Regional Key Comparison SIM.QM-K111 – Propane in nitrogen

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Field

Amount of substance

Subject

Comparison of 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) [4], 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 binary mixture of propane in nitrogen has been chosen at a nominal amount-of-substance fraction level of 1000 µmol mol^{-1} [6]. The key comparison design follows that of the key comparisons for gas mixture that are prepared gravimetrically [2].

2 Design and organization of the key comparison

2.1 Participants

Table 1 lists the participants in this key comparison.

Table 1: List of participants

Acronym	Country	Institute
INMETRO	BR	Instituto Nacional de Metrologia, Qualidade e Tecnologia, Xerém RJ, Brasil
CENAM	MX	Centro Nacional de Metrología, Querétaro, México

2.2 Measurement standards

A set of mixtures were prepared gravimetrically by INMETRO. For the preparation, pure propane was used from VSL (cylinder number D247762) and nitrogen from White Martins Gases, grade 6.0. The mixtures were verified against a set of INMETRO PSMs. The propane was subjected to a purity analysis in accordance with ISO 19229 [3] prior to use for preparation of the gas mixtures.

The filling pressure in the cylinders was approximately 100 bar. 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 were calculated in accordance with ISO 6142-1:2015 [4]. The amount-of-substance 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 value.

The nominal amount-of-substance fraction of propane was 1000 µmol/mol.

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 concentration ranges. The laboratories were also requested to submit a summary of their uncertainty evaluation used for estimating the uncertainty of their result.

2.4 Schedule

The schedule of this key comparison was as follows (table 2).

Table 2: Key comparison schedule

Date	Stage
September 2014	Agreement of protocol
November 2014	Registration of participants
January 2015	Preparation of mixtures
February2015	Verification of mixture compositions
June2015	Dispatch of mixtures
February 2016	Reports and cylinder arrived at Inmetro
April 2016	Re-verification of the mixtures
October 2016	Draft A report available
May 2017	*Draft B report available*

2.5 Measurement equation

The key comparison reference values are based on the weighing data, 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:

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

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

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

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

The equation for calculating the associated standard uncertainty reads as

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

The validity of the mixtures has been demonstrated by verifying the composition as calculated from the preparation data with that obtained from (analytical chemical) measurement. In order to have a positive demonstration of the preparation data including uncertainty, the following condition should be met [5]

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

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 key comparison, an approach has been chosen which is consistent with CCQM-K3 [6] and CCQM-K111 [6].

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

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

The values for $u_{i,ver}$ are given in the tables containing the results of this key comparison.

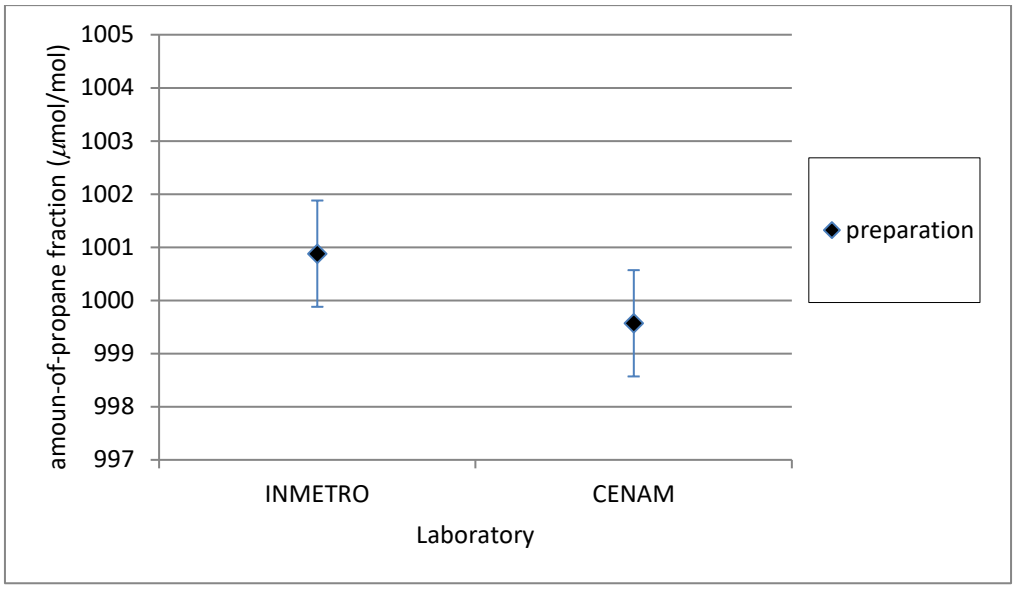

Figure 1: Preparation data of the transfer standards used in this key comparison

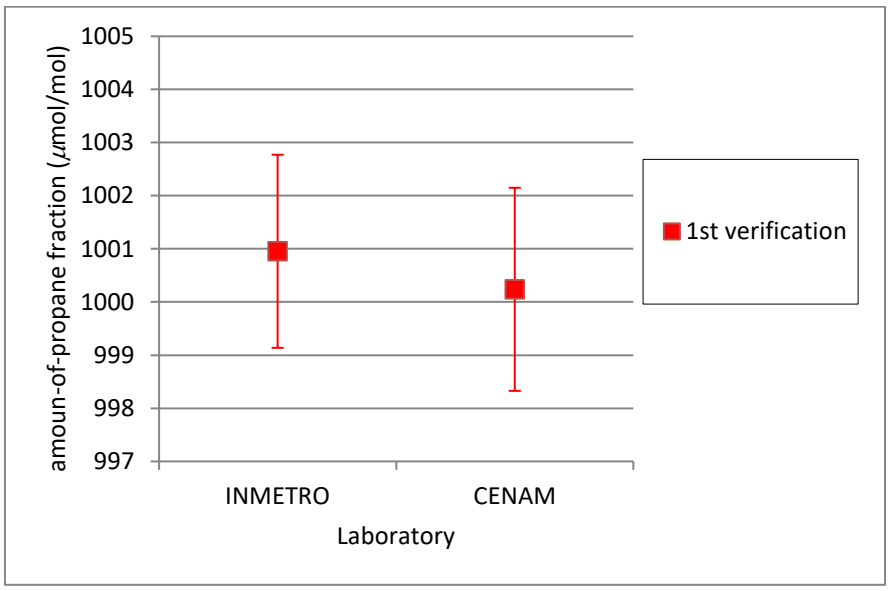

Figure 2: First verification data of the transfer standards used in this key comparison

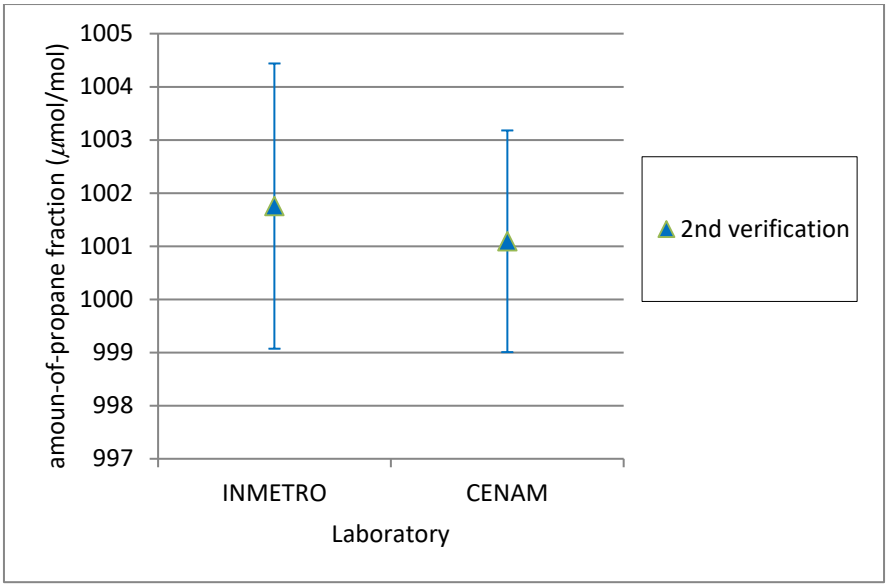

Figure 3: Second verification data of the transfer standards used in this key comparison

The preparation and verification data agree well (see figure **Erreur ! Source du renvoi introuvable.**, 2 and 3).

2.6 Measurement methods

The measurement methods used by the participants are described in annex A 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 3.

Table 3: Summary of calibration methods and metrological traceability

Laboratory code	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
INMETRO	06/07 April 2016 and 16/17/19 May 2016	ISO 6143	Own standards (ISO 6142-1:2015)	Nitrogen	GC-NGA-FID
CENAM	02/03/04 December 2015	ISO 6143	Own standards (ISO 6142-1:2015)	Nitrogen	GC-FID

2.7 Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as

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

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

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

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

The standard uncertainty of d_i can be expressed as

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

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.

2.8 Link to CCQM-K111

INMETRO participated in the key comparison, CCQM-K111 (1000 µmol/mol propane in nitrogen). Therefore, the results of SIM.QM-K111 will be relating with CCQM-K111 through the results of INMETRO and the Laboratory coordinator VSL. The results from INMETRO in CCQM-K111 is presented in table 4.

Table 4: Linking CCQM-K111 through INMETRO´s results

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	%u	%U	x_{lab}	U_{lab}	%U	k_{lab}	di	k	$U_{(di)}$	$u_{(di)}$
INMETRO	153926	991.4	0.264	0.347	0.044	0.088	990.9	2.3	0.23	2	-0.54	2	2.46	1.23
VSL	153513	993.4	0.265	0.348	0.044	0.088	993.4	0.7	0.07	2	0.0	2	1.12	0.56

3 Results

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

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

Table 5: Results of SIM.QM-K111

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	d_i	k	$U_{(di)}$
CENAM	D958424	999.57	0.706	1.78	1.91	998.9	1.7	2	-0.67	2	4.18
INMETRO	D543677	1000.88	0.705	1.67	1.82	1001.0	2.0	2	0.12	2	4.15

In figure 4 the degrees of equivalence for all participating laboratories are given relative to the gravimetric value. The uncertainties are, as required by the MRA [7], given as 95% confidence intervals. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been

[2] As defined in the MRA [7], a degree of equivalence is given by Δx and $U(\Delta x)$.

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.

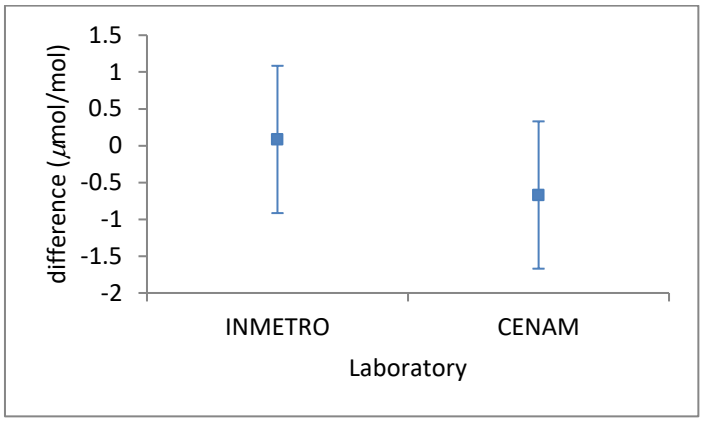

Figure 4: Degrees of equivalence

4 Supported CMC claims

The results of this key comparison can be used to support CMC claims as described in the final report of CCQM-K111 [6]:

1) For core capabilities, as track A key comparison;
2) For propane in nitrogen, as track B key comparison.

The support of CMC claims is described in more detail in the "GAWG strategy for comparisons and CMC claims" [6].

5 Discussion and conclusions

The results in this Track A key comparison on 1000 µmol.mol^{-1} propane in nitrogen are very good. All results are within ± 0.07 % of the KCRV.

References

[1] Van der Veen A.M.H., Van der Hout J.W., Ziel P.R., Oudwater R.J., Fioravante A.L., Augusto C.R., Brum M.C., Uehara S., Akima D., Bae H.K., Kang N., Woo J.C., Liaskos C.E., Roderick G.C., Brewer P.H., Brown A.S., Bartlett S., Downey M.L., Konopelko L.A., Kolobova A.V., Pankov A.A., Orshanskaya A.A., Efremova O.V., "International Comparison CCQM-K111 – Propane in nitrogen", Final Report, Metrologia Technical Supplement, Metrologia Techn. Suppl. **54** (2017), 08009

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

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[6] Van der Veen A.M.H, De Leer E.W.B., Perrochet J.-F., Wang Lin Zhen, Heine H.-J., Knopf D., Richter W., Barbe J., Marschal A., Vargha G., Deák E., Takahashi C., Kim J.S., Kim Y.D., Kim B.M., Kustikov Y.A., Khatskevitch E.A., Pankratov V.V., Popova T.A., Konopelko L., Musil S., Holland P., Milton M.J.T., Miller W.R., Guenther F.R., International Comparison CCQM-K3, Final Report, 2000

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

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Project reference

SIM.QM-K111

Completion date

July 2016

Measurement report CENAM

Laboratory name: CENTRO NACIONAL DE METROLOGIA (CENAM)
Cylinder number: D958424

Measurement #1

Component	Date dd/mm/yy	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
Propane	02/12/2015	999.08	0.12	4

Measurement #2

Component	Date dd/mm/yy	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
Propane	03/12/2015	998.734	0.077	4

Measurement #3

Component	Date dd/mm/yy	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
Propane	04/12/2015	998.849	0.054	4

Note: Each replica was obtained of 5 replicates grouped as submeasurements

Final results:

Component	Date dd/mm/yy	Result (μmol/mol)	Expanded uncertainty (μmol/mol)	Coverage factor
Propane	05/12/2015	998.9	1.7	2

Calibration Standards

CENAM according to guide ISO 6143 prepared four propane gravimetric standards in aluminium cylinder in the range of 950 to 1100 µmol / mol.

Calibration standars:

Number cylinder	Amount of substance fraction µmol/mol	U µmol/mol
FF24439	1097.48	0.32
FF24466	1048.22	0.32
FF24461	998.79	0.32
FF24457	949.10	0.32

Instrumentation

The measurements were performed using an Agilent Technologies gas chromatograph, model 6890 (G1540A), with FID detector at 250 °C, hydrogen flow 40.0 ml/min, air flow 450 ml/min, makeup flow 45 ml, Split Injector at 150 °C, total flow 98.0 ml/min, split ratio - 18:1; HP-PLOT Q column of 30 m x 530 µm x 4.0 µm at constant flow, helium flow 5.0 ml/min, average speed 51 cm/s; oven isothermally operated at 100 °C in a run time of 4.20 min, loop: 1 ml .

The sample is supplied to CG regulated to 200 ml/min with mass flow controller MKS, gas cylinders are set to a manual valve of 7 ports.

Calibration method and value assignment

Four standards are used for the calibration curve, considering the linear adjusted model least squares generalized as the program xgenline V1.0.

The calibration was done according to ISO 6143.

Measurement sequence was $S_1MS_2MS_3MS_4MS_1$.The sample was measured for three days, with 4 replicates per day of measurement

Uncertainty evaluation

The uncertainty value was estimated as $U = k \cdot u_c$, where u_c is the combined standard uncertainty estimated according to the "Guide to Expression of Uncertainty in Measurement, BIMP, First edition - September 2008". The expanded uncertainty, U, with a coverage factor k = 2 defines a confidence level of approximately 95%.

The uncertainty was calculated according the software xgenline V1.0, two sources of uncertainty were considered: uncertainty of the model (certificate – type A) and uncertainty of the variation between days (analysis – type A). Model source considers the uncertainty of measurement standards as a type B uncertainty produced by the preparation of CENAM´s PSMs.

Uncertainty evaluation

Uncertainty source Xi	Estimate xi, µmol/mol	Evaluation type (A or B)	Assumed distribution	Standard uncertainty u(xi) µmol/mol	Sensitivity coefficient ci	Contribution to standard uncertainty ui(y), µmol/mol
Variation between days	----------	A	Normal	0.216	1	20.63
Model	----------	A	Normal	0.831	1	79.37

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) International Organization for Standardization, ISO 6143:2001 Gas analysis -- Comparison methods for determining and checking the composition of calibration gas mixtures, First edition
(3) Guide to Expression of Uncertainty in Measurement, BIMP, Firts edition - September 2008"

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Measurement report INMETRO

Laboratory name: Inmetro / Lanag

Cylinder number: D543677

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Propane	16-05-2016	1001.76×10^{-6}	0.27	9

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Propane	17-05-2016	1002.16×10^{-6}	0.21	9

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Propane	18-05-2016	998.98×10^{-6}	0.26	9

Final Results

Component	Result (mol/mol)	Coverage factor	Assigned expanded uncertainty (mol/mol)
Propane	1001.0×10^{-6}	2	2.0×10^{-6}

Calibration standards

All primary gas standards mixtures (PSMs) for the measurement of propane are binary mixtures in nitrogen. Preparation is performed according ISO 6142-1:2015. The standard uncertainty is based on the uncertainty of the gravimetric preparation process and the purity analysis of the parent gases.

Table 4: Purity table of propane.

Chemical symbol	Amount fraction x (mol/mol)	Standard uncertainty u_x (mol/mol)
C_2H_6	0.00000517	0.00000014
C_3H_8	**0.99998752**	**0.00000023**
n-C_4H_{10}	0.00000137	0.00000012
i-C_4H_{10}	0.00000414	0.00000008
CO	0.00000060	0.00000005
CO2	0.00000120	0.00000010

Table 2: Purity table of nitrogen.

Chemical symbol	Amount fraction x (mol/mol)	Standard uncertainty u_x (mol/mol)
N2	0.999999400	0.000000200
CO	0.000000050	0.000000290
H_2O	0.000000250	0.000000140
O_2	0.000000250	0.000000140
C_xH_y*	0.000000050	0.000000029

* total hydrocarbons

Table 5: Calibration standards

Mixture code	***x* × 10^{-6} (mol/mol)**	**u_x × 10^{-6} (mol/mol)**
PSM117518	300.25	0.07
PSM133643	500.47	0.11
PSM113641	999.77	0.26
PSM110255	2000.43	0.27
PSM113658	3498.36	0.68
PSM127528	3853.67	0.63

Instrumentation

The measurements were performed using a gas chromatograph for natural gas (GC-NGA, CP-3800sp Varian), with a flame ionization detector, coupled to a gas sampling valve (Vici), with the following method conditions (table 4).

Table 4: GC-NGA method conditions

Parameter	Settings
Injector temperature	150°C
Split ratio	20:1
Column	CP-cil 5CB column, WCOT silica, l: 60 m, id: 0,25 mm
Column pressure	30,3 psi
Sample flow	3 ml/min
Column temperature	150 °C
FID temperature	250°C
FID flow´s	H_2: 30 ml/min, Air 300 ml/min, make up 29 ml/min

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 the 2nd and 3rd day of analyses the reducers were disconnected and connected to a different cylinder, also a different position on the multi position valve was used to connect the cylinder. The flushing and setting of the flow was done equal to the first measurement.

The calibration was done according to ISO 6143:2001. The calibration curve was made using the software XLgenline, the curve model for the data resulted in a straight line function, which was used for the value assignment. The goodness of fit for all 3 measurements was lower than 2.

Uncertainty evaluation

The uncertainty was calculated according to ISO 6143:2001, 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 repeatability (analysis – type A)
- Uncertainty of the area (analysis – type A)

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) International Organization for Standardization, ISO 6143:2001 Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures, First edition

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