainties listed in Table 21, using Equation 3.

Since the standards used to analyze the CCQM sample were prepared in a balance of nitrogen, an additional source of uncertainty was considered, to account for any potential bias in the assigned value relating to the presence of oxygen in the CCQM sample matrix. This uncertainty, u_{matrix}, was incorporated into the overall uncertainty, u, such that:

$$u = \sqrt{u_c^2 + u_{matrix}^2} \qquad (5)$$

The final uncertainty is expressed as:

$$U = ku$$

where the coverage factor *k* is equal to 2. The true value is therefore asserted to lie in the interval defined by the assigned amount fraction ± *U*, with a confidence of approximately 95 % [4].

References

[1] International Organization for Standardization, ISO 6142-1:2015 Gas analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures.

[2] M.J.T. Milton, P.M. Harris, I.M. Smith, A.S. Brown, and B.A. Goody, Implementation of a generalized least-squares method for determining calibration curves from data with general uncertainty structures, *Metrologia*, 4(4), S291–S298 (2006).

[3] International Organization for Standardization, ISO 6143:2001 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures, 2nd edition.

[4] JCGM 100:2008, Evaluation of measurement data – Guide to the expression of uncertainty in measurement (Gum 1995 with minor corrections), Joint Committee for Guides in Metrology, BIPM, Sèvres, France (2008).

Annex F Measurement report of NMISA

Cylinder number: D34 0045

Nominal amount fraction ranges for the comparison sample are indicated in Table 1.

Table 1: Nominal amount fraction ranges for the comparison

Component	Amount fraction range
Carbon dioxide (CO_2)	2 – 5 cmol/mol
Carbon monoxide (CO)	0.5 – 2 cmol/mol
Oxygen (O_2)	1 – 4 cmol/mol
Propane (C_3H_8)	100 – 300 µmol/mol

F.1 Results

Measurement #1

Components	Date (dd/mm/yy)	Results (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
O_2	05-06-2020	3.0×10^{-2}	0.11	4	5.6×10^{-5}
CO_2	03-06-2020	2.0×10^{-2}	0.11	5	1.5×10^{-5}
C_3H_8	11-05-2020	2.0×10^{-4}	0.30	3	6.3×10^{-7}
CO	05-06-2020	1.0×10^{-2}	0.11	4	6.1×10^{-6}

Measurement #2

Components	Date (dd/mm/yy)	Results (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
O_2	02-09-2020	3.0×10^{-2}	0.06	5	3.9×10^{-5}
CO_2	05-06-2020	2.0×10^{-2}	0.11	4	1.5×10^{-5}

C_3H_8	18-05-2020	2.0 x 10^{-4}	0.13	4	3.3 x 10^{-7}
CO	05-06-2020	1.0 x 10^{-2}	0.03	4	2.8 x 10^{-6}

Measurement #3

Components	Date (dd/mm/yy)	Results (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
O_2	28-10-2020	3.0 x 10^{-2}	0.11	4	6.1 x 10^{-5}
CO_2	02-09-2020	2.0 x 10^{-2}	0.28	4	3.2 x 10^{-5}
C_3H_8	20-05-2020	2.0 x 10^{-4}	0.18	4	4.1 x 10^{-7}
CO	02-09-2020	1.0 x 10^{-2}	0.22	4	1.7 x 10^{-5}

Measurement #4

Components	Date (dd/mm/yy)	Results (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
C_3H_8	25-05-2020	2.0 x 10^{-4}	0.45	6	9.2 x 10^{-7}
CO	02-09-2020	1.0 x 10^{-2}	0.22	4	1.7 x 10^{-5}

Measurement #5

Components	Date (dd/mm/yy)	Results (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
C_3H_8	02-06-2020	2.0 x 10^{-4}	0.31	3	6.9 x 10^{-7}

Comparison sample results

Component	Results (mol/mol)	Expanded uncertainty. (mol/mol)	Coverage factor at 95 % confidence
Oxygen	3.0 x 10^{-2}	1.2 x 10^{-4}	U (k = 2)
Carbon dioxide	2.0 x 10^{-2}	4.9 x 10^{-5}	U (k = 2)
Propane	2.0 x 10^{-4}	1.3 x 10^{-6}	U (k = 2)
Carbon monoxide	1.0 x 10^{-2}	2.9 x 10^{-5}	U (k = 2)

F.2 Measurement methods

An Agilent 7890B gas chromatography coupled with different detectors was used for the value assignment of the four components in the comparison sample. A flame Ionisation detector (FID) was used for analysis of C_3H_8 and CO, thermal conductivity detector (TCD) was used for the analysis of (CO and CO_2) and micro- electron capture detector (μ-ECD) was used for the analysis of O_2 in the comparison sample. The comparison sample and NMISA prepared PSGMs were connected to the sampler box using 1/16-inch sulfinert treated tubing. Data acquisition was done using Agilent Chemstation offline software. The cylinders were connected to a double stage regulator which was purged several times before use. The sample flow was set at 35 ml/min using the mass flow controller for all the gas chromatography. Seven injections were done with minimum of three replicates taken for the calculations of the comparison sample amount fraction.

Table 2: Analytical conditions for carbon monoxide and carbon dioxide

Instrument: Agilent 7890B	RGA system (TCD)	NCD system (TCD)	GC-FID
Parameters:			
Column	Shin Carbon ST, 2 m x 1/8” OD x 2 mm ID, 80/100 2 mm ID, 80/100	Shin Carbon ST, 2 m x 1/8” OD x 2 mm ID, 80/100	Shin Carbon ST, 2 m x 1/8” OD x 2 mm ID, 80/100
Oven temperature	35 °C for 3 min, 120 °C for 4 min at 120 °C/min	80°C isothermal,	60 °C for 4 min, 100 °C for 5.5 min at 100 °C/min
Detector temperature	275 °C	275 °C	250°C
Carrier gas	Hydrogen	Hydrogen	Helium
Sample flow	35 ml/min	35 ml/min	35 ml/min

Table 3: Analytical conditions for oxygen and propane

Components	**O_2**	**C_3H_8**	
Instruments: Agilent 7890B	GC - µECD	RGA System (FID)	NCD system (FID)
Parameters:			
Column	Porapak Q, 3m x 1/8” OD x 2 mm ID, 80/100	HP-PLOT Al_2O_3 KCl 50 m x 0.320 mm x 8 µm plot column	Porapak Q, 3m x 1/8” OD x 2 mm ID, 80/100
Oven temperature	60 ºC	80 ºC isothermal	135 ºC isothermal
Detector temperature	175 ºC	250 ºC	250 ºC
Carrier gas	Nitrogen	Helium	Helium
Sample flow	35 ml/min	35 ml/min	35 ml/min

F.3 Calibration standards

The multi-component containing carbon monoxide, carbon dioxide, propane and oxygen primary standard gas mixtures (PSGMs) in nitrogen used for calibration were prepared in accordance with ISO 6142-1:2015 (Gas analysis – Preparation of calibration gas mixtures – Gravimetric method). The gravimetric amount fraction for propane was a three-steps dilution from high purity of propane (Source Air Liquide), carbon monoxide was a two-steps dilution from high purity CO 4.5 (Source Air Liquide), CO_2 and O_2 were a one-step dilution from high purity of CO_2 and O_2 (Source Air Products Southern Africa), and BIP nitrogen (Source Air Products Southern Africa) as the diluent gas. Production diagram of the multi-component primary standard gas mixtures is shown in figure 1 and 2. The gravimetric amount fractions of the prepared PSGMs are detailed in table 4. The gravimetric amount fractions of the primary standard gas mixtures were verified using ISO 6143:2001 (Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures).

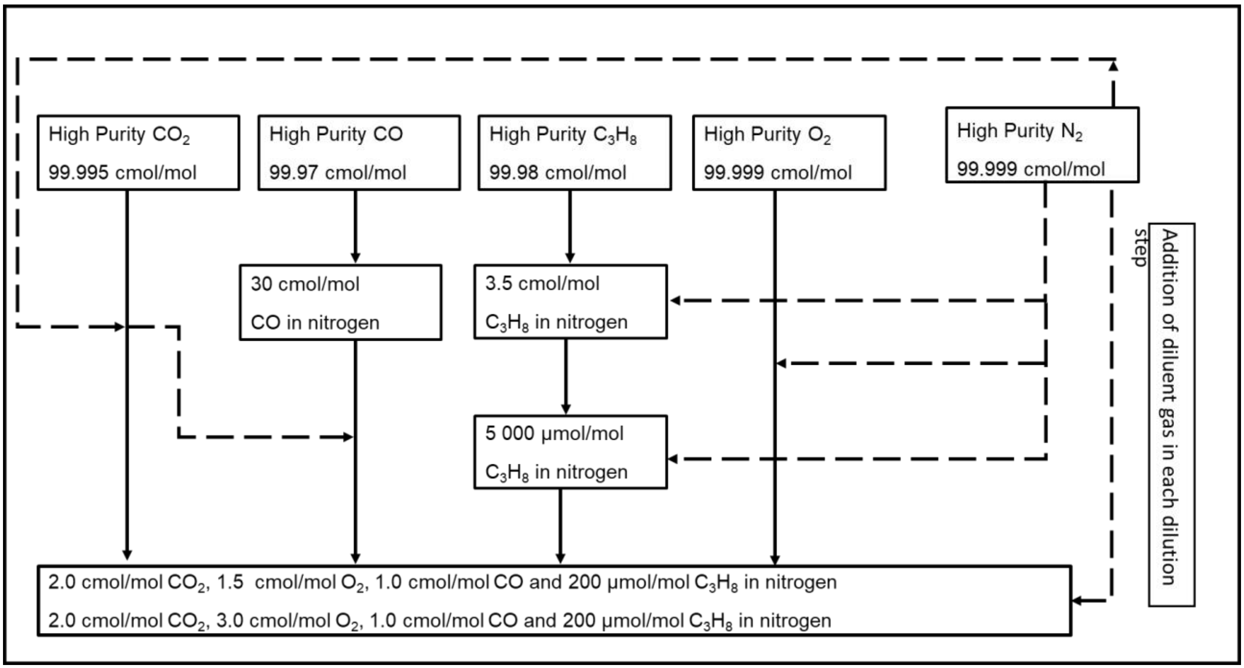


Figure 1: Production diagram for multi-component of carbon dioxide, carbon monoxide, propane and oxygen primary standard gas mixtures prepared for the single-point calibration.

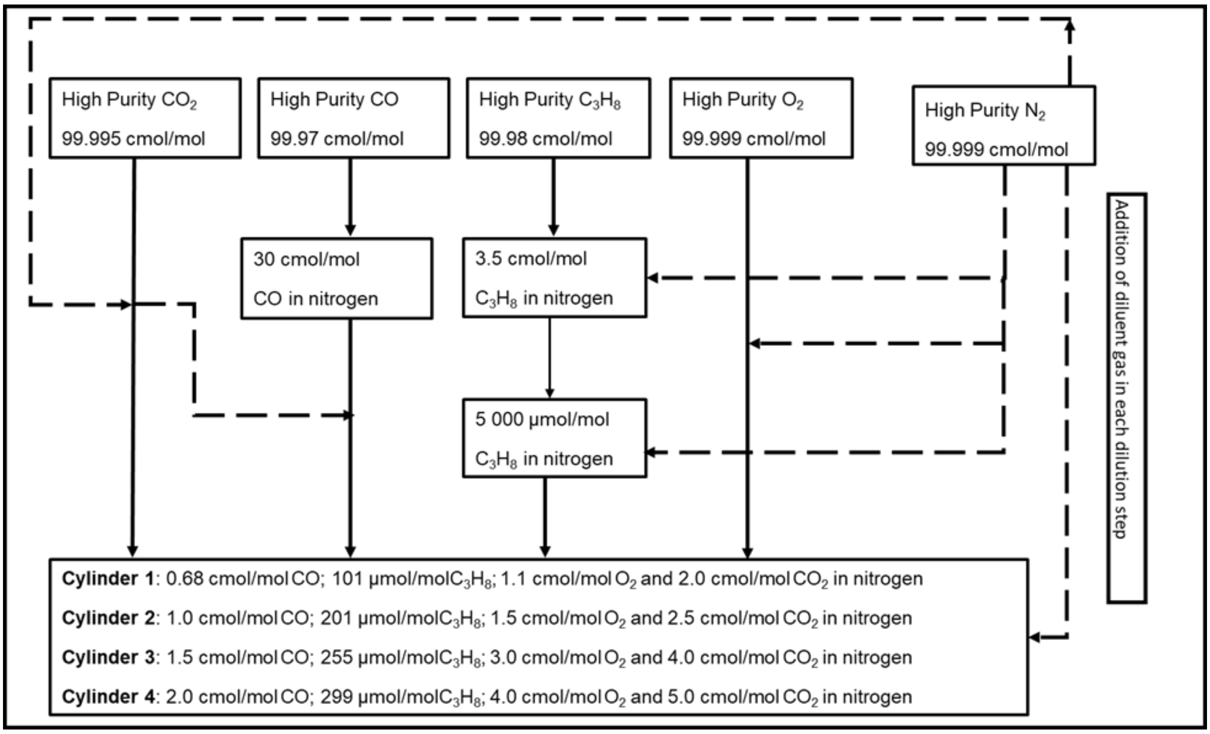


Figure 2: Production diagram for multi-component of carbon dioxide, carbon monoxide, propane and oxygen primary standard gas mixtures prepared for the multi-point calibration.

Table 4: Gravimetric amount fractions and uncertainties for primary standards gas mixtures

Cylinder number	Component	Gravimetric amount fraction (mol/mol)	Expanded uncertainty (*k* =2), (mol/mol)
D62 6592	C_3H_8	1.0×10^{-4}	2.0×10^{-8}
	CO	6.8×10^{-3}	9.0×10^{-7}
	O_2	1.1×10^{-2}	2.4×10^{-6}
	CO_2	2.0×10^{-2}	2.2×10^{-6}
D73 2166	C_3H_8	2.0×10^{-4}	3.4×10^{-8}
	CO	1.0×10^{-2}	1.2×10^{-6}
	O_2	1.5×10^{-2}	3.1×10^{-6}
	CO_2	2.5×10^{-2}	$2{,}7 \times 10^{-6}$
D62 6668	C_3H_8	2.5×10^{-4}	4.1×10^{-8}
	CO	1.5×10^{-2}	1.3×10^{-6}
	O_2	3.0×10^{-2}	3.4×10^{-6}
	CO_2	4.0×10^{-2}	3.3×10^{-6}
D62 6625	C_3H_8	3.0×10^{-4}	4.7×10^{-8}
	CO	2.0×10^{-2}	1.4×10^{-6}
	O_2	4.0×10^{-2}	3.1×10^{-6}
	CO_2	5.0×10^{-2}	3.6×10^{-6}
D62 6490	C_3H_8	2.0×10^{-4}	3.6×10^{-8}
	CO	1.0×10^{-2}	1.2×10^{-6}
	O_2	3.0×10^{-2}	3.6×10^{-6}
	CO_2	2.0×10^{-2}	2.7×10^{-6}
D67 9612	C_3H_8	2.0×10^{-4}	3.5×10^{-8}
	CO	1.0×10^{-2}	1.2×10^{-6}
	O_2	3.0×10^{-2}	3.6×10^{-6}
	CO_2	2.0×10^{-2}	2.7×10^{-6}
D62 6501	C_3H_8	2.0×10^{-4}	3.4×10^{-8}
	CO	1.0×10^{-2}	1.2×10^{-6}
	O_2	3.0×10^{-2}	3.4×10^{-6}
	CO_2	2.0×10^{-2}	2.5×10^{-6}

F.4 Instrument calibration

F.4.1 Carbon monoxide (CO) and carbon dioxide (CO_2)

The quantification of CO and CO_2 amount fractions in the comparison sample were obtained using a single point calibration method on the gas chromatography (GC) coupled with thermal conductivity detector (TCD). A calibration standard with similar amount fraction as the comparison sample was used for value assignment of CO and CO_2 components in the comparison sample. The calibration standard and the comparison sample were connected on the multi-position sampler box to the GC. The amount fraction of the comparison sample was calculated using the following model equation:

$$x_{sample} = \frac{y_{Sample}}{y_{Reference}} \times x_{reference} \qquad (1)$$

F.4.2 Oxygen (O_2)

The quantification of O_2 amount fraction in the comparison sample was attained using a single point calibration method on the gas chromatography coupled with a micro-electron capture detector (μECD). A calibration standard with similar amount fraction as the comparison sample was used to value assign the O_2 in the comparison sample. Both the calibration standard and comparison sample were introduced to the GC through the multi-position sampler box.

F.4.3 Propane (C_3H_8)

The determination of propane amount fraction in the comparison sample was done using the multi-point calibration method. The calibration standards used are listed in Table 4. The calibration standards and comparison sample were connected randomly on the gas chromatography coupled with flame ionization detector (GC-FID). The generated data was analysed using a generalized least square method using the XLgenlinev1.1 software.

The second-order polynomial mathematical function was used for multi-point calibration:

$$x = b_0 + b_1 y + b_2 y^2 \qquad (2)$$

F.5 Purity assessment of high purity gases

Purity assessment of the high purity gases was performed using traceable primary standard gas mixtures containing components and mole fractions similar to those found in high purity gases. Table 5 to 9 shows purity table for high purity gases used to prepare standards used to value-assign comparison sample.

Table 5: Purity analysis for high purity Built-in purifier nitrogen

Component	Amount fraction (cmol/mol)	Expanded uncertainty (cmol/mol), *k=2*
CH_4	5.0×10^{-6}	5.8×10^{-6}
CO_2	2.7×10^{-5}	2.7×10^{-6}
CO	1.3×10^{-5}	1.4×10^{-5}
H_2O	1.0×10^{-6}	1.2×10^{-6}
O_2	4.7×10^{-7}	4.7×10^{-8}
Ar	1.8×10^{-2}	1.8×10^{-3}
N_2	1.0×10^{2}	1.8×10^{-3}

Table 6: Purity analysis for high purity carbon dioxide

Component	Amount fraction (cmol/mol)	Expanded uncertainty (cmol/mol), *k=2*
CH_4	6.2×10^{-4}	6.2×10^{-5}
H_2O	2.0×10^{-4}	2.3×10^{-4}
O_2	5.4×10^{-4}	5.4×10^{-5}
Ar	1.4×10^{-4}	1.4×10^{-5}
N_2	1.6×10^{-2}	1.6×10^{-3}
CO_2	1.0×10^{2}	1.6×10^{-3}

Table 7: Purity analysis for high purity carbon monoxide

Component	Amount fraction (cmol/mol)	Expanded uncertainty (cmol/mol), *k=2*
CH_4	1.0×10^{-4}	1.2×10^{-4}
CO_2	5.0×10^{-5}	5.8×10^{-5}
H_2	2.4×10^{-3}	1.2×10^{-4}
H_2O	1.5×10^{-4}	1.7×10^{-4}
C_3H_8	1.9×10^{-5}	1.9×10^{-6}
O_2	5.9×10^{-4}	5.9×10^{-5}
Ar	2.8×10^{-4}	2.8×10^{-5}
N_2	2.5×10^{-4}	2.9×10^{-4}
CO	1.0×10^{2}	3.8×10^{-4}

Table 8: Purity analysis for high purity oxygen

Component	Amount fraction (cmol/mol)	Expanded uncertainty (cmol/mol), *k=2*
CH_4	5.0×10^{-6}	5.8×10^{-6}
CO_2	2.6×10^{-5}	2.6×10^{-6}
CO	1.0×10^{-5}	1.2×10^{-5}
H_2O	1.0×10^{-4}	1.2×10^{-4}
H_2	6.7×10^{-3}	6.7×10^{-4}
Ar	3.2×10^{-5}	3.2×10^{-6}
N_2	5.4×10^{-4}	5.4×10^{-4}
O_2	1.0×10^{2}	8.7×10^{-4}

Table 9: Purity table for high purity propane

Component	Amount fraction (cmol/mol)	Expanded uncertainty (cmol/mol), *k=2*
CH_4	1.1×10^{-5}	1.1×10^{-6}
CO	2.1×10^{-5}	2.1×10^{-6}
H_2	7.6×10^{-3}	3.8×10^{-4}
CO_2	2.3×10^{-5}	2.3×10^{-6}
H_2O	2.5×10^{-4}	2.9×10^{-4}
O_2	5.4×10^{-4}	5.4×10^{-5}
Ar	1.4×10^{-4}	1.4×10^{-5}
N_2	1.1×10^{-2}	1.1×10^{-3}
C_3H_8	1.0×10^{2}	1.2×10^{-3}

F.6 Sample handling

Upon receipt of the comparison sample, it was kept in a temperature-controlled laboratory to stabilize to the laboratory's environmental conditions before the measurements could commence. The comparison sample and calibration standards cylinders were connected through a double stage regulator, fitted with Swagelok quick connectors, and purged before connected to the automatic sampler box with a 16-port multi-position valve. The sample flow rate was set at 35 ml/min and controlled by mass flow controller.

F.7 Uncertainty evaluation

F.7.1 General

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method, and the target uncertainty of the result, they must be considered or can be neglected.

The uncertainty contributors associated with the final measurement are as follows:

a) Verification uncertainty (repeatability)
b) Stability (Estimated standard deviation of the mean)

The verification uncertainty includes the gravimetric uncertainty of the standards and uncertainty from purity analysis.

The results yielded an average amount fraction and standard deviation was calculated. The predicted amount fraction for each component in the samples were averaged, and a standard deviation calculated as shown in Equation 3. The uncertainties of each measurement were combined as shown in Equation 4 below:

$$S = \sqrt{\frac{\Sigma(x-\overline{x})^2}{(n-1)}} \tag{3}$$

$$u_c = \sqrt{\Sigma(u_{Meas(i)}{}^2)/n} \tag{4}$$

Where u_c is the combined uncertainty, $u_{Meas(i)}$ is the standard uncertainty of measurement i and n, the total number of measurements. The combined standard uncertainty was converted to an expanded uncertainty by multiplying by a coverage factor k = 2, at a confidence level of 95,45%.

An example of verification uncertainty contribution for propane results.

Table 10: Uncertainty budget for propane results

Measurement date	Verification amount fraction (µmol/mol)	Verification uncertainty (µmol/mol)
11-05-2020	200.87	0.63
18-05-2020	200.08	0.33
20-05-2020	200.02	0.41
25-05-2020	200.29	0.92
02-06-2020	200.49	0.69
Average	**200.35**	
Std deviation	**0.34**	
ESDM (stability)	**0.15**	
Verification	**0.63**	
uc	**0.65**	
U (k=2)	**1.30**	
%REU	**0.65**	

F.7.2 Detailed uncertainty budget:

The uncertainty contributors and corresponding relative expanded uncertainties are detailed in table 10 for each component.

Table 11: Uncertainty evaluation

Component	**Uncertainty source** ***X_I***	**Evaluation Type (A or B)**	**Assumed distribution**	**Standard uncertainty** $u(x_i)$,(cmol/mol)	**Expanded Uncertainty,** U(k=2) (cmol/mol)	**% REU**
Carbon monoxide	Verification	Type A	Normal	$1,5 \times 10^{-3}$	$2,9 \times 10^{-3}$	0,30 %
	Stability	Type A	Normal	$2,1 \times 10^{-4}$		
Carbon Dioxide	Verification	Type A	Normal	$4,3 \times 10^{-3}$	$8,5 \times 10^{-1}$	0,43 %
	Stability	Type A	Normal	$9,5 \times 10^{-4}$		
Oxygen	Verification	Type A	Normal	$5,8 \times 10^{-3}$	$1,2 \times 10^{-2}$	0,39 %
	Stability	Type A	Normal	$1,2 \times 10^{-3}$		
Propane	Verification	Type A	Normal	$6,5 \times 10^{-5}$	$1,3 \times 10^{-4}$	0,65 %
	Stability	Type A	Normal	$1,5 \times 10^{-5}$		

- Sensitivity coefficient, $c_1 = 1$

Annex G Measurement report of NPL

G.1 Results

Cylinder number: 8500

G.2 Calibration standards

Preliminary analysis of the CCQM-K3.2019 comparison mixture against existing NPL in-house standards was conducted to determine the nominal amount fractions. Based on these analyses, two matching NPL Primary Reference Materials (PRMs) were prepared (2707 and 2910) independently in accordance with ISO 6142-1, each from different premixtures (figure 1) to match the results of the initial analysis. Mixtures A672, 2861, 2876 & 2917 were newly prepared from source gases (purity shown in tables 2 – 6), before further dilution to produce calibration mixture 2707. Existing NPL in-house PRMs (A489, 2650, 2032 & 2032) were used as validation standards for the newly prepared parents and were also used to produce a second matching calibration mixture 2910. All mixtures were prepared in 10 L cylinders with SPECTRA-SEAL passivation (BOC) that had been evacuated to < 5×10^{-7} mBar prior to use. The amount fractions were determined by gravimetry and are shown in table 1.

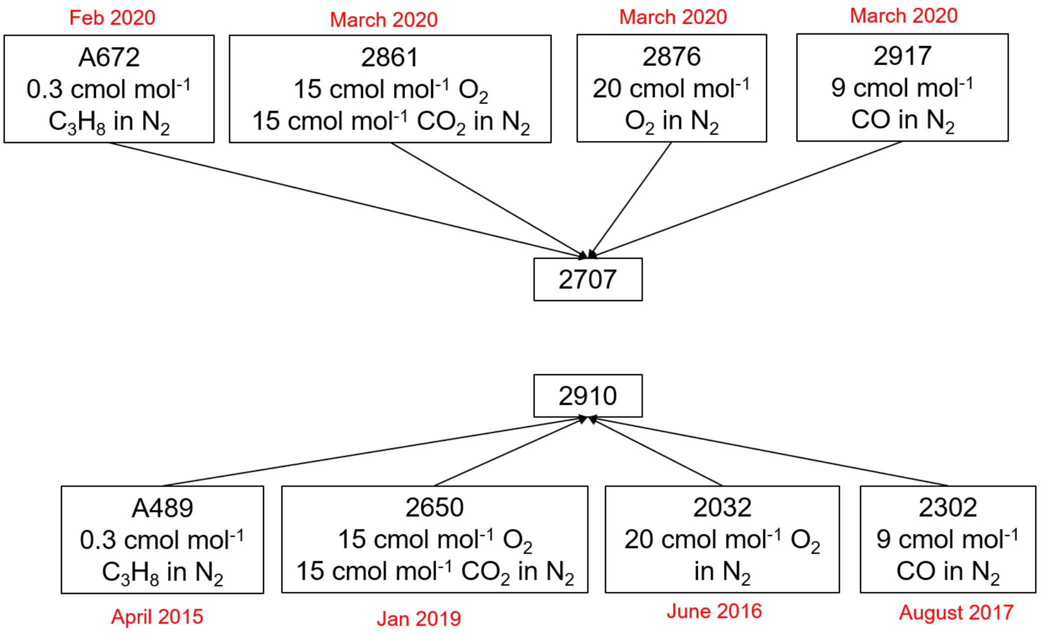


Figure 6. **Preparation hierarchies for two NPL PRMs used as calibration standards to certify the comparison mixture.**

Table 1. Amount fractions (cmol mol^{-1}) of two matching NPL PRMs (uncertainties are from gravimetry only).

	Oxygen	Carbon dioxide	Carbon monoxide	Propane
NPL2707	3.11 ± 0.00047	2.00 ± 0.00029	1.00 ± 0.00023	0.0197 ± 0.000007
NPL2910	3.10 ± 0.00061	2.00 ± 0.00037	0.996 ± 0.00030	0.0199 ± 0.000009

G.3 Purity tables

Table 2. Oxygen purity table.

Component	Amount Fraction (μmol mol^{-1})	Expanded Uncertainty (μmol mol^{-1})
O_2	999999.80	0.09
N_2	0.08	0.05
CO	0.10	0.07
CH_4	0.03	0.02

Table 3. Carbon dioxide purity table.

Component	Amount Fraction (μmol mol^{-1})	Expanded Uncertainty (μmol mol^{-1})
CO_2	999999.80	0.06
N_2	0.05	0.03
O_2	0.05	0.03

CO	0.05	0.03
Ar	0.05	0.03

Table 4. Carbon monoxide purity table.

Component	Amount Fraction (µmol mol^{-1})	Expanded Uncertainty (µmol mol^{-1})
CO	999975.1	2.0
N_2	11.1	0.5
O_2	12.0	0.5
CO_2	0.80	0.05
H_2O	1.0	0.5
C_XH_Y	0.010	0.006

Table 5. Propane purity table.

Component	Amount Fraction (µmol mol^{-1})	Expanded Uncertainty (µmol mol^{-1})
Propane	999949	6
n-butane	3.3	0.5
neopentane	39.0	4.6
C_5-unknown	9.0	1.2

Table 6. Nitrogen Purity table.

Component	Amount Fraction (µmol mol^{-1})	Expanded Uncertainty (µmol mol^{-1})
N_2	999999.5	0.9
Ar	0.50	0.05
CO	0.00030	0.00015
O_2	0.0050	0.0025
C_XH_Y	0.005	0.005
H_2O	0.0050	0.0020
NO	0.00050	0.00025
SO_2	0.00050	0.00025
CH_4	0.0010	0.0010
H_2	0.0010	0.0010

NPL PRMs 2707 and 2910 were validated by measurement against each other and existing NPL in-house mixtures of similar amount fraction. They were then used to assign analytical values to the CCQM-K3.2019 mixture.

G.4 Instrumentation

Oxygen, carbon dioxide, and carbon monoxide were analysed by gas chromatography with a thermal conductivity detector (GC-TCD) (model: Agilent 7890B). Three columns were used:

- HP-PLOT Q PT - 15m x 0.53mm x 40μm (pre-separation)
- FS Tubing 0.25mm - cut to 1.5m (carbon dioxide)
- HP-PLOT MolSieve 30m x 0.53mm x 50μm (oxygen and carbon monoxide)

Propane was analysed by GC using either a DB-624 (75m × 0.53 μm, df = 3 μm; J&W) or PLOT (50m × 0.53 μm, df = 10 μm, J&W) column with a flame ionisation detector (GC-FID). A further measurement for oxygen was made using a paramagnetic analyser (model: Horiba – MPA-510).

G.5 Calibration method and value assignment

The GC-TCD and GC-FID analyses were performed using a switching method (A-B-A-B- etc), alternating between a calibration standard and the CCQM-K3.2019 comparison mixture. All lines were thoroughly purged before measurement, and gas continually flowed at 30 sccm for the duration of the analysis. For each replicate measurement, a ratio (r) of the peak area of the component in the CCQM-K3.2019 (b) compared to the NPL PRM (2707 or 2910) was calculated, accounting for any drift by using the average of the peak areas immediately before (a_1) and after (a_2).

$$r = \frac{2b}{a_1+a_2} \qquad \text{Eq. 1}$$

The average ratio ($\bar{r}$) of n replicate measurements was then calculated and

$$\bar{r} = \frac{\sum r}{n} \qquad \text{Eq. 2}$$

The paramagnetic analyser switches between two ports, a reference inlet which takes a continuous flow of pure nitrogen (Air Products BIP+) and a sample inlet. Gas flowing to the sample inlet switches between a zero gas (nitrogen, Air Products BIP+), NPL PRM as calibration standard (2707 or 2910) and the CCMQ-K3.2019 comparison mixture, following the sequence: zero-cal-comp-comp-cal-zero. Upon switching to a new gas, a wait time of 100 seconds allows the analyser response to stabilise, before a data point is recorded every second for 100 seconds. The sequence is repeated four times, providing eight unique measurements of the ratio between the analyser response to the comparison mixture (v_u) and NPL PRM (v_s), minus the offset from the response to the zero gas (v_z).

$$r = \left(\frac{v_u - v_z}{v_s - v_z}\right) \qquad \text{Eq. 3}$$

The unknown amount fraction (x_u), for the given component was calculated by multiplying the gravimetric amount fraction in the NPL PRM (x_s) by the average of the ratio measurements ($\bar{r}$).

$$x_u = x_s\bar{r} \qquad \text{Eq. 4}$$

In order to evaluate any bias present from the coelution of argon and oxygen in GC-TCD analyses, additional measurements of the argon amount fraction in NPL cylinder 2707 and the CCQM-K3.2019 comparison mixture were made using GC with pulsed discharge helium ionisation detector (GC-PDHID) that utilizes a molsieve capillary column (5A, 80m × 0.53mm × 0.50µm) to separate argon from oxygen. A 10 µmol mol^{-1} argon in helium NPL PRM was used for comparison. Similar amount fractions (<10 µmol mol^{-1}) were observed in both mixtures, which indicates a negligible bias on the oxygen amount fraction measurements determined by the GC-TCD analyses. This is consistent with the agreement in observed results between the GC-TCD and the paramagnetic analyser, which is not susceptible to interference from the presence of argon.

G.6 Uncertainty evaluation

Following the measurement equation above, the combined uncertainty $u(x_u)$ is calculated by:

$$\frac{u(x_u)}{x_u} = \sqrt{\frac{u(x_s)^2}{{x_s}^2} + \frac{u(\bar{r})^2}{\bar{r}^2}} \qquad \text{Eq. 5}$$

The standard uncertainty $u(x_s)$ comes from the gravimetry and the standard uncertainty $u(\bar{r})$ is the standard deviation of the mean of the ratio measurements. Sensitivity coefficients are calculated by taking the partial derivative with respect to each measurement input. The following table shows an example uncertainty budget for one measurement of a single component.

Table 7. Uncertainty budget for one measurement of carbon monoxide.

	unit	example value	standard unc	Sensitivity coefficient	unc contribution	unc type	distribution
x_s	cmol/mol	1.00015	0.00023	0.99474	0.00023	A	normal
$\bar{r}$	-	0.99474	0.00187	1.00015	0.00187	A	normal
x_u	cmol/mol	0.99489					
$u(x_u)$	cmol/mol	0.00188					
$U(x_u)$	cmol/mol	0.00377					

For each component, all measurements are combined by taking a weighted average, according to the uncertainty in each measurement, to give x_f. Sensitivity coefficients are given to provide equal input from each measurement, giving the uncertainty for the final measurement $u(x_f)$.

Table 8. Determination of final amount fraction and uncertainty of carbon monoxide.

	unit	value	standard unc	Sensitivity coefficient	unc contribution	unc type	Distribution
x_1	cmol/mol	0.99489	0.00188	0.25	0.00047	A	normal
x_2	cmol/mol	0.99450	0.00246	0.25	0.00062	A	normal

x_3	cmol/mol	0.99358	0.00173	0.25	0.00043	A	normal
x_4	cmol/mol	0.99501	0.00105	0.25	0.00026	A	normal
x_f	cmol/mol	0.99456					
u(x_f)	cmol/mol	0.00093					
U(x_f)	cmol/mol	0.00185					

Detailed results are in the accompanying report file ‘NPL_CCQM-K3.2019 Report form Submitted’.

References

International Organisation for Standardisation. ISO 6142−1 Gas analysis - Preparation of calibration gas mixtures - Part 1: Gravimetric method for Class I mixtures. ISO: Geneva, Switzerland, 2015.

Annex H Measurement report of VNIIM

H.1 Results

Cylinder number: 8449

Table 1: Measurement #1

Component	Date (dd/mm/yy)	Result (%)	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	-	-

Table 2: Measurement #2

Component	Date (dd/mm/yy)	Result (%)	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	-	-

Table 3: Measurement #3

Component	Date (dd/mm/yy)	Result (%)	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
Nitrogen	-	balance	-	-

Table 4: Measurement #4

Component	Date (dd/mm/yy)	Result (%)	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	-	-

Table 5:Results

Component	Date (dd/mm/yy)	Result (%)	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		-	-	-

H.2 Calibration standards

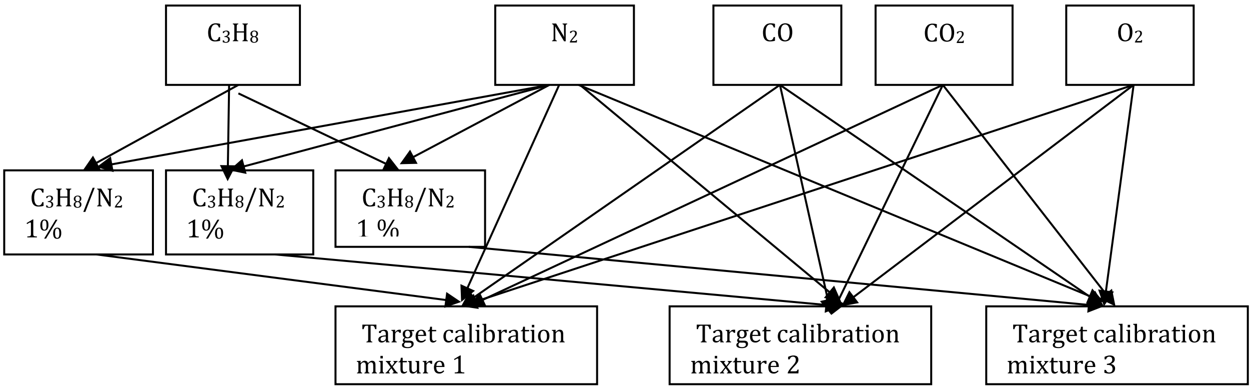
Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to [1] were used as calibration standards.

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 %	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	-
Cylinder number	Component	Mole fraction (%)	Standard uncertainty due to weighing and purity (%)
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

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

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

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

H.3 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

H.4 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 $X_x = X_{st} \frac{A_x}{(A'_{st}+A''_{st})/2}$,

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.

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.

H.5 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

The contribution $u_i(y)$ is calculated according to the following formula:

$$u_i(y)=c_i*u(x_i),$$

c_i - sensitivity coefficient,
$u(x_i)$ - standard uncertainty.

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

Annex I Measurement report of VSL

I.1 Results

Cylinder number : 8457 E

Table 15 Results of measurement 1

Component	Date	Fraction x_1 (cmol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty $u(x_1)$ (cmol/mol)
Oxygen	10-03-2020	2.89346	0.02%	5	0.00056
Carbon dioxide	21-02-2020	2.01516	0.03%	5	0.00062
Propane	18-03-2020	0.0203110	0.02%	5	0.0000040
Carbon monoxide	21-02-2020	1.01494	0.02%	5	0.00018

Table 16 Results of measurement 2

Component	Date	Fraction x_2 (cmol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty $u(x_2)$ (cmol/mol)
Oxygen	12-03-2020	2.89500	0.03%	5	0.00097

Carbon dioxide	25-02-2020	2.01574	0.02%	5	0.00048
Propane	31-03-2020	0.0203090	0.02%	5	0.0000040
Carbon monoxide	25-02-2020	1.01546	0.02%	5	0.00023

Table 17 Results of measurement 3

Component	Date	Fraction x_3 (cmol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty $u(x_3)$ (cmol/mol)
Oxygen	16-03-2020	2.89500	0.03%	5	0.00097
Carbon dioxide	28-02-2020	2.01519	0.03%	5	0.00132
Propane	02-04-2020	0.0203090	0.02%	5	0.0000040
Carbon monoxide	28-02-2020	1.01546	0.02%	5	0.00023

Table 18 results of measurement 4

Component	Date	Fraction x_4 (cmol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty $u(x_4)$ (cmol/mol)
Oxygen	06-04-2020	2.89322	0.03%	5	0.00096
Carbon dioxide	06-03-2020	2.01510	0.02%	5	0.00033
Propane	-	-	-	-	-
Carbon monoxide	06-03-2020	1.01637	0.02%	5	0.00023

Table 19 Results of measurement 5

Component	Date	Fraction x_5 (cmol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty $u(x_5)$ (cmol/mol)
Oxygen	18-05-2020	2.89233	0.03%	5	0.00082
Carbon dioxide	-	-	-	-	-
Propane	-	-	-	-	-
Carbon monoxide	-	-	-	-	-

I.2 PSMs preparation method

The preparation of PSMs (Primary Standard Mixtures) is carried out in accordance with ISO 6142-1 [1]. Carbon dioxide was transferred from the pure gas. Oxygen with amount fractions up to 3 cmol/mol was transferred from the pure gas. For lower fractions, one–step dilution was used. Carbon monoxide was transferred from the premixture obtained with one dilution step from the pure gas. Propane was transferred from the premixture obtained with two dilution steps. In the Table 20 to Table 24 the purity data of the pure gases are given for the PSM with code VSL244236. Other PSMs have been prepared similarly using the same source gases. The purity analysis of these parent gases was performed in accordance with ISO 19229 [4], using a variety of analytical techniques. In cases where an expected impurity is not detected, the limit of detection is taken as basis for assigning a value to the corresponding amount fraction, assuming a rectangular distribution. The associated standard uncertainty is computed accordingly.

For the preparation of the PSMs, an automatic weighing device was used. The standard deviation of each weighing was typically between 1 to 2 mg resulting in gravimetric relative standard uncertainty of about 0.01- 0.02% on the amount fraction. The calculations of uncertainty of the gravimetric gas mixtures preparation have been published in [2][3]. As an example, the weighing data of the PSMs with a code VSL244236 are presented in the Table 25.

The composition of the gravimetrically prepared mixtures is calculated using the formulae for the amount fraction given in ISO 6142-1. For propagating the uncertainty due to weighing, purity of the parent gases and the atomic weights, the formula of ISO 6142-1 is used, thus ignoring the correlations that exist between the masses recorded for the transferred gases and the molar masses. The magnitude of these effects has recently been evaluated for the preparation of synthetic natural gas mixtures, where these correlation effects are substantially greater. The approach regularly used by VSL is consistent with ISO 6142-1, and deviates in the same way from the requirements of the Guide to the expression of Uncertainty in Measurement (GUM) [6] as the documentary standard does.

I.2.1 Purity data of the parent gases

Table 20 Purity data of carbon dioxide

Component	AP7582 (mol/mol)	
	x	u(x)
Argon	0.00000071	0.00000021
Carbon dioxide	0.99999447	0.00000300
Nitrogen	0.00000411	0.00000082
Oxygen	0.00000071	0.00000021

Table 21 Purity data of oxygen

Component	LI3195 (mol/mol)	
	x	u(x)
Argon	0.00000100000	0.00000057735
Methane	0.00000004290	0.00000000140

Component	LI3195 (mol/mol)	
	x	u(x)
Carbon monoxide	0.00000010000	0.00000005774
Carbon dioxide	0.00000000100	0.00000000058
Water	0.00000050000	0.00000028868
Nitrogen	0.00000050000	0.00000028868
Oxygen	0.99999785600	0.00000070946
Nitrous oxide	0.00000000010	0.00000000006

Table 22 Purity data of carbon monoxide

Component	AP1706 (mol/mol)	
	x	u(x)
Argon	0.000000570	0.000000120
Methane	0.000000027	0.000000005
Carbon monoxide	0.999995243	0.000002000
Carbon dioxide	0.000000150	0.000000090
Hydrogen	0.000000500	0.000000290
Water	0.000002400	0.000001000
Nitrogen	0.000000880	0.000000160
Oxygen	0.000000230	0.000000050

Table 23 Purity data of propane

Component	AP4621 (mol/mol)	
	x	u(x)
Argon	0.000004000	0.000002000
Ethane	0.000060300	0.000001400
Propene	0.000047000	0.000000600
Propane	0.999828919	0.000010000
1,3-butadiene	0.000000146	0.000000010
iso-butene	0.000000145	0.000000005
n-butane	0.000000590	0.000000030
iso-butane	0.000044800	0.000001500
Nitrogen	0.000010100	0.000001200
Oxygen	0.000004000	0.000002000

Table 24 Purity data of nitrogen

Component	APN26B (mol/mol)	
	x	u(x)
Argon	0.000005000	0.000003000
Methane	0.000000001	0.000000001
Carbon monoxide	0.000000001	0.000000001
Carbon dioxide	0.000000010	0.000000006
Hydrogen	0.000000025	0.000000015
Water	0.000000010	0.000000006
Nitrogen	0.999994900	0.000006000
Oxygen	0.000000100	0.000000030

The weighing data of the preparation of VSL244236, one of the PSMs used for calibration, data are given in Table 25. The “S” denotes the sample cylinder and the “R” the reference cylinder. The amount fractions with associated uncertainty for all components of VSL244236 are shown in Table 26.

Table 25 Weighing data of VSL244236

	Vacuum	Propane VSL144466	Carbon dioxide AP7582	Oxygen VSL320158	Carbon monoxide VSL448168	Nitrogen APN26B
S	7950.072	7997.027	8094.538	8127.874	8159.024	8765.388
R	8037.901	8037.897	8037.896	8037.897	8037.905	8037.903
S	7950.073	7997.028	8094.540	8127.875	8159.025	8765.387
R	8037.899	8037.9	8037.896	8037.900	8037.904	8037.901
S	7950.075	7997.027	8094.538	8127.877	8159.025	8765.390
R	8037.901	8037.898	8037.895	8037.899	8037.905	8037.904
S	7950.075	7997.030	8094.539	8127.878	8159.024	8765.389
R	8037.901	8037.901	8037.896	8037.9	8037.904	8037.904
S	7950.074	7997.029	8094.542	8127.877	8159.023	8765.38700

The standard atomic weights of 2019 have been used to compute the molar masses, save Argon, for which the standard atomic weight of 2013 has been used. The latter standard atomic weight considers mainly air as source of argon, which is consistent with the origin of the high-purity argon used by VSL. The stated uncertainty with the standard atomic weights has been interpreted in accordance with the guidance in ISO 6142-1 [1].

Table 26 Purity table of VSL244236

Component	VSL149269 (mol/mol)	
	x	u(x)
Argon	0.000004487976	0.000002347301
Methane	0.000000002976	0.000000000569
Carbon monoxide	0.020038453880	0.000003278136
Carbon dioxide	0.079846190313	0.000004677196
Ethane	0.000000036172	0.000000000840
Propene	0.000000028193	0.000000000360
Propane	0.000599757170	0.000000093711
1.3-butadiene	0.000000000088	0.000000000006
iso-butene	0.000000000087	0.000000000003
n-butane	0.000000000354	0.000000000018
iso-butane	0.000000026874	0.000000000900
Hydrogen	0.000000032006	0.000000013096
Water	0.000000066901	0.000000021378
Nitrogen	0.879482034100	0.000007380432
Oxygen	0.020028882909	0.000003058161
Nitrous oxide	0.000000000002	0.000000000001

I.3 Instrumentation

The measurements were performed on two different systems. The verification of carbon dioxide, carbon monoxide and propane were carried out using an Agilent 6890 gas chromatograph equipped with two channels and helium carrier gas. Measurements for carbon dioxide and carbon monoxide were performed within one measurement method on the channel equipped with TCD detector. First, a sample of 1mL was injected on 3ft Molsieve 13x column. As soon as carbon monoxide has eluted, the flow of the gasses was switched to 10 ft Porapak N to separate carbon dioxide. The temperature program starts at 35 °C, followed by 4 min at 180°C after elution of CO_2. The measurements of propane were performed separately using a method dedicated to this component on the same GC using 10 ft Porapak N column with an FID detector. There is no temperature program and the channel is kept at 145 °C.

The verification of oxygen was performed on the Agilent 7890A GC, configured for the analysis of the composition of natural gas and biogas. For the measurement of oxygen in automotive gas mixtures a method was set to measure only that component using one of three existing channels. Oxygen was separated and detected on the auxiliary channel equipped with a 500 µL sample loop, a Hayesep Q/ Molsieve 5A column with a TCD detector and argon as a carrier gas. The temperature program for the auxiliary channel starts at 35 °C and it is kept isothermal until the end of analysis.

I.4 Calibration method and value assignment

All PSMs used for the measurements of the key comparison are multi compound mixtures containing only components of interest. Depending on fraction of the component 6-8 injections were done for each cylinder. The first 1-3 injection were deleted to eliminate possible carry-over effects. The calculation of the averaged area and standard deviation were done always with 5 last injections. As the recorded peak areas are generally prone to drift due to, e.g., fluctuations in ambient pressure, these peak areas are usually corrected for this influence. The correction method based on the recorded ambient pressure was used for the results obtained with TCD detector. The data obtained with FID detector were not corrected at all.

Correction of the observed peak areas A for influence of the ambient pressure p was done using

$$y = \frac{p_0}{p} A$$

where p_0 the reference pressure (101325 Pa). The choice of the reference pressure is arbitrary.

After the corrections the calibration curve was obtained in accordance with ISO 6143 [7]**.** For all components a quadratic curve was used.

I.4.1 Results

An overview of the analytical results, obtained calibration functions and assigned value for all components for the second set of the measurements are given in Table 27 to Table 34 and in Figure 7 to Figure 10.

Table 27 Results of the PSM's for carbon dioxide measurement obtained on 25-02-2020

	x	u(x)	y	u(y)
	cmol/mol		a.u.	
VSL243984	1.00032	0.00013	3755.57	0.58
VSL299720	3.98331	0.00045	14960.15	2.35
VSL244160	5.98677	0.00045	22479.54	3.72
VSL244236	7.98462	0.00047	29970.15	7.88
VSL651981	10.00855	0.00048	37514.68	4.17

Figure 7 Calibration data and residuals for carbon dioxide done on 25-02-2020

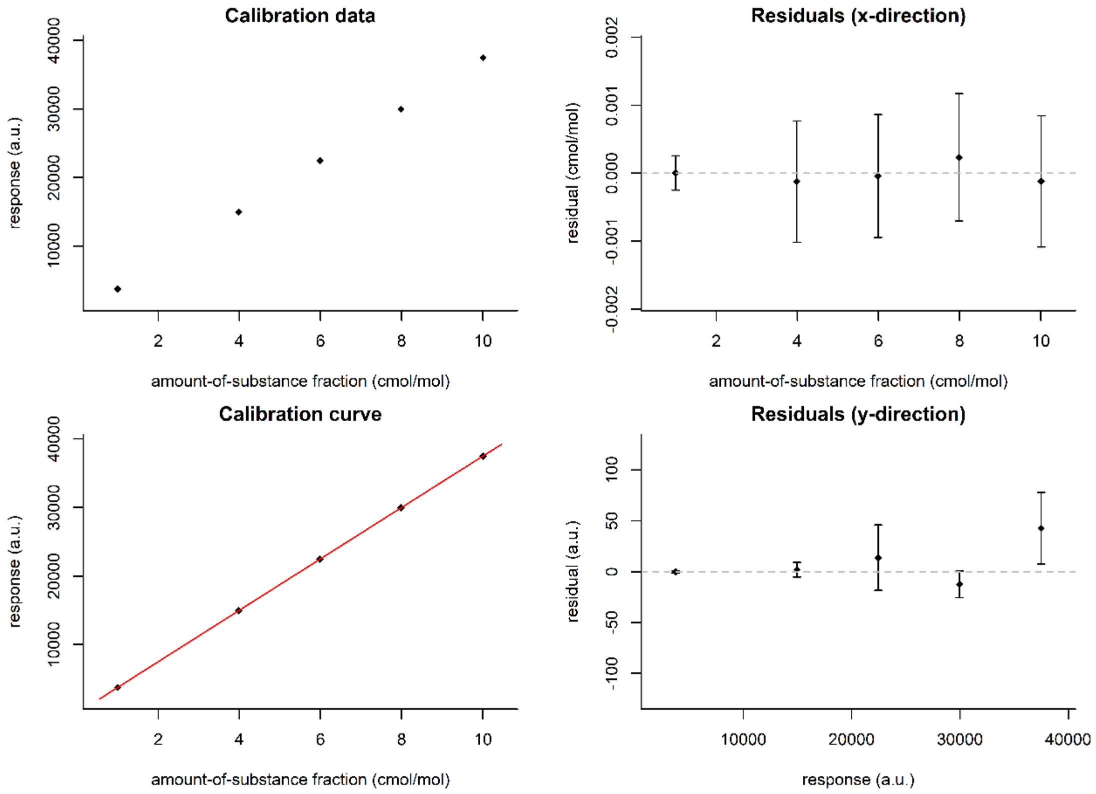


Table 28 Result of interpolation for carbon dioxide in the measurement done on 25-02-2020

	y	u(y)	x_2	$u(x_2)$
	a.u.		cmol/mol	
8457 E	7573.95	1.38	2.01574	0.00048

Table 29 Results of the PSM's for carbon monoxide measurement obtained on 25-02-2020

	x	u(x)	y	u(y)
	cmol/mol		a.u.	
VSL299720	0.50049	0.00008	1570.55	0.32
VSL244160	0.99950	0.00014	3166.74	0.61
VSL244236	2.00385	0.00033	6386.45	1.26
VSL243718	3.49782	0.00069	11196.36	2.42
VSL651981	3.99305	0.00064	12789.48	2.25

Figure 8 Calibration data and residuals for carbon monoxide done on 25-02-2020

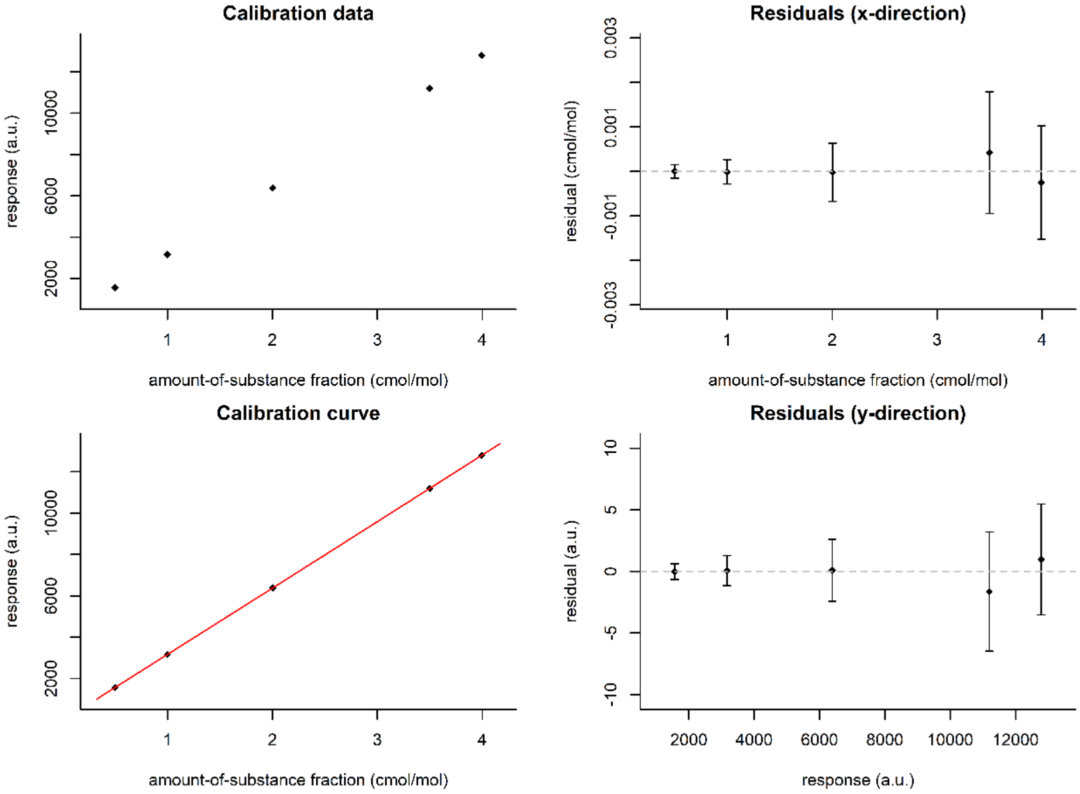


Table 30 Result of interpolation for carbon monoxide in the measurement done on 25-02-2020

	y	u(y)	x_2	u(x_2)
	a.u.		cmol/mol	
8457 E	3217.92	0.44	1.01546	0.00023

Table 31 Results of the PSM's for propane measurement obtained on 31-03-2020

	x	u(x)	y	u(y)
	µmol/mol		a.u.	
VSL249511	100.079	0.027	2237.60	0.21
VSL299720	200.592	0.050	4478.86	0.62
VSL244160	403.092	0.080	8985.55	0.94
VSL244236	599.757	0.094	13347.13	0.97
VSL651981	1002.049	0.241	22240.83	1.18

Figure 9 Calibration data and residuals for propane done on 31-03-2020

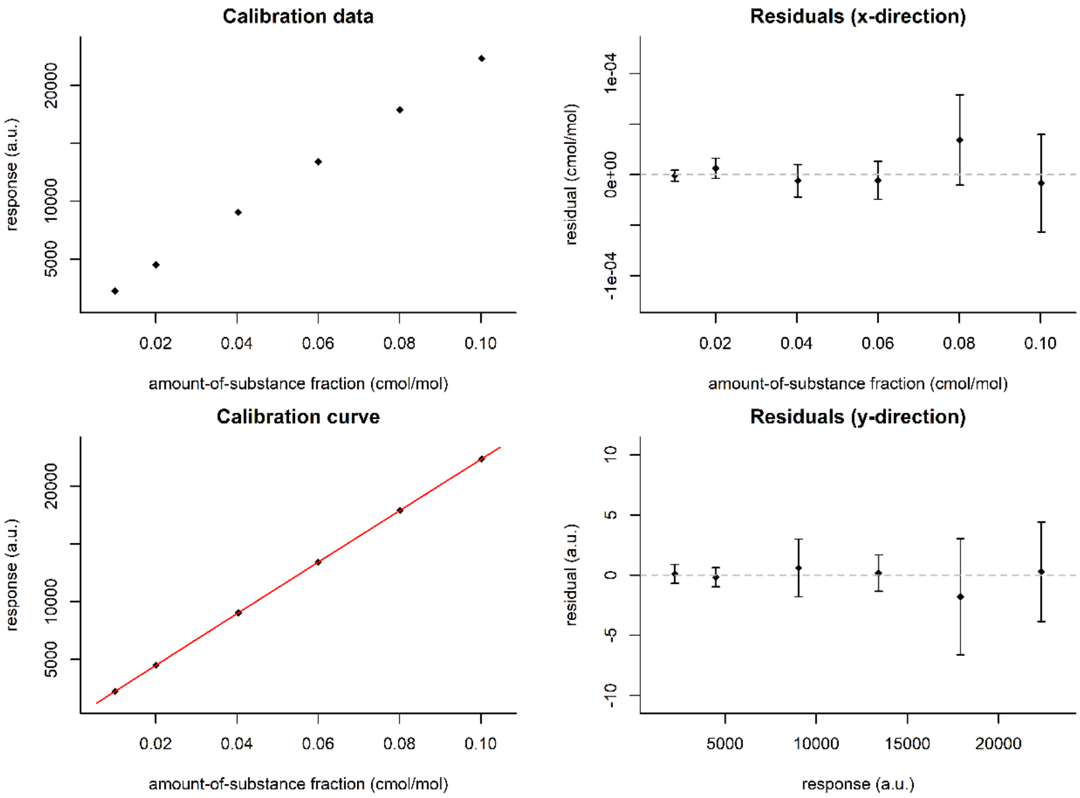


Table 32 Result of interpolation for propane in the measurement done on 31-03-2020

	y	u(y)	x_2	$u(x_2)$
	a.u.		cmol/mol	
8457 E	4559.53	0.46	0.0203090	0.0000040

Table 33 Results of the PSM's for oxygen measurement obtained on 16-03-2020

	x	u(x)	y	u(y)
	cmol/mol		a.u.	
VSL248709	0.699399	0.000138	278.69	0.09
VSL243984	1.002356	0.000141	399.85	0.13
VSL244236	2.002888	0.000306	798.87	0.08
VSL651981	4.999327	0.000559	1993.97	0.39
VSL244160	9.956061	0.000617	3969.17	0.39

Figure 10 Calibration data and residuals for oxygen obtained on 16-03-2020

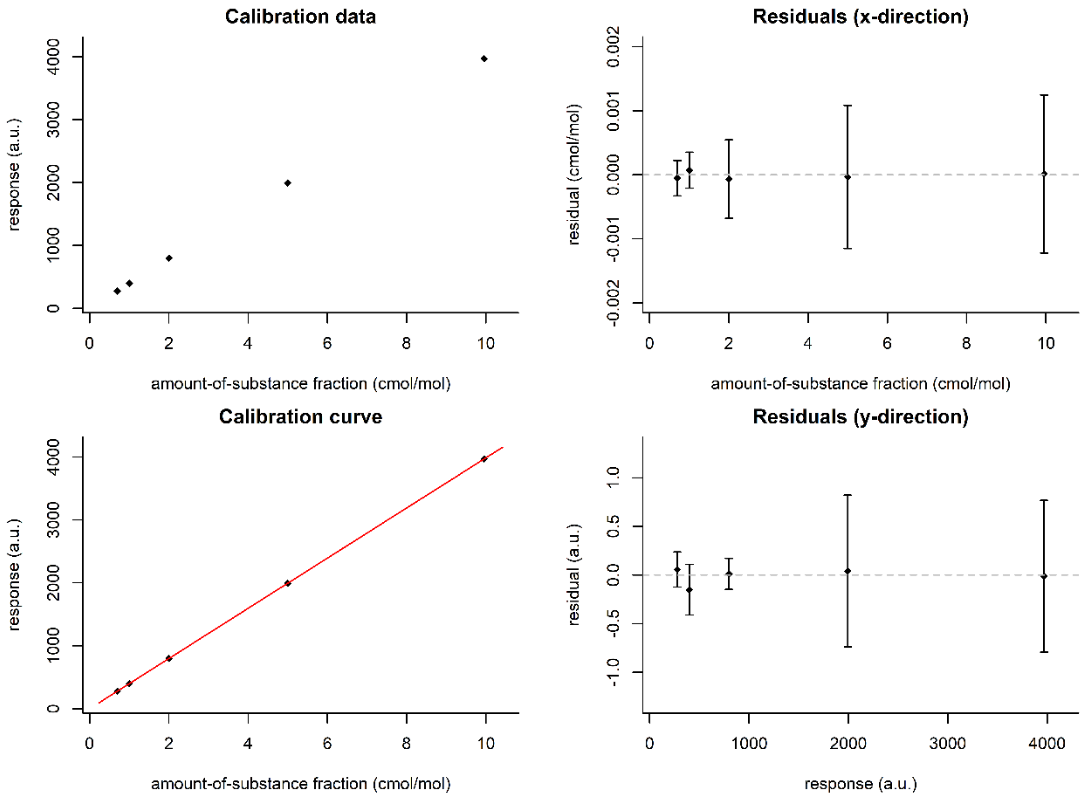


Table 34 Result of interpolation for oxygen in the measurement done on 16-03-2020

	y	u(y)	x_2	$u(x_2)$
	a.u.		cmol/mol	
8457 E	1154.81	0.34	2.89500	0.00097

I.5 Uncertainty evaluation

The standard uncertainty associated with the assigned values has been obtained based on the calibration functions as determined in accordance with ISO 6143 [7]. The values and standard uncertainties have been obtained as described in [8]. The mean of each amount fraction is calculated using the DerSimonian-Laird model. In Table 35, the results are given. τ denotes the excess standard deviation, σ denotes the within-group standard deviation, and μ the mean. The standard uncertainty associated with μ and τ and σ has been taken as basis for the stated expanded uncertainty. The expanded uncertainty has been obtained using a coverage factor k=2.

Table 35: Summary of the results for the measurements of 8457 E and the mean value with standard uncertainty (cmol/mol)

Component	Carbon dioxide	Carbon monoxide	Propane	Oxygen
x_1	2.01516	1.01494	0.020311	2.89346
u(x_1)	0.00062	0.00018	0.000004	0.00056
x_2	2.01574	1.01546	0.020309	2.895
u(x_2)	0.00048	0.00023	0.000004	0.00097
x_3	2.01513	1.01545	0.02031	2.89502
u(x_3)	0.00054	0.0002	0.000005	0.00066
x_4	2.0151	1.01637	-	2.89322
u(x_4)	0.00033	0.00023	-	0.00096
x_5	-		-	2.89233
u(x_5)	-		-	0.00082
τ	0	0.05466	0	0.02953
σ	0.02789	0.02495	0.02146	0.0205
μ	2.01525	1.01554	0.020310	2.89381
u(μ)	0.001008	0.000609	0.000010	0.001158

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