Supplementary Comparison SIM.QM-S06 – Automotive exhaust gases (CO, CO_2, C_3H_8)

Final report

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Field

Amount of substance

Subject

Supplementary comparison of carbon monoxide, carbon dioxide and propane in nitrogen (model 1).

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1 Introduction

This RMO supplementary comparison aims to assess the analytical capabilities of laboratories for measuring the composition of automotive (or even autogas or vehicle) emissions mixtures composed mainly of carbon monoxide, carbon dioxide and propane in nitrogen (Model 1). The amount-of-substance fractions analysed are relevant for implementing regulations with regard to automotive exhaust gas measurements.

A previous Track A key comparison of automotive exhaust gases was recently coordinated by VSL – CCQM-K3.2019 [1], with the participation of INMETRO. Nevertheless, the ranges from the gas mixture components are different from the ones from the Track A comparison. Besides, this present supplementary comparison doesn´t include the component oxygen. For this reason, it was previously arranged this supplementary comparison.

2 Design and organisation of the key comparison

2.1 Participants

Table 1 lists the participants in this supplementary comparison.

Table 1: List of participants

Acronym	Country	Institute
INMETRO	BR	Instituto Nacional de Metrologia, Qualidade e Technologia, Xerém RJ, Brasil
INACAL	PE	Instituto Nacional de Calidad, San Isidro, Peru
LATU	UR	Laboratorio Tecnológico del Uruguay, Montevideo, Uruguay

2.2 Measurement standards

Three primary reference mixture standards (PRM) were gravimetrically produced by INMETRO. The certified values of amount fractions of the components in the mixtures are given in Table 2.

Table 2 Gravimetric composition of mixtures, given in amount fractions

Component	PRM 1 – M692245 amount fraction	PRM 2 – M692268 amount fraction	PRM 3 – M692236 amount fraction
Carbon monoxide **(cmol/mol)**	1,002 ± 0,006	1,003 ± 0,006	1,00 ± 0,006
Carbon dioxide **(cmol/mol)**	10,01 ± 0,06	10,001 ± 0,065	9,92 ± 0,07
Propane **(μmol/mol)**	998,56 ± 12,68	1002,6 ± 10,63	1006,16 ± 10,71

The filling pressure in the cylinders was approximately 10 MPa. Aluminium cylinders having a 5 dm^3 water volume from Luxfer UK with an Aculife IV treatment were used.

INMETRO analyzed all the standards before dispatch and after return of the cylinders at INMETRO. The mixtures were verified by INMETRO with a calibration using a set of its own PRMs.

The amount fractions as obtained from gravimetric preparation procedure were used as supplementary comparison reference values (SCRVs). Each cylinder had its own reference values and associated expanded uncertainties. The expanded uncertainties included a contribution from the analytical verification of the gas mixtures.

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. 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 supplementary comparison was as follows (table 3).

Table 3: Supplementary comparison schedule

Date	Event
December 2015	Agreement of protocol
February 2016	Registration of participants
November 2019	Preparation of PRM mixtures
April 2021	Dispatch of the mixtures
May 2022	Receipt of the mixture at LATU and INACAL
December 2022	Reports from participants
January 2023	Receipt of the mixtures
March 2023	Re-verification of the returned mixture
June 2023	Draft A report available
November 2023	Draft B report available

2.5 Assessment of the standards

The supplementary comparison reference values are based on the certified values of INMETRO's PRM sent to participants. All mixtures underwent verification at INMETRO prior to shipping them to the participants. All cylinders were verified after the return to INMETRO. This re-verification was done within the stability time established at INMETRO certificate of the returned PRM. Thus, the supplementary comparison reference value ($x_{SCRV,i}$) is the amount of substance composition of INMETRO certificate of the PRM.

The validity of the mixtures has been demonstrated by INMETRO verifying the composition (first analytical verification). In order to have a positive demonstration of the certification data (including uncertainty, the following condition should be met:

$$|x_{\text{PRM,}} - x_{\text{ver,}}| \leq 2\sqrt{u_{PRM,i}^2 + u_{ver,i}^2} \quad (1)$$

The factor 2 is a coverage factor (normal distribution, 95% level of confidence).

The verification analysis at INMETRO was performed with the following instrument:
Micro GC (Agilent) Model: 490
Channel 1: 10m MS5A Heated Injector, Backflush
Channel 2: 10m PPU Heated Injector, Backflush
Channel 3: 10m AL2O3-KCL Heated Injector, Backflush

The reverification analysis were done with the following instrument:
GC CP-3800sp (Varian)
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.

The GC was calibrated with a suite of 6 (six) Primary Reference gas Mixtures (PRM) from INMETRO, in accordance with ISO 6142-1 [2]. For the measurements before shipment and those after return of the transfer standards, the same calibration function has been used. The errors-in-variables regression has been performed in accordance with ISO 6143 [3]. A calibration function was only accepted if the goodness-of-fit, as required by ISO 6143, did not exceed a value of 2. For all components, a quadratic polynomial has been used, satisfying the goodness-of-fit criterion.

The stability study analysis demonstrated that within the uncertainty of these measurements, the certified values of the supplementary comparison mixtures agreed for both first verification analysis (May 2021) and re-verification analysis (March 2023). From the Figures 1 through 3, it is readily seen that the stability is rather good for all components: carbon monoxide (Figure 1), carbon dioxide (Figure 2),and propane (Figure 3), considering all 3 mixtures dispatched, as the verification analysis step was approved with few differences between the mean value assigned and the amount fraction of these components.

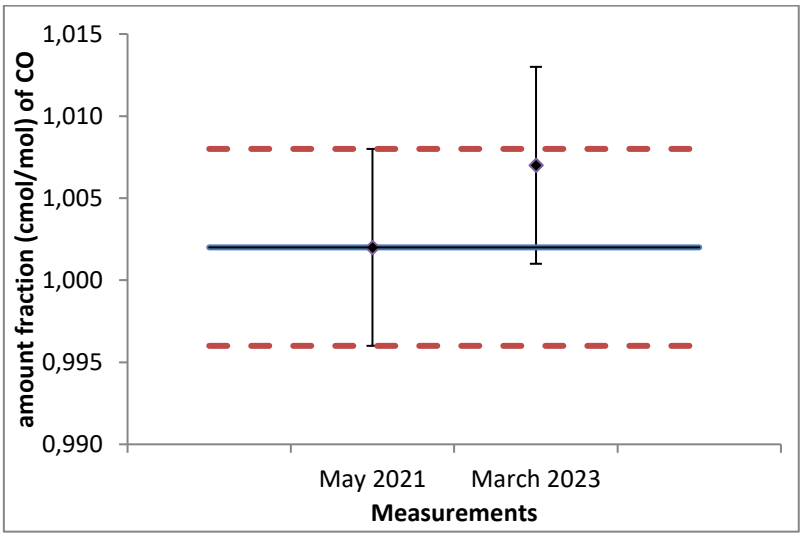

Figure 1 – Carbon monoxide stability analysis

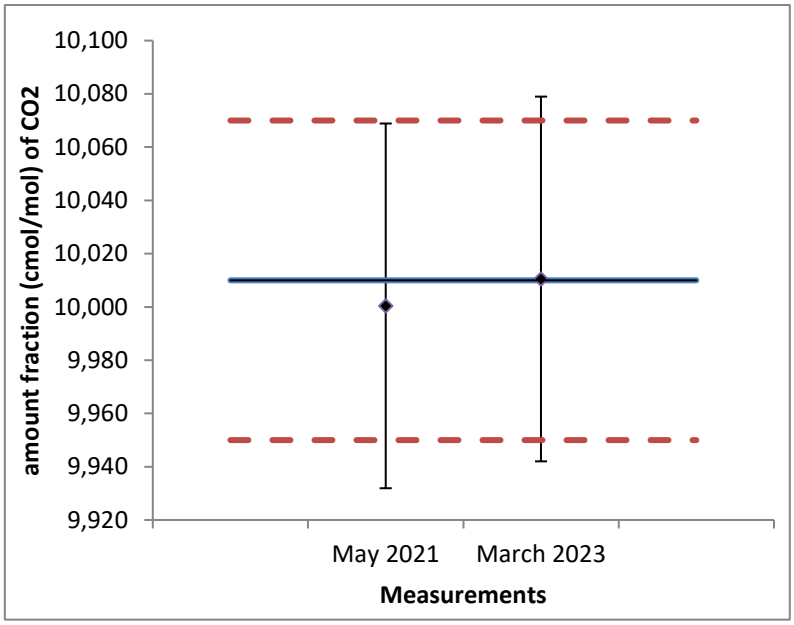

Figure 2 – Carbon dioxide stability analysis

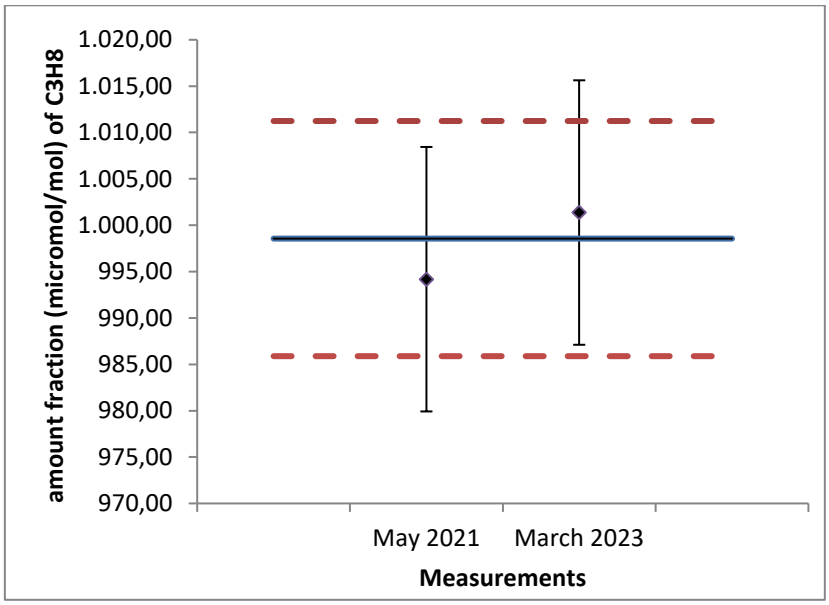

Figure 3 – Propane stability analysis

2.6 Participants measurements

The measurement methods used by the participants are described in annexes 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 4.

Table 4: Summary of calibration methods and metrological traceability of participants

Laboratory code	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
INMETRO	21, 26 May 2021, February 1st, and 06, 10 March 2023	ISO 6143	INMETRO standards	Nitrogen	GC-FID/TCD
INACAL	18, 25 November, 02, 16 December 2022	ISO 6143	INMETRO standards	Nitrogen	GC-FID/TCD
LATU	30, 31 May, 01 June 2022	ISO 6143	INMETRO standards	Nitrogen	GC-FID/TCD

2.7 Measurement equation and Degree of equivalence

As mentioned before, the supplementary comparison reference values are based on the certified values of the three INMETRO PRMs sent to participants. Thus, the supplementary comparison reference value ($x_{i,SCRV}$) is the amount of substance composition of INMETRO certificate of the PRM. Each cylinder had its own reference values, $x_{i,SCRV}$, and associated expanded uncertainties $u(x_{i,SCRV})$. The expanded uncertainties included a contribution from the gravimetrical production, $u(x_{i,prep})$, and the analytical verification of the gas mixtures, $u(x_{i,ver})$,. The reference value for each one of the three PRMs were evaluated against the participant results.

A unilateral degree of equivalence in supplementary comparisons is defined as:

$$\Delta x_i = d_i = x_i - x_{i,\mathrm{SCRV}}, \qquad (2)$$

The standard uncertainty of the difference d_i has a covered factor 2 (normal distribution, 95 % level of confidence).. Here $x_{i,SCRV}$ denotes the supplementary comparison reference value (the amount fraction from preparation, $x_{i,prep}$), and x_i the result of laboratory i.

The standard uncertainty of d_i ($u(d_i)$) is defined as:

$$u^2(d_i) = u^2(x_i) + u^2(x_{i,SCRV}) \qquad (3)$$

Where, the standard uncertainty of d_i ($u(d_i)$) is the combined standard uncertainty of the reference value comprised with that from preparation and that from verification for the mixture involved.

3 Results

In this section, the results of the supplementary comparison are summarised. In the Tables 5, 6, and 7, followed by the graph results (Figures 4, 5 and 6), the degree-of-equivalences are presented separately by each of the three mixture components of the automotive emissions primary standards.

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

In the tables, the following data is presented:

x_{prep} amount fraction, from preparation (cmol mol^{-1})

u_{prep} standard uncertainty of xprep (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})

d difference between laboratory result and reference value (cmol mol^{-1})

U(d) Expanded uncertainty of difference di, at 95 % level of confidence3 (cmol mol^{-1})

Table 5: Carbon monoxide results

Lab	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{SCRV}	x_{lab}	U_{lab}	d	U(d)
INMETRO	M692245	1,002	0,0001	0,003	0,003	1,003	0,009	0,0007	0,011
LATU	M692268	1,003	0,0001	0,003	0,003	1,0081	0,0075	0,0051	0,0096
INACAL	M692236	1,0	0,0001	0,003	0,003	1,000	0,012	0,0	0,013

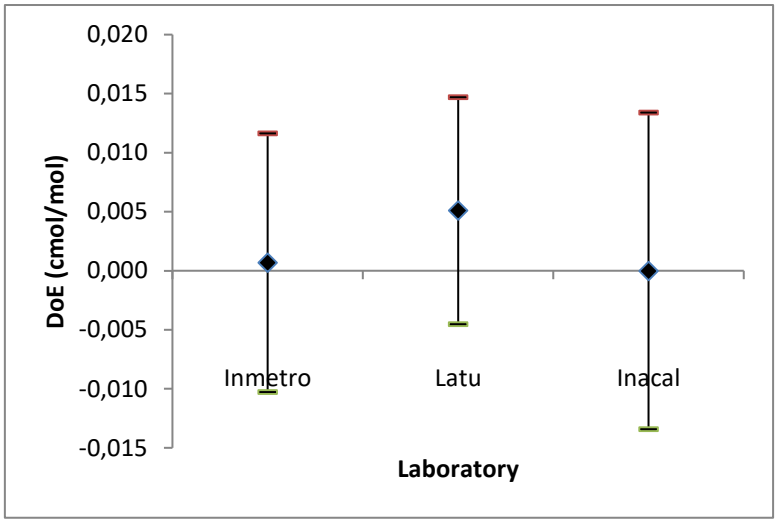

Figure 4 – Degrees-of-equivalence (DoE) for carbon monoxide

Table 6: Carbon dioxide results

Lab	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{SCRV}	x_{lab}	U_{lab}	d	U(d)
INMETRO	M692245	10,01	0,0006	0,030	0,030	10,01	0,07	-0,0003	0,09
LATU	M692268	10,00	0,0006	0,033	0,033	10,0	0,08	-0,0010	0,10
INACAL	M692236	9,92	0,0006	0,035	0,035	9,92	0,11	0	0,13

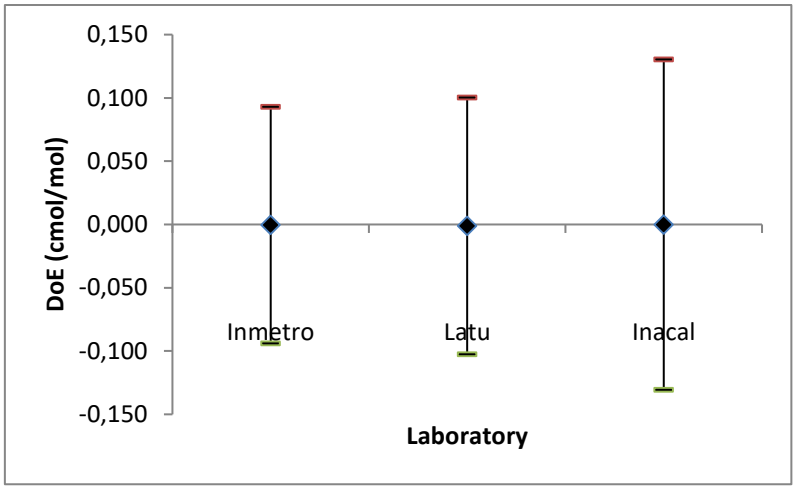

Figure 5 – Degrees-of-equivalence (DoE) for carbon dioxide

Table 7: Propane results

Lab	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{SCRV}	x_{lab}	U_{lab}	d	U(d)
INMETRO	M692245	998,56	0,31	6,33	6,34	998,3	9,2	-0,26	15,67
LATU	M692268	1002,60	0,32	5,31	5,32	1005,0	10,0	2,40	14,60
INACAL	M692236	1006,16	0,29	5,35	5,36	1002,0	9,8	-4,16	14,50

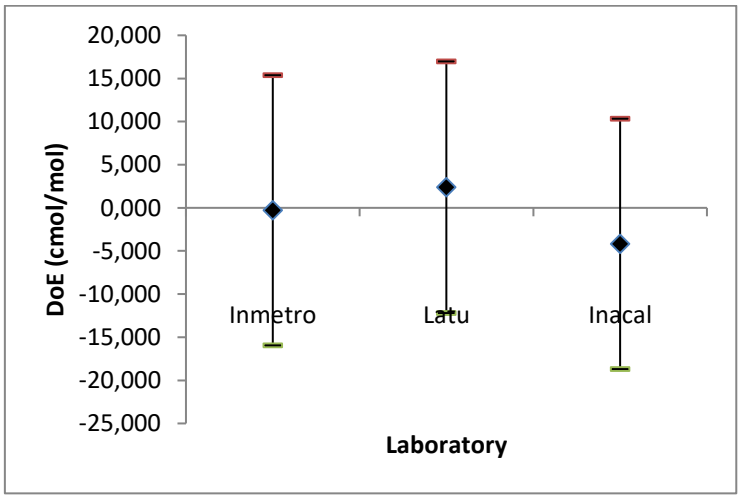

Figure 6 – Degrees-of-equivalence (DoE) for propane

4 Supported CMC

The results of this supplementary comparison can be used to support CMC claims for the composition automotive emissions mixtures in the following ranges (see table 8). CMCs outside the listed ranges are not supported by the results of this key comparison without further evidence.

Table 8: Supported component ranges

Component	Amount fraction
Carbon monoxide	0,01 to 50 cmol/mol

Carbon dioxide	0,01 to 50 cmol/mol
Propane	0,01 to 10 cmol/mol

Proposed CMCs at the annex D in this document are calculated by considering the INMETRO's performance in the CCQM-K3:2019 to be consistent with the CCQM-K3:2019 results and support the participant NMIs' CMC submissions and their reviewers. For example, an excess uncertainty is added into the submitted uncertainty of INMETRO for calculating uncertainties in the proposed CMCs when its result is not consistent with its key comparison reference value.

5 Discussion and conclusions

According to results presented in this Model 1 supplementary comparison, all participants' results agree well with the SCRV of this supplementary comparison of autogas or automotive emissions.

Coordinator

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Project reference

SIM-QM-S06

Completion date

June 2023

References

[1] International comparison CCQM-K3.2019 automotive exhaust gases. Adriaan M H van der Veen, Ewelina T Zalewska, Janneke I T van Wijk, Midori Kobayashi, Dai Akima, Shinji Uehara, Andreia L Fioravante, Cristiane R Augusto, Claudia C Ribeiro, Viviane Silva, Florbela Dias, Alda Botas, Carlos Costa, Joengsoon Lee, Jinbok Lee, Jeongsik Lim, Hyun-Kil Bae, Namgoo Kang, Christina E Cecelski, Kimberly J Harris, Walter R Miller Jr, Jennifer Carney, James Tshilongo, Napo G Ntsasa, Mudalo I Jozela, Nompumelelo Leshabane, Prelly Mohweledi Marebane, David R Worton, Eric B Mussell Webber, Sergi Moreno, Paul J Brewer, Leonid A Konopelko, Anna V Kolobova, V V Pankratov and Olga V Efremova. Metrologia, Volume 60, Number 1A, 2023.

[2] International Organization for Standardization, ISO 6142-1:2015 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods, 2nd edition

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

[4] CIPM, “Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes”, Sèvres (F), October 1999

[5] CCQM-GAWG strategy for comparisons and CMC claims https://www.bipm.org/documents/20126/58994067/GAWG19-41-CCQM-GAWG_strategy_for_comparisons_and_CMC_claims.pdf/52b1395e-a2cc-3f9c-053d-bb205c831b4f

Annex A:

Measurement reports of INMETRO

Report Form SIM.QM-S6 Autogas emissions in Nitrogen

Laboratory name: INMETRO

Cylinder number: M692245

Measurement #1

Component	Date dd/mm/yy	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Carbon Monoxide	21/05/2021	1,002 x10^{-2}	0,09	7
Carbon Dioxide	21/05/2021	10,0004 x10^{-2}	0,11	7
Propane	21/05/2021	994,18 x10-6	0,22	7

Measurement #2

Component	Date dd/mm/yy	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Carbon Monoxide	26/05/2021	0,999 x10^{-2}	0,02	7
Carbon Dioxide	26/05/2021	10,0182 x10^{-2}	0,11	7
Propane	01/02/2023	1001,37 x10-6	0,28	7

Measurement #3

Component	Date dd/mm/yy	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Carbon Monoxide	06/03/2023	1,007 x10^{-2}	0,28	7
Carbon Dioxide	06/03/2023	10,0105 x10^{-2}	0,18	7
Propane	10/03/2023	999,34 x10^{-6}	0,11	6

Final results:

Component	Date dd/mm/yy	Result (mol/mol)	Expanded uncertainty (mol/mol)	Coverage factor
Carbon Monoxide	13/03/2023	$1{,}003 \times 10^{-2}$	0,009	2
Carbon Dioxide	13/03/2023	10,01	0,07	2
Propane	13/03/2023	$998{,}30 \times 10^{-6}$	9,21	2

Calibration standards

Six calibration standards of carbon dioxide, carbon monoxide and propane in nitrogen were used in this study for value assignment of the sample cylinder. These calibrants were obtained from the National Metrology Institute of Brazil, INMETRO. Information about the standards is detailed in the table below.

Mixture identification	Analyte	Amount fraction (mol/mol)	Expanded uncertainty (mol/mol)
PSM112273	Carbon dioxide	1,536E-02	0,008E-02
	Carbon monoxide	0,2601E-02	0,0009E-02
	Propane	79,7E-06	1,06E-06
PSM112259	Carbon dioxide	3,518E-02	0,022E-02
	Carbon monoxide	0,585 E-02	0,005E-02
	Propane	196,08 E-06	1,31E-06
PSM112247	Carbon dioxide	7,387 E-02	0,033 E-02
	Carbon monoxide	2,462 E-02	0,012 E-02
	Propane	739,02 E-06	5,52 E-06
PSM112279	Carbon dioxide	11,803 E-02	0,037 E-02
	Carbon monoxide	3,52 E-02	0,015 E-02
	Propane	1527,4 E-06	8,11 E-06
PSM1112263	Carbon dioxide	14,996 E-02	0,058 E-02
	Carbon monoxide	4,981 E-02	0,035 E-02
	Propane	2016,84 E-06	11,97 E-06
PSM112274	Carbon dioxide	10,74 E-02	0,00065 E-02
	Carbon monoxide	1,07 E-02	0,0001 E-02
	Propane	1066,99 E-06	5,79 E-06

Instrumentation

GC CP-3800sp (Varian)

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.

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 9 times were the first and second injections was dictated. The calibration of the instrument was done according to ISO 6143. The calibration curve was made using the software XLgenline. The goodness of fit for all measurements was lower than 2.

Uncertainty evaluation

The uncertainty was calculated according to ISO 6143 using the software XLgenline. The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95%. 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)

References

- International Organization for Standardization. (2001) *Gas Analysis—Comparison methods for determining and checking the composition of calibration gas mixtures.* (Norma ISO nº6143:2001). https://www.iso.org/standard/24665.html

Authorship

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Annex B:

Measurement reports of INACAL

Report Form SIM-QM-S6 Autogas emissions in Nitrogen

Laboratory name: Instituto Nacional de Calidad (INACAL)

Cylinder number: M692236

Measurement #1

Component	Date dd/mm/yy	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Propane	18/11/2022	$1002{,}36 \times 10^{-6}$	0,27	10
Carbon Monoxide	18/11/2022	$1{,}0044 \times 10^{-2}$	0,42	10
Carbon Dioxide	18/11/2022	$9{,}945 \times 10^{-2}$	0,41	10

Measurement #2

Component	Date dd/mm/yy	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Propane	25/11/2022	$999{,}30 \times 10^{-6}$	0,36	10
Carbon Monoxide	25/11/2022	$0{,}9988 \times 10^{-2}$	0,44	10
Carbon Dioxide	25/11/2022	$9{,}893 \times 10^{-2}$	0,46	10

Measurement #3

Component	Date dd/mm/yy	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Propane	02/12/2022	$1004{,}42 \times 10^{-6}$	0,29	10
Carbon Monoxide	02/12/2022	$1{,}0006 \times 10^{-2}$	0,44	10
Carbon Dioxide	02/12/2022	$9{,}920 \times 10^{-2}$	0,29	10

Measurement #4

Component	Date dd/mm/yy	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Propane	16/12/2022	$1002{,}00 \times 10^{-6}$	0,35	10
Carbon Monoxide	16/12/2022	$0{,}9976 \times 10^{-2}$	0,36	10
Carbon Dioxide	16/12/2022	$9{,}911 \times 10^{-2}$	0,48	10

Note: Please copy this table as many times as needed for reporting additional measurements

Final results:

Component	Date dd/mm/yy	Result (mol/mol)	Expanded uncertainty (mol/mol)	Coverage factor
Propane	29/12/2022	$1002{,}0 \times 10^{-6}$	$9{,}8 \times 10^{-6}$	2
Carbon Monoxide	29/12/2022	$1{,}000 \times 10^{-2}$	$0{,}012 \times 10^{-2}$	2
Carbon Dioxide	29/12/2022	$9{,}92 \times 10^{-2}$	$0{,}11 \times 10^{-2}$	2

Analytical method

We used a gas chromatograph 7890B (brand Agilent Technologiest) equipped with both flame ionization detector (FID) and thermal conductivity detector (TCD), it was set up with four valves, ones is a multiposicion valve, a gas sampling valve and two pressurized valves. The FID detector was used to measure propane and the TCD detector was used to measure carbon dioxide and carbono monoxide. This chromatograph has a preventive maintenance program.

Also, The GC 7890 was equipped with three packed columns and a capillary column:

3 ft 1/8 HayeSeQ 80/100 mesh

6 ft 1/8 HayeSeQ 80/100 mesh

10 ft 1/8 Molsieve 13X 45/60 mesh

50 m x 200 µm x 0,5 µm PONA:

The method conditions were the following:

Table 1 : GC 7890 – GV2022R3

Parameters	**Settings**
Oven	40 °C, 40 °C for 10.5 min, at 50 °C/min to 200 °C, 200 °C for 1 min
Injector temperature	250 °C
Split ratio	80:1
Column flow #1 (to FID)	0,55 mL/min (He)
Column flow #2 (to TCD)	30 mL/min (He)
Valve box temperature	100 °C
Detector FID	220 °C, air 350 mL/min, H2 35 mL/min, makeup gas 30 mL/min
Detector TCD	150 °C, reference gas 45 mL/min, make up gas 2 mL/min
Sample loop	250 µL y 1 mL
Time events	Valve 3 OFF 0.01 min Valve 1 ON 0.05 min Valve 1 OFF 0.5 min Valve 2 ON 2 min Valve 3 ON 4.7 min Valve 2 OFF 4.8 min

Sample handling:

The SIM-QM-S6 cylinder M692236 and the calibration standards were manually rolled and then equipped with a pressure regulator. Sampling takes place with multiposition valve sample boxes and a pressure regulator of High-Sensitivity as described in the work instructions for routine analyses.

Calibration curve:

The calibration curve was carried out according to the ISO 6143. Five calibration standards and one control standard were used, which were provided by INMETRO:

Table 2: Standards and control

Cilindro	N° certificado	Propane (10^{-6} mol/mol)	Carbon dioxide (10^{-2} mol/mol)	Carbono monoxide (10^{-2} mol/mol)
M692244	1220198	79,11 ± 0,84	1,4778 ± 0,0090	0,2454 ± 0,0009
M692251	1220496	300,04 ± 2,94	2,963 ± 0,014	0,504 ± 0,003
M692254	1220889	997,25 ± 8,97	9,928 ± 0,049	1,006 ± 0,004
M692237	1220832	1521,64 ± 10,07	11,964 ± 0,038	3,452 ± 0,015
M692233	1220840	2007,83 ± 12,94	14,970 ± 0,057	4,992 ± 0,035
M692258 (CTRL)	1220803	603,64 ± 3,80	5,939 ± 0,027	2,016 ± 0,012

The calibration curve was made using the generalized least squares (GLS) in the XLGENLINE software, the selected analysis function was a second order polynomial, which was used for the measurements. The goodness of fit for all 4 measurements was lower than 2.

Uncertainty evaluation

The uncertainty was calculated according to ISO 6143 using XLGENLINE software. The measurement uncertainty was estimated from the uncertainty associated with the amount-of-substance fractions of each component of the calibration standard, the standard deviation of the mean of the analyses of the calibration standards and the repeatability standard deviation of sample mixture

The final results is the average of the four measurements, the pooled uncertainty from evaluating the data from calibration of the GC (by XLGENLINE) was combined with the repeatability standard deviation of sample mixture. The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95% .

Below, we described the uncertainty budget of each componente of the sample:

Propane

Description	Value, x	Method of evaluation	Probability distribution	Sensitivity coefficients ci	Standard uncertainties u(xi)	Contribution uncertainty |ci| *u(xi)
Software (XLGENLINE)	1002,0 X10^{-6} mol/mol	A,B	Normal	1	3,61 X10^{-6} mol/mol	3,61 X10^{-6} mol/mol
Repeatability	---	A	Normal	1	3,34 X10^{-6} mol/mol	3,34 X10^{-6} mol/mol

	u(x)	4,9 X10^{-6} mol/mol
	U (k=2)	9,8 X10^{-6} mol/mol

Carbon Monoxide

Description	Value, x	Method of evaluation	Probability distribution	Sensitivity coefficients ci	Standard uncertainties u(xi)	Contribution uncertainty |ci| *u(xi)
Software (XLGENLINE)	1,000 X10^{-2} mol/mol	A,B	Normal	1	0,0031 X10^{-2} mol/mol	0,0031 X10^{-2} mol/mol
Repeatability	---	A	Normal	1	0,0050 X10^{-2} mol/mol	0,0050 X10^{-2} mol/mol
					u(x)	0,0060 X10^{-2} mol/mol
					U (k=2)	0,012 X10^{-2} mol/mol

Carbon Dioxide

Description	Value, x	Method of evaluation	Probability distribution	Sensitivity coefficients ci	Standard uncertainties u(xi)	Contribution uncertainty |ci| *u(xi)
Software (XLGENLINE)	9,92 X10^{-2} mol/mol	A,B	Normal	1	0,029 X10^{-2} mol/mol	0,029 X10^{-2} mol/mol
Repeatability	---	A	Normal	1	0,044 X10^{-2} mol/mol	0,044 X10^{-2} mol/mol
					u(x)	0,053 X10^{-2} mol/mol
					U (k=2)	0,11 X10^{-2} mol/mol

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Annex C:
Measurement reports of LATU

Report Form SIM.QM-S6 Autogas emissions in Nitrogen

Laboratory name: LATU

Cylinder number: M692268

Measurement #1

Component	Date dd/mm/yy	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
Propane	30/05/2022	0.0010037 x10^6	0.05	6
Carbon Monoxide	30/05/2022	0.010042 x10^6	0.07	6
Carbon Dioxide	30/05/2022	0.09999 x10^6	0.11	6

Measurement #2

Component	Date dd/mm/yy	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
Propane	31/05/2022	0.0010042 x10^6	0.06	6
Carbon Monoxide	31/05/2022	0.010058 x10^6	0.02	6
Carbon Dioxide	31/05/2022	0.09996 x10^6	0.09	6

Measurement #3

Component	Date dd/mm/yy	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
Propane	01/06/2022	0.0010065 x10^6	0.04	6
Carbon Monoxide	01/06/2022	0.010142 x10^6	0.05	6
Carbon Dioxide	01/06/2022	0.10005 x10^6	0.12	6

Note: Please copy this table as many times as needed for reporting additional measurements

Final results:

Component	Date dd/mm/yy	Result (μmol/mol)	Expanded uncertainty (μmol/mol)	Coverage factor
Propane	24/08/2022	(0.001005) x10^6	(0.000010) x10^6	2
Carbon Monoxide	24/08/2022	(0.010081) x10^6	(0.000075) x10^6	2
Carbon Dioxide	24/08/2022	(0.10000) x10^6	(0.00078) x10^6	2

Calibration standards

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

Six calibration standards of carbon dioxide, carbon monoxide and propane in nitrogen were used in this study for value assignment of the sample cylinder. These calibrants were obtained from the National Metrology Institute of Brazil, INMETRO. Information about the standards is detailed in the table below.

Cylinder identification	Analyte	Amount fraction (mol/mol)	Expanded uncertainty (mol/mol)
M692238	Carbon dioxide	1,5E-02	1,0E-04
	Carbon monoxide	2,5E-03	9,0E-06
	Propane	8,1E-05	7,8E-07
M692253	Carbon dioxide	3,1E-02	1,6E-04
	Carbon monoxide	4,8E-03	3,0E-05
	Propane	3,0E-04	3,1E-06
M692264	Carbon dioxide	6,0E-02	2,7E-04
	Carbon monoxide	2,0E-02	1,2E-04
	Propane	6,0E-04	3,3E-06
M692265	Carbon dioxide	1,0E-01	7,8E-04
	Carbon monoxide	9,8E-03	4,0E-05
	Propane	1,0E-03	8,9E-06
M692252	Carbon dioxide	1,2E-01	3,9E-04
	Carbon monoxide	3,5E-02	1,5E-04
	Propane	1,5E-03	8,2E-06
M692270	Carbon dioxide	1,5E-01	5,6E-04
	Carbon monoxide	5,0E-02	3,7E-04
	Propane	2,0E-03	9,8E-06

Instrumentation

Principles, make, type, configuration, data collection etc.

A Thermo Scientific TRACE 1300 gas chromatograph with flame ionization detector (FID) and thermal conductivity detector (TCD) was used. Carbon dioxide and carbon monoxide were analyzed using the TCD detector and propane using the FID detector.

Carrier gas: Helium

Chromatography columns:

Rt-Q-BOND PLOT 30m, 0.53mm ID, 20µm – FID

ShinCarbon ST 100/120 2m, 1mm ID, 1/16"OD – TCD

Temperature program: 40 ºC (3 min), ramp 8,3 ºC/min to 140 ºC (12 min).

Sample loop:

500 µL – FID

250 µL – TCD

Data collection: Chromeleon 7. Thermo Fischer Scientific.

Calibration method and value assignment

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

The gas chromatograph was calibrated by using six calibration standards of carbon dioxide, carbon monoxide and propane in nitrogen from INMETRO, according to ISO 6143. Three calibration curves were measured on three different days and were used to calculate the final result for each analyzed gas.

These calibration curves were calculated using XLGENLINE version 1.1, obtaining second order regressions for carbon dioxide and propane, and linear regressions for carbon monoxide. The value of goodness-of-fit, Γ, for each calibration curve was less than 2, in agreement with ISO 6143.

Sample content and its standard uncertainty were calculated using the software previously mentioned, considering the amount fraction of each primary reference material with their associated standard uncertainty and the measured responses of each calibration point with their standard deviations.

Measurement sequence: 6 standards in random order and sample cylinder.

Uncertainty evaluation

Description of the evaluation of measurement uncertainty, including the expressions used.

Calibration uncertainty was calculated by using the mathematical models for multi-point calibrations. This is a combination of the standard uncertainty of the calibration curve and the repeatability of six different readings of the sample cylinder along with the standard uncertainty of the primary reference gas mixtures. This

uncertainty was calculated by using the software XLGENLINE version 1.1, according to ISO 6143. The largest uncertainty of three days of measurement was selected as the calibration uncertainty.

This calibration uncertainty was combined with a drift contribution for the three days of measurement and, since the combination of these two uncertainties for carbon dioxide and propane were lower than the highest standard uncertainty from the reference gas mixtures, a third contribution was included for these gases.

Standard uncertainty for propane and carbon dioxide:

$$u_{sample} = \sqrt{u_{calibration}^2 + u_{drift}^2 + u_{PRM}^2}$$

Standard uncertainty for carbon monoxide:

$$u_{sample} = \sqrt{u_{calibration}^2 + u_{drift}^2}$$

The expanded uncertainty is the sample standard uncertainty multiplied by the coverage factor *k*=2

Uncertainty budget – Propane:

Uncertainty source	Evaluation type (A or B)	Distribution	Standard uncertainty (mol/mol)	Sensitivity coefficient
Calibration	A	Normal	1.8E-06	1
Drift	B	Rectangular	8.0E-07	1
PRMs	B	Rectangular	4.7E-06	1
Combined standard uncertainty		5.1E-06 mol/mol		
Expanded uncertainty		1.0E-05 mol/mol		

Uncertainty budget – Carbon monoxide:

Uncertainty source	Evaluation type (A or B)	Distribution	Standard uncertainty (mol/mol)	Sensitivity coefficient
Calibration	A	Normal	2.3E-05	1
Drift	B	Rectangular	2.9E-05	1
Combined standard uncertainty		3.7E-05 mol/mol		
Expanded uncertainty		7.5E-05 mol/mol		

Uncertainty budget – Carbon dioxide:

Uncertainty source	Evaluation type (A or B)	Distribution	Standard uncertainty (mol/mol)	Sensitivity coefficient
Calibration	A	Normal	1.9E-04	1
Drift	B	Rectangular	2.7E-05	1
PRMs	B	Rectangular	3.4E-04	1
Combined standard uncertainty		3.9E-04 mol/mol		
Expanded uncertainty		7.8E-04 mol/mol		

References

- International Organization for Standardization. (2001) *Gas Analysis—Comparison methods for determining and checking the composition of calibration gas mixtures.* (Norma ISO nº6143:2001). https://www.iso.org/standard/24665.html

- International Organization for Standardization. (2017) *General requirements for the competence of testing and calibration laboratories.* (Norma ISO/IEC nº17025:2017). https://www.iso.org/standard/66912.html

- Smith I. (2010) Software for determining polynomial calibration functions by generalised least squares: user manual. *Technical Report MS 11* (Teddington, UK: National Physical Laboratory).

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Annex D:

CMC new uncertainties linking Inmetro´s results in CCQM-K3

carbon dioxide													consistent with CCQM-K3.2019		extra uncertainty added only for CO and C3H8 since INMETRO results are not consistent in CCQM-K3.201 extra uncertainty							
Lab	Cylinder	x_{prep}	U_{KCRV}	x_{lab}	$U_{lab\,(k=2)}$	U_{lab} (%rel)	d	$U_{(d),\,k=2}$	x_{KCRV_k3}	$U(x_{KCRV\_K}$	x_{lab_K3}	U_{lab_K3}	$d_{\_k3}$	$U(d_{\_k3})$	$U_{lab\_CMC\_SIM.QM}$	$U_{lab\_SIM.QM-S6}$ (%rel)	x_{LB} (nmol/mo	CMC_1(nmol/mc	x_{tp} (micromol/m	CMC_2 (%	x_{UB} (cmol/mol)	d (k3 to SIM_QM_S6)
Inmetro	M692245	10,01	0,06	10,01	0,07	0,70%	-0,0003	0,092	1,999	0,002	1,993	0,010	0,0063	0,101	0,07	0,70	350	350	10	0,70	50	0 INMETRO result is consistent in CCQM-K3.2019
Latu	M692268	10,001	0,065	10	0,08	0,80%	-0,0010	0,103							0,08	0,80	401	401	10	0,80	50	0 LATU result is traceable to INMETRO
Inacal	M692236	9,92	0,07	9,92	0,11	1,11%	0,0000	0,130							0,11	1,11	555	555	10	1,11	50	0 INACAL result is traceable to INMETRO
Carbon monoxide													not consistent with CCQM-K3.2019									
Lab	Cylinder	x_{prep}	U_{KCRV}	x_{lab}	$U_{lab\,(k=2)}$	U_{lab} (%rel)	d	$U_{(d),\,k=2}$	x_{KCRV_k3}	$U(x_{KCRV\_K}$	x_{lab_K3}	U_{lab_K3}	$d_{\_k3}$	$U(d_{\_k3})$	$U_{lab\_CMC\_SIM.QM}$	$U_{lab\_QMC\_SIM.QM-S6}$ (%	x_{LB} (nmol/mc	CMC_1(nmol/mc	x_{tp} (micromol/m	CMC_2 (%	x_{UB} (cmol/mol)	d (k3 to SIM_QM_S6)
Inmetro	M692245	1,002	0,006	1,003	0,009	0,90%	0,0010	0,011	0,999	0,0008	0,999	0,004	-0,0062	0,0041	0,015	1,53	153	153	10	1,53	50	**-0,0062** INMETRO result is not consistent in CCQM-K3.2019
Latu	M692268	1,003	0,006	1,0081	0,0075	0,74%	0,0051	0,010							0,008	0,74	74	74	10	0,74	50	**-0,0062** LATU result is traceable to INMETRO
Inacal	M692236	1	0,006	1	0,012	1,20%	0,0000	0,013							0,012	1,20	120	120	10	1,20	50	**-0,0062** INACAL result is traceable to INMETRO
Propane													not consistent with CCQM-K3.2019									
Lab	Cylinder	x_{prep}	U_{KCRV}	x_{lab}	$U_{lab\,(k=2)}$	U_{lab} (%rel)	d	$U_{(d),\,k=2}$	x_{KCRV_k3}	$U(x_{KCRV\_K}$	x_{lab_K3}	U_{lab_K3}	$d_{\_k3}$	$U(d_{\_k3})$	$U_{lab\_CMC\_SIM.QM}$	$U_{lab\_QMC\_SIM.QM-S6}$ (%	x_{LB} (nmol/mc	CMC_1(nmol/mc	x_{tp} (micromol/m	CMC_2 (%	x_{UB} (cmol/mol)	d (k3 to SIM_QM_S6)
Inmetro	M692245	0,099856	0,001268	0,09983	0,00092	0,92%	-0,00003	0,00157	0,02016	0,00002	0,02002	0,00011	-0,00014	0,00011	0,002	1,69	839	839	10	1,69	50	**-0,0007** INMETRO result is not consistent in CCQM-K3.2019
Latu	M692268	0,10026	0,001063	0,10050	0,0010	1,00%	0,00024	0,00146					-0,007 relative d_{k3}		0,002	1,73	855	855	10	1,73	50	**-0,0007** LATU result is traceable to INMETRO
Inacal	M692236	0,100616	0,001071	0,10020	0,00098	0,98%	-0,00042	0,00145					-0,00071 d for 0.1 cmol/mol (S6 nominal va		0,002	1,72	852	852	10	1,72	50	**-0,0007** INACAL result is traceable to INMETRO