# International Comparison EURAMET.QM-K3.2019 – Automotive exhaust gases

Ruben P. Ziel[1], E. Zalewska[1], Adriaan M.H. van der Veen[1], Heinrich Kipphardt[2], Dirk Tuma[2], Andres Rojo Esteban[3], Teresa Esperanza Fernandez Vicente[3], Tatiana Mace[4], Christophe Sutour[4], Fabrice Marioni[4], Judit Fűkő[5], László Szűcs[5], Tamás Büki[5], Zsófia Szilágyi Nagyné[5], Dariusz Cieciora[6], Grzegorz Ochman[6], Przemysław Romanowski[6], Anna Lis[6], Magdalena Garnuszek[6], Miroslava Valkova[7], Andreas Ackermann[8], Celine Pascale[8], Bernhard Niederhauser[8], Tanıl Tarhan[9], Aylin Boztepe[9], Jan Beránek[10], Miroslav Bárta[10]

[1]*Van Swinden Laboratorium (VSL), Chemistry Group, Thijsseweg 11, 2629 JA Delft, The Netherlands*
[2]*Bundesanstalt für Materialforschung und -prüfung (BAM), Richard-Willstätter-Str. 11, 12489 Berlin, Germany*
[3]*Centro Español de Metrología (CEM), Calle Alfar 2, 28760 Tres Cantos (Madrid), Spain*
[4]*Laboratoire national de métrologie et d'essais (LNE), 23 Avenue Albert Bartholomé, 75015 Paris, France*
[5]*Government Office of the Capital City Budapest (BFKH), Németvölgyi út 37-39. C/107, 1124 Budapest, Hungary*
[6]*Główny Urząd Miar – Central Office of Measures (GUM), ul. Elektoralna 2, 00-950 Warszawa, Poland*
[7]*Slovak Institute of Metrology (SMU), Karloveská 63, SK-842 55 Bratislava, Slovak Republic*
[8]*METAS - Federal Institute of Metrology (METAS), Lindenweg 50, CH-3003 Bern - Wabern, Switzerland*
[9]*TUBITAK National Metrology Institute (UME), Barış Mah. Dr. Zeki Acar Cad. No:1, 41470 Gebze Kocaeli, Turkey*
[10]*Český metrologický institut OI Praha (CMI), Radiová 1136/3, 102 00 Praha 10 – Hostivař, Czech Republic*

## Field

Amount of substance

## Subject

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

## Table of contents

# 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. The key comparison design follows that of the key comparisons CCQM-K3 [2] and CCQM-K111 [3].

# 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 |
|---|---|---|
| BAM | DE | Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany |
| CEM | ES | Centro Español de Metrología, Madrid, Spain |
| LNE | FR | Laboratoire national de métrologie et d'essais, Paris, France |
| BFKH | HU | Government Office of the Capital City Budapest, BFKH Budapest, Hungary |
| GUM | PL | Główny Urząd Miar, Warszawa, Poland |
| SMU | SK | Slovak Institute of Metrology, Bratislava, Slovak Republic |
| METAS | CH | METAS - Federal Institute of Metrology, Bern - Wabern, Switzerland |
| UME | TR | TUBITAK National Metrology Institute (UME), Gebze Kocaeli, Turkey |
| CMI | CZ | Český metrologický institute, Praha, Czech Republic |
| VSL | NL | Van Swinden Laboratorium, Delft, The Netherlands |

## 2.2 Measurement standards

A set of mixtures was prepared gravimetrically by VSL for the CCQM-K3.2019 key comparison [4]. The same set of standards was used for this EURAMET key comparison. The set of standards was verified before shipment to the participants and after their return.

For the preparation, carbon dioxide grade 5.5 was used from Air Products. Oxygen grade 6.0 was used from Linde. Carbon monoxide grade 4.7 was used from Air Products. Propane grade 3.5 was used from Air Products and nitrogen from Air Products, grade 6.0 BIP+. Carbon dioxide and oxygen were transferred as pure gas. Carbon monoxide was transferred from a premixture obtained by one gravimetric dilution step from the pure gas. Propane was transferred from a premixture obtained by two subsequent gravimetric dilution steps. The mixtures were verified against a set of VSL PSMs. All used 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 of 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 calculated from gravimetry and purity verification of the parent gases were used as key comparison reference values (KCRVs). Each individual cylinder had its own reference values and associated expanded uncertainties. The expanded uncertainties included a contribution from the verification of the gas mixtures.

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

**Table 2 Nominal composition of mixtures, given in amount fractions**

| Component | Amount fraction<br>$x$ |
|---|---|
| Carbon monoxide | 0.5 cmol $mol^{-1}$ – 2 cmol $mol^{-1}$ |
| Carbon dioxide | 2 cmol $mol^{-1}$ – 5 cmol $mol^{-1}$ |
| Oxygen | 1 cmol $mol^{-1}$ – 4 cmol $mol^{-1}$ |
| Propane | 100 µmol $mol^{-1}$ – 300 µmol $mol^{-1}$ |
| 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 submittable measurement value, 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 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/February 2021 | Re-verification of mixture compositions |
| May 2021 | Dispatch of mixtures |
| August 2021 | Reports and cylinders arrived back at VSL |
| September 2021 | Re-verification of the mixtures |
| January 2022 | 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 contributions have been considered:

1. gravimetric preparation (weighing process) ($x_{i,\mathrm{grav}}$)
2. purity of the parent gases ($\Delta x_{i,\mathrm{purity}}$)
3. stability of the gas mixture ($\Delta x_{i,\mathrm{stab}}$)
4. 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 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 [1]

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

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 [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

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

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

The relative difference from verification is defined as

$$e_{ij} = \frac{x_{\mathrm{anal},ij} - x_{\mathrm{prep},ij}}{x_{\mathrm{prep},ij}} \tag{5}$$

and expressed as percentage. $x_{\mathrm{prep},ij}$ denotes the amount fraction as calculated from static gravimetric preparation for mixture *i* and verification *j*, and $x_{\mathrm{anal},ij}$ the amount fraction obtained from the analytical verification. The results of the verification of the mixtures are summarised in Tables 4–7.

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

$$e_{ij} = \mu_i + B_i + \varepsilon_{ij} \qquad (6)$$

where $\mu_i$ denotes the mean relative difference for mixture *i*, $B_i$ a reproducibility effect in the verification measurements and $\varepsilon_{ij}$ a random measurement error term. Both $B_i$ and $\varepsilon_{ij}$ are assumed to be normally distributed with zero mean and variances $\tau_i^2$ and $\sigma_i^2$, 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 [7]

$$\log L(\mu, \tau^2) = -\frac{1}{2}\sum_j \log\left(2\pi\left(\sigma_j^2 + \tau^2\right)\right) - \frac{1}{2}\sum_j \log\frac{\left(e_j - \mu\right)^2}{\left(\sigma_j^2 + \tau^2\right)} \qquad (7)$$

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 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).

The calculations have been performed using the metafor package [8] and R [9]. The standard uncertainty of the difference was calculated using the procedures of ISO 6143 [10] (in the case of a multipoint calibration) and ISO 12963 [11] (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) [12] to obtain the standard uncertainty associated with the relative difference.

Table 4 shows the verification results of the mixtures for carbon dioxide. The values for the excess standard deviation ($\tau$) vary appreciably which is partly due to the low number of degrees of freedom on which they are based. The within-group standard uncertainty ($\sigma$) is very similar for each of the mixtures. All mixtures save D340045 and 8451 E 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 0.032 %. With this standard uncertainty, also D340045 and 8451 E meets the criterion of ISO 6143.

Table 5 summarises the verification results of the mixtures for carbon monoxide. All mixtures save 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 $\tau$ 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 but one of the mixtures pass the criterion of ISO 6143. For mixture 8449 E, the standard uncertainty is set at 0.050 %. The deviation seen in the verification is larger than for the other mixtures. The larger verification uncertainty has no adverse effect on the evaluation of the result of the NMI receiving this mixture.

**Table 4: Verification results for carbon dioxide, expressed as relative differences with respect to the amount fractions as calculated from preparation (%)**

| Mixture | $e_1$ | $u(e_1)$ | $e_2$ | $u(e_2)$ | $e_3$ | $u(e_3)$ | $e_4$ | $u(e_4)$ | $e_5$ | $u(e_5)$ | $\tau$ | $\sigma$ | $\bar{e}$ | $u(\bar{e})$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ML 6817 | 0.00 | 0.03 | 0.00 | 0.05 | 0.02 | 0.01 | −0.04 | 0.02 | −0.01 | 0.02 | 0.02 | 0.03 | −0.004 | 0.013 |
| 8500 E | −0.06 | 0.03 | −0.10 | 0.04 | 0.00 | 0.01 | 0.08 | 0.01 | 0.00 | 0.01 | 0.06 | 0.02 | −0.010 | 0.029 |
| MR 8468 | 0.09 | 0.02 | −0.06 | 0.06 | −0.08 | 0.01 | −0.03 | 0.01 | 0.02 | 0.01 | 0.07 | 0.03 | −0.009 | 0.031 |
| D751979 | 0.03 | 0.03 | 0.07 | 0.05 | −0.07 | 0.02 | −0.02 | 0.02 | −0.03 | 0.02 | 0.04 | 0.03 | −0.016 | 0.020 |
| ML 6812 | −0.03 | 0.04 | −0.18 | 0.06 | 0.01 | 0.01 | 0.00 | 0.03 | 0.16 | 0.03 | 0.11 | 0.04 | −0.001 | 0.051 |
| D340045 | 0.05 | 0.03 | 0.10 | 0.04 | 0.09 | 0.02 | −0.01 | 0.02 | 0.05 | 0.02 | 0.04 | 0.03 | 0.052 | 0.020 |
| 8449 E | −0.05 | 0.04 | −0.05 | 0.04 | 0.04 | 0.02 | −0.02 | 0.01 | −0.18 | 0.01 | 0.08 | 0.03 | −0.053 | 0.038 |
| 8451 E | −0.07 | 0.04 | 0.03 | 0.05 | 0.05 | 0.01 | 0.02 | 0.01 | 0.04 | 0.01 | 0.02 | 0.03 | 0.031 | 0.011 |
| 8457 E | 0.11 | 0.03 | −0.10 | 0.05 | −0.04 | 0.01 | −0.04 | 0.03 | −0.15 | 0.03 | 0.09 | 0.03 | −0.043 | 0.044 |

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

| Mixture | $e_1$ | $u(e_1)$ | $e_2$ | $u(e_2)$ | $e_3$ | $u(e_3)$ | $e_4$ | $u(e_4)$ | $\tau$ | $\sigma$ | $\bar{e}$ | $u(\bar{e})$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ML 6817 | 0.02 | 0.02 | 0.00 | 0.03 | 0.01 | 0.01 | 0.01 | 0.02 | 0.00 | 0.02 | 0.011 | 0.008 |
| 8500 E | −0.12 | 0.02 | −0.16 | 0.02 | 0.03 | 0.01 | 0.01 | 0.02 | 0.09 | 0.02 | −0.059 | 0.047 |
| MR 8468 | 0.01 | 0.02 | −0.07 | 0.03 | −0.04 | 0.01 | −0.10 | 0.03 | 0.04 | 0.02 | −0.046 | 0.023 |
| D751979 | −0.03 | 0.02 | 0.01 | 0.02 | 0.01 | 0.01 | 0.16 | 0.02 | 0.08 | 0.02 | 0.038 | 0.042 |
| ML 6812 | −0.02 | 0.03 | −0.18 | 0.02 | 0.01 | 0.03 | 0.05 | 0.04 | 0.10 | 0.03 | −0.037 | 0.051 |
| D340045 | −0.11 | 0.02 | −0.07 | 0.02 | 0.02 | 0.01 | 0.01 | 0.02 | 0.06 | 0.02 | −0.037 | 0.032 |
| 8449 E | −0.12 | 0.02 | −0.11 | 0.03 | 0.03 | 0.02 | −0.14 | 0.02 | 0.08 | 0.02 | −0.084 | 0.040 |
| 8451 E | −0.10 | 0.02 | −0.06 | 0.02 | −0.05 | 0.01 | 0.07 | 0.02 | 0.07 | 0.02 | −0.034 | 0.037 |
| 8457 E | −0.02 | 0.03 | −0.15 | 0.02 | 0.01 | 0.02 | −0.23 | 0.03 | 0.11 | 0.02 | −0.097 | 0.056 |

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

| Mixture | $e_1$ | $u(e_1)$ | $e_2$ | $u(e_2)$ | $e_3$ | $u(e_3)$ | $\tau$ | $\sigma$ | $\bar{e}$ | $u(\bar{e})$ |
|---|---|---|---|---|---|---|---|---|---|---|
| ML 6817 | −0.06 | 0.03 | 0.06 | 0.02 | 0.00 | 0.01 | 0.05 | 0.02 | 0.004 | 0.033 |
| 8500 E | −0.01 | 0.02 | 0.02 | 0.02 | −0.01 | 0.02 | 0.00 | 0.02 | −0.003 | 0.011 |
| MR 8468 | −0.04 | 0.02 | −0.04 | 0.02 | 0.00 | 0.02 | 0.01 | 0.02 | −0.026 | 0.013 |
| D751979 | 0.01 | 0.02 | −0.02 | 0.02 | −0.05 | 0.02 | 0.02 | 0.02 | −0.020 | 0.017 |
| ML 6812 | −0.07 | 0.02 | 0.14 | 0.02 | 0.00 | 0.02 | 0.11 | 0.02 | 0.024 | 0.062 |
| D340045 | −0.04 | 0.02 | 0.01 | 0.02 | 0.04 | 0.02 | 0.03 | 0.02 | 0.005 | 0.023 |
| 8449 E | −0.03 | 0.03 | 0.02 | 0.02 | 0.03 | 0.02 | 0.02 | 0.02 | 0.010 | 0.018 |
| 8451 E | −0.08 | 0.02 | 0.03 | 0.02 | 0.03 | 0.01 | 0.06 | 0.02 | −0.006 | 0.036 |
| 8457 E | −0.05 | 0.02 | −0.02 | 0.02 | -0.03 | 0.01 | 0.00 | 0.02 | −0.031 | 0.010 |

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

| Mixture | $e_1$ | $u(e_1)$ | $e_2$ | $u(e_2)$ | $e_3$ | $u(e_3)$ | $\tau$ | $\sigma$ | $\bar{e}$ | $u(\bar{e})$ |
|---|---|---|---|---|---|---|---|---|---|---|
| ML 6817 | 0.01 | 0.02 | −0.04 | 0.02 | 0.09 | 0.02 | 0.06 | 0.02 | 0.020 | 0.038 |
| 8500 E | −0.03 | 0.02 | −0.02 | 0.03 | −0.27 | 0.02 | 0.14 | 0.02 | −0.107 | 0.082 |
| MR 8468 | −0.05 | 0.03 | −0.01 | 0.02 | 0.04 | 0.03 | 0.04 | 0.03 | −0.008 | 0.025 |
| D751979 | −0.04 | 0.02 | −0.02 | 0.02 | 0.13 | 0.02 | 0.09 | 0.02 | 0.024 | 0.054 |
| ML 6812 | 0.04 | 0.03 | −0.02 | 0.02 | 0.14 | 0.03 | 0.08 | 0.03 | 0.051 | 0.047 |
| D340045 | −0.01 | 0.02 | 0.02 | 0.02 | −0.05 | 0.02 | 0.03 | 0.02 | −0.014 | 0.020 |
| 8449 E | 0.03 | 0.02 | 0.05 | 0.02 | −0.04 | 0.02 | 0.04 | 0.02 | 0.014 | 0.027 |
| 8451 E | 0.05 | 0.02 | 0.00 | 0.02 | −0.04 | 0.02 | 0.04 | 0.02 | 0.002 | 0.025 |
| 8457 E | 0.03 | 0.02 | −0.07 | 0.02 | −0.05 | 0.02 | 0.05 | 0.02 | −0.032 | 0.029 |

Table 6 summarises the verification results of the mixtures for propane. All mixtures save 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 $\tau$ are appreciably different. For the verification uncertainty, the pooled standard uncertainty of all verifications is used, which is 0.028 %. With this standard uncertainty, all mixtures pass the criterion of ISO 6143.

Table 7 summarises the verification results of the mixtures for oxygen. All mixtures 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 $\tau$ are appreciably different. For the verification uncertainty, the pooled standard uncertainty of all verifications is used, which is 0.041 %. With this standard uncertainty, all mixtures pass the criterion of ISO 6143.

## 2.6 Measurement methods

The measurement methods used by the participants are described in the measurement reports annexed to 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 8.

**Table 8: Summary of calibration methods and metrological traceability**

| Laboratory | Measurement period | Calibration | Traceability | Matrix standards | Measurement technique |
|---|---|---|---|---|---|
| BAM | 1 July to 12 August 2021 | two-point calibration with bracketing (TPC) protocol | Own standards (ISO 6142) | Nitrogen | GC with TCD and methanizer/FID |
| CEM | 16 July to 17 August 2021 | ISO 6143 | Own standards (ISO 6142) | Nitrogen | micro-GC-TCD |
| LNE | 16 August to 24 August 2021 | Single-point calibration | Own standards (ISO 6142) | Nitrogen | PDHID detector ($O_2$) and a FID with methanizer (CO, $CO_2$ and $C_3H_8$) |
| BFKH | 19 July to 26 August 2021 | Single-point calibration | Own standards | Nitrogen | GC-FID and GC-TCD |
| GUM | 28 June to 4 August 2021 | ISO 6143 | Own standards (ISO 6142) | Nitrogen | GC-FID and GC-TCD |
| SMU | 28 June to 27 July 2021 | ISO 6143 | Own standards (ISO 6142) | Nitrogen | GC-FID ($C_3H_8$) and GC-TCD (CO, $CO_2$ & $O_2$) |
| METAS | 2 June to 6 September 2021 | ISO 6143 | Own standards and NPL & VSL standards | Nitrogen | GC-FID with methanizer (CO, $CO_2$ & $C_3H_8$) and paramagnetic measurement system ($O_2$) |
| UME | 2 July to 9 September 2021 | ISO 6143 | Own standards (ISO 6142) | Nitrogen | GC-FID (CO, $CO_2$ and $C_3H_8$) and GC-TCD ($O_2$) |
| CMI | 5 July to 16 August 2021 | Four-point linear model | Own standards (ISO 6142) | Nitrogen | GC with 2x TCD and FID |

## 2.7 Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as

$$\Delta x_i = d_i = x_i - x_{i,\mathrm{KCRV}}, \tag{8}$$

and the uncertainty of the difference $d_i$ at 95 % level of confidence. Here, $x_{i,\mathrm{ref}}$ 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

$$\Delta x_i = d_i = x_i - x_{i,\mathrm{ref}}. \tag{9}$$

The standard uncertainty of $d_i$ can be expressed as

$$u^2(d_i) = u^2(x_i) + u^2\left(x_{i,\mathrm{prep}}\right) + u^2\left(\Delta x_{i,\mathrm{ver}}\right), \tag{10}$$

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

# 3 Results

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

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

**Table 9: Results for the amount fraction carbon dioxide**

| Laboratory | Cylinder | $x_{\mathrm{prep}}$ (cmol/mol) | $u_{\mathrm{prep}}$ (cmol/mol) | $u_{\mathrm{ver}}$ (cmol/mol) | $u_{\mathrm{ref}}$ (cmol/mol) | $x_{\mathrm{lab}}$ (cmol/mol) | $U_{\mathrm{lab}}$ (cmol/mol) | $k_{\mathrm{lab}}$ | $d_i$ (cmol/mol) | $k$ | $U(d_i)$ (cmol/mol) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| BAM | ML 6817 | 1.9951 | 0.0004 | 0.0006 | 0.0008 | 1.9963 | 0.0060 | 2 | 0.0012 | 2 | 0.0062 |
| CEM | 8500 E | 1.9998 | 0.0004 | 0.0006 | 0.0008 | 2.016 | 0.013 | 2 | 0.0162 | 2 | 0.0131 |
| LNE | 8457 E | 2.0138 | 0.0004 | 0.0006 | 0.0008 | 2.007 | 0.017 | 2 | −0.0068 | 2 | 0.0171 |
| BFKH | 8451 E | 1.9846 | 0.0004 | 0.0006 | 0.0008 | 1.9831 | 0.0018 | 2 | −0.0015 | 2 | 0.0023 |
| GUM | D340045 | 1.9965 | 0.0004 | 0.0006 | 0.0008 | 1.9947 | 0.0070 | 2 | −0.0018 | 2 | 0.0072 |
| SMU | 8449 E | 2.0025 | 0.0004 | 0.0006 | 0.0008 | 2.0027 | 0.0060 | 2 | 0.0002 | 2 | 0.0062 |
| METAS | MR 8468 | 2.0018 | 0.0004 | 0.0006 | 0.0008 | 2.005 | 0.007 | 2 | 0.0032 | 2 | 0.0072 |
| UME | D751979 | 1.9731 | 0.0004 | 0.0006 | 0.0007 | 1.9752 | 0.0038 | 2 | 0.0021 | 2 | 0.0041 |
| CMI | ML 6812 | 1.9993 | 0.0004 | 0.0006 | 0.0008 | 2.0002 | 0.0051 | 2 | 0.0009 | 2 | 0.0053 |

---

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

[2] As defined in the MRA [8], a degree of equivalence is given by *d* and *U(d).*

Table 9 shows the results for the amount fraction carbon dioxide. All results but one (CEM) are consistent with the key comparison reference value. The degrees of equivalence are plotted in Figure 1.

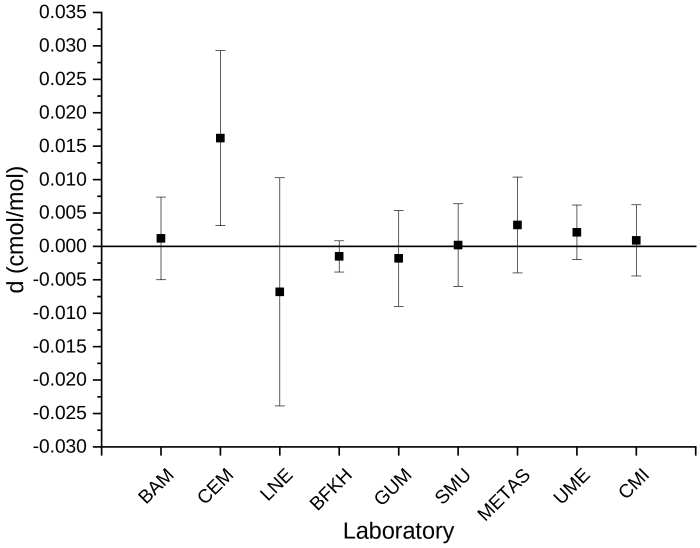


**Figure 1: Degrees of equivalence for the amount fraction carbon dioxide**

Table 10 shows the results for the amount fraction carbon monoxide. All results, save that of METAS 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 monoxide**

| Laboratory | Cylinder | $x_{\text{prep}}$ (cmol/mol) | $u_{\text{prep}}$ (cmol/mol) | $u_{\text{ver}}$ (cmol/mol) | $u_{\text{ref}}$ (cmol/mol) | $x_{\text{lab}}$ (cmol/mol) | $U_{\text{lab}}$ (cmol/mol) | $k_{\text{lab}}$ | $d_i$ (cmol/mol) | $k$ | $U(d_i)$ (cmol/mol) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| BAM | ML 6817 | 1.0135 | 0.0002 | 0.0004 | 0.0004 | 1.0145 | 0.0030 | 2 | 0.0010 | 2 | 0.0031 |
| CEM | 8500 E | 0.9939 | 0.0002 | 0.0004 | 0.0004 | 0.9962 | 0.0046 | 2 | 0.0023 | 2 | 0.0047 |
| LNE | 8457 E | 1.0162 | 0.0002 | 0.0004 | 0.0004 | 1.0130 | 0.0080 | 2 | −0.0032 | 2 | 0.0080 |
| BFKH | 8451 E | 1.0026 | 0.0002 | 0.0004 | 0.0004 | 1.0021 | 0.0017 | 2 | −0.0005 | 2 | 0.0019 |
| GUM | D340045 | 1.0010 | 0.0002 | 0.0004 | 0.0004 | 1.0032 | 0.0040 | 2 | 0.0022 | 2 | 0.0041 |
| SMU | 8449 E | 1.0007 | 0.0002 | 0.0004 | 0.0004 | 1.0008 | 0.0030 | 2 | 0.0001 | 2 | 0.0031 |
| METAS | MR 8468 | 1.0033 | 0.0002 | 0.0005 | 0.0005 | 1.0087 | 0.0040 | 2 | 0.0054 | 2 | 0.0041 |
| UME | D751979 | 1.0100 | 0.0002 | 0.0004 | 0.0004 | 1.0118 | 0.0020 | 2 | 0.0018 | 2 | 0.0022 |
| CMI | ML 6812 | 1.0052 | 0.0002 | 0.0004 | 0.0004 | 1.0024 | 0.0052 | 2 | −0.0028 | 2 | 0.0053 |

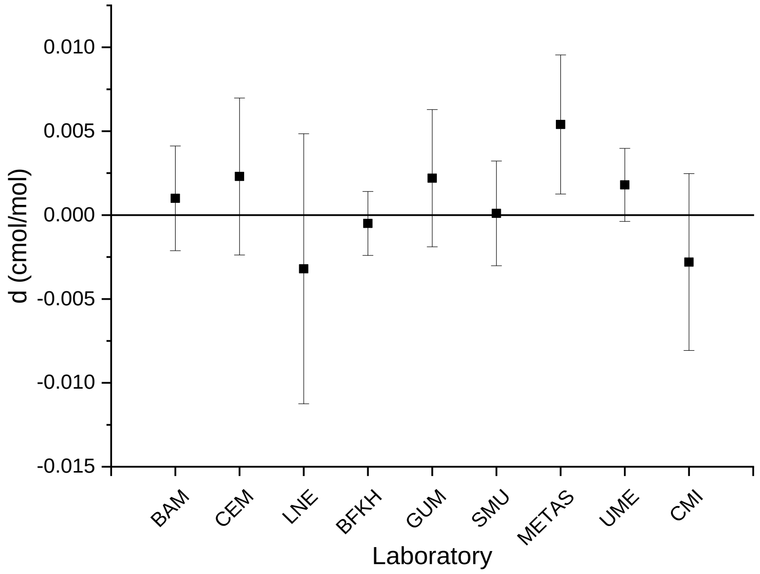


**Figure 2: Degrees of equivalence for the amount fraction carbon monoxide**

In Table 11 the results for the amount fraction propane are shown. All results, save those from BFKH and UME are consistent with the key comparison reference value. The degrees of equivalence are plotted in Figure 3.

**Table 11: Results for the amount fraction propane**

| Laboratory | Cylinder | $x_{\mathrm{prep}}$ (cmol/mol) | $u_{\mathrm{prep}}$ (cmol/mol) | $u_{\mathrm{ver}}$ (cmol/mol) | $u_{\mathrm{ref}}$ (cmol/mol) | $x_{\mathrm{lab}}$ (cmol/mol) | $U_{\mathrm{lab}}$ (cmol/mol) | $k_{\mathrm{lab}}$ | $d_i$ (cmol/mol) | $k$ | $U(d_i)$ (cmol/mol) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| BAM | ML 6817 | 0.019981 | 0.000005 | 0.000007 | 0.000009 | 0.019976 | 0.000080 | 2 | −0.000005 | 2 | 0.000082 |
| CEM | 8500 E | 0.020116 | 0.000005 | 0.000007 | 0.000009 | 0.02001 | 0.00029 | 2 | −0.000106 | 2 | 0.000291 |
| LNE | 8457 E | 0.020327 | 0.000005 | 0.000007 | 0.000009 | 0.02027 | 0.00013 | 2 | −0.000057 | 2 | 0.000131 |
| BFKH | 8451 E | 0.020017 | 0.000005 | 0.000007 | 0.000009 | 0.020052 | 0.000028 | 2 | 0.000035 | 2 | 0.000033 |
| GUM | D340045 | 0.019986 | 0.000005 | 0.000007 | 0.000009 | 0.019968 | 0.000078 | 2 | −0.000018 | 2 | 0.000080 |
| SMU | 8449 E | 0.019868 | 0.000005 | 0.000007 | 0.000009 | 0.019906 | 0.000061 | 2 | 0.000038 | 2 | 0.000063 |
| METAS | MR 8468 | 0.019954 | 0.000005 | 0.000007 | 0.000009 | 0.01995 | 0.00008 | 2 | −0.000004 | 2 | 0.000082 |
| UME | D751979 | 0.019665 | 0.000005 | 0.000007 | 0.000009 | 0.01973 | 0.00004 | 2 | 0.000065 | 2 | 0.000044 |
| CMI | ML 6812 | 0.020163 | 0.000005 | 0.000007 | 0.000009 | 0.02015 | 0.00044 | 2 | −0.000013 | 2 | 0.000440 |

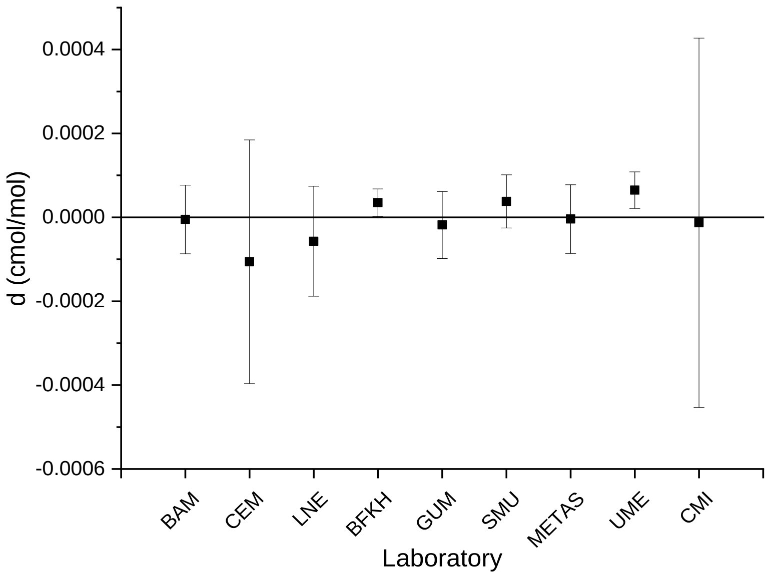


**Figure 3: Degrees of equivalence for the amount fraction propane**

Table 12 shows the results for the amount fraction oxygen. The result from BFKH is discrepant with respect to the key comparison reference value. The degrees of equivalence are plotted in Figure 4.

**Table 12: Results for the amount fraction oxygen**

| Laboratory | Cylinder | $x_{\text{prep}}$ (cmol/mol) | $u_{\text{prep}}$ (cmol/mol) | $u_{\text{ver}}$ (cmol/mol) | $u_{\text{ref}}$ (cmol/mol) | $x_{\text{lab}}$ (cmol/mol) | $U_{\text{lab}}$ (cmol/mol) | $k_{\text{lab}}$ | $d_i$ (cmol/mol) | $k$ | $U(d_i)$ (cmol/mol) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| BAM | ML 6817 | 2.9698 | 0.0006 | 0.0012 | 0.0014 | 2.9733 | 0.0089 | 2 | 0.0035 | 2 | 0.0093 |
| CEM | 8500 E | 3.0137 | 0.0006 | 0.0012 | 0.0014 | 3.028 | 0.021 | 2 | 0.0143 | 2 | 0.0212 |
| LNE | 8457 E | 2.8924 | 0.0006 | 0.0012 | 0.0013 | 2.918 | 0.027 | 2 | 0.0256 | 2 | 0.0271 |
| BFKH | 8451 E | 3.0080 | 0.0006 | 0.0012 | 0.0014 | 3.0031 | 0.0028 | 2 | −0.0049 | 2 | 0.0039 |
| GUM | D340045 | 3.0016 | 0.0006 | 0.0012 | 0.0014 | 3.0037 | 0.0098 | 2 | 0.0021 | 2 | 0.0102 |
| SMU | 8449 E | 3.0116 | 0.0006 | 0.0012 | 0.0014 | 3.011 | 0.013 | 2 | −0.0006 | 2 | 0.0133 |
| METAS | MR 8468 | 2.9833 | 0.0006 | 0.0012 | 0.0014 | 2.972 | 0.012 | 2 | −0.0113 | 2 | 0.0123 |
| UME | D751979 | 3.0649 | 0.0006 | 0.0013 | 0.0014 | 3.0641 | 0.0038 | 2 | −0.0008 | 2 | 0.0047 |
| CMI | ML 6812 | 2.9606 | 0.0006 | 0.0012 | 0.0014 | 2.9619 | 0.0099 | 2 | 0.0013 | 2 | 0.0103 |

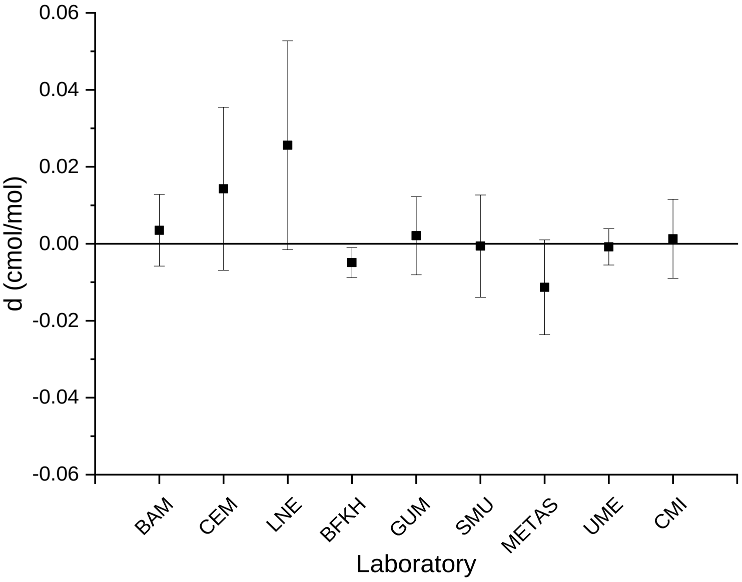


**Figure 4: Degrees of equivalence for the amount fraction oxygen**

# 4 Supported CMC claims

The results of this key comparison can be used to support CMC claims in two different ways, as detailed in the report of CCQM-K3.2019 [4].

# 5 Discussion and conclusions

The results in this key comparison show generally good agreement. Most results agree within 0.3 % 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 key comparisons (e.g., CCQM-K120 Carbon dioxide, CCQM-K111 Propane, CCQM-K51 Carbon monoxide).

# 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, 1st edition

[2] 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

[3] 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 Techn. Suppl. 54 (2017), 08009

[4] Van der Veen A.M.H., Zalewska E., Kobayashi M., Akima D., Uehara S., Fioravante A.L., Augusto C.R., Ribeiro C.C., Silva V., Dias F., Botas A., Costa C., Lee J.S., Lee J.B., Lim J., Bae H., Kang N., Cecelski C.E., Harris K.J., Miller Jr. W.R., Carney J., Tshilongo J., Ntsasa N.G., Jozela M.I., Leshabane N., Marebane P.M., Worton D.R., Mussell Webber E.B., Moreno S., Brewer

P.J., Konopelko L.A., Kolobova A.V. , Meshkov A.V., Efremova O.V., “International Comparison CCQM-K3.2019 Automotive exhaust gases”, Final Report, Metrologia Techn. Suppl., to be published

[5] International Organization for Standardization, ISO 19229:2019 Gas analysis — Gas analysis — Purity analysis and the treatment of purity data, 2nd edition

[6] Van der Veen A.M.H., Brinkmann F.N.C., Arnautovic M., Besley L., Heine H.-J., Lopez Esteban T., Sega M., Kato K., Kim J.S., Perez Castorena A., Rakowska A., Milton M.J.T., Guenther F.R., Francy R., Dlugokencky E., “International comparison CCQM-P41 Greenhouse gases. 2. Direct comparison of primary standard gas mixtures”, Metrologia 44 (2007), Techn. Suppl. 08003

[7] Brockwell S.E., Gordon I.R., “A comparison of statistical methods for meta-analysis”, Statistics in Medicine 20 (2001), pp. 825-840

[8] Viechtbauer, W., Conducting meta-analyses in R with the metafor package. Journal of Statistical Software, 36(3) (2010)., 1–48

[9] R Core Team (2020). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/

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

[11] International Organization for Standardization, ISO 12963:2017 Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration

[12] International Organization for Standardization, ISO/IEC Guide 98-3:2008 Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995), 1st edition

## Coordinator

VSL
Chemistry Group
Ruben P. Ziel
Thijsseweg 11
2629 JA Delft
The Netherlands

## Project reference

EURAMET.QM-K3.2019

## Completion date

January 2022

# Annex A Measurement report of BAM

## A.1 Background

EURAMET.QM-K3.2019 is an international interlaboratory comparison for automotive gases organized by VSL. The study covers an $O_2$ containing automotive gas. This report provides the results of BAM as a participant.

## A.2 Choice of method

For the determination of the components the method of choice was GC with TCD or FID detection and optionally methanizer/FID for the determination of CO and $CO_2$.

## A.3 Sample: labeling, packing, pre-information

The sample was provided by VSL in a 5-L aluminum cylinder with cylinder number ML 6817 equipped with a valve which has DIN 477 thread No. 1 (hydrogen). The initial pressure upon receipt was not measured, the final pressure after finishing the measurement campaign was 6.4 MPa.

## A.4 Sample pretreatment

No heating or rolling was applied. The sample was stored at indoor laboratory conditions.

## A.5 Devices used and flushing

A DIN 477 No. 1 (hydrogen)-VRC ¼″ fitting was adapted to the sample cylinder. A reduction valve, a needle valve for dosing, and a closing valve with an outlet to Swagelok 1/16″ capillaries were attached. For the two simultaneously employed calibration gases a similar assembly was used but with a DIN 477 No. 14 (test gas) thread. The assembly for both the sample cylinder and the calibration gases were frequently connected and disconnected to the cylinder valve when it was mounted to the two GC analyzers used in this measuring campaign.

A freshly installed assembly was evacuated down to a pressure of approximately $10^{-3}$ mbar and then filled with gas from the cylinder prior to the actual analysis. The evacuating/flushing procedure was repeated five times before the analysis was started.

## A.6 Measurement instruments & settings

A specially designed Siemens Maxum II process gas analyzer was used applying "method 1" (an established standard method to certify gas samples) which executes a sequence of 44 consecutive injections. The instrument is equipped with TCD detectors and has six different separation channels that are adapted for assigned analytes. All installed columns are custom-fit packed columns. The oven was set to 60 °C and operated in isothermal mode with helium as carrier gas for five of the six channels. Injection volumes vary between 30 and 500 µL depending on the channel. Details on Maxum operation can be found in the BAM SOP "GAS-StAA-027".

Channel 1 is for helium and hydrogen with $N_2$ as a carrier gas and two columns of type Hayesep (guard) and Molsieve (separation) columns.

Channel 2 is for methane with two Hayesep (guard and separation) columns.

Channel 3 is for methane, carbon dioxide, ethene, and ethane with two Hayesep (guard and separation) columns.

Channel 4 is for propene and propane with a Sorbitolchrom (guard), a TCEP-Carboblack (guard), and a TCEP-Unibeads (separation) column.

Channel 5 is for oxygen, nitrogen, and carbon monoxide with Shincarbon (guard) and Molsieve (separation) columns.

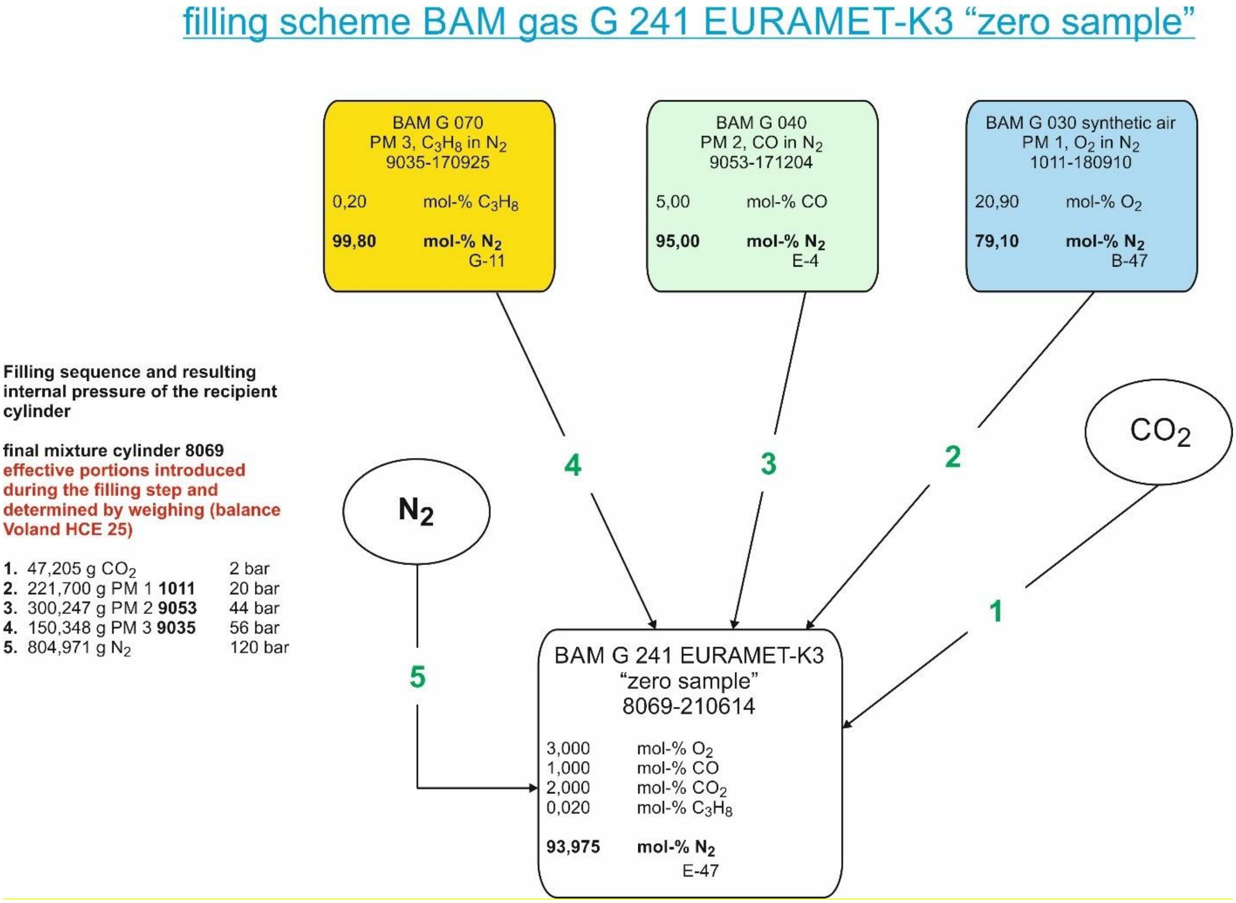
Channel 6 is for isobutane, n-butane, neopentane, isopentane, n-pentane, and n-hexane with two Wax-20M-Carboblack (guard and separation) columns.

Additionally, a Thermo Scientific Trace 1310 analytical GC was used. It is equipped with two channels, namely a channel for permanent gases with backflush on a Restek HayesepQ and separation on a Restek Molsieve micro-packed column with TCD detection and channel for hydrocarbons with a Restek Rtx-1® capillary column for hydrocarbons and a methanizer/FID detector. A valve control circuit allows for building methods with a switch protocol.

Oxygen was determined on the channel for permanent gases. $CO_2$ and CO were visible there as well but directed on the hydrocarbon channel with a methanizer and measured together with the propane. The method operated in an isothermal mode at 80 °C.

## A.7 Calibration

Three calibration gases were prepared independently from high-purity gases by a gravimetric method according to DIN EN ISO 6142-1:2015 as shown in the following general scheme:



Filling steps and resulting pressure in the recipient cylinder (calculated amounts and pressures to create the targeted composition; the pressures are calculated for room temperature):
1, 2, 3, … indicates a filling step with pure gases or gas mixtures, respectively.

Gas cylinders (with individual component masses > 30 g) were weighed on a balance of type Voland HCE 25 with an uncertainty of $U(m)$ = 15 mg (Type B).

Premixture 1 (PM 1; cylinder no. 1011) Premixture 2 (PM 2; cylinder no. 9053)

388,439 g $O_2$
1287,088 g $N_2$
Total: 1675,527 g

81,191 g CO
1542,096 g $N_2$
Total: 1623,286 g

Premixture 3a (4 mol-% propane in $N_2$, cylinder no. 8005, not shown in the scheme)
90,684 g $C_3H_8$
1381,160 g $N_2$
Total: 1471,844 g

Premixture 3 (PM 3; cylinder no. 9035)

80,178 g PM 3a
1490,110 g $N_2$
Total: 1570,288 g

The composition (from gravimetry) of the calibration gases was:

| Cylinder no. | | Oxygen | Carbon-monoxide | Carbon-dioxide | Propane |
|---|---|---|---|---|---|
| 8036-210614 | $x_{\text{zert}}$ / % | 2.854457 | 0.950082 | 1.898046 | 0.019002 |
| | $u(x_{zert})$ / % | 0.000114 | 0.000095 | 0.000313 | 0.000005 |
| | $u_{\text{rel}}(x_{\text{zert}})$ | 4.0E-05 | 1.0E-04 | 1.7E-04 | 2.7E-04 |
| | $U_{\text{rel}}(x_{\text{zert}})$ | 8.0E-05 | 2.0E-04 | 3.3E-04 | 5.4E-04 |
| 8092-210614 | $x_{\text{zert}}$ / % | 3.149334 | 1.049895 | 2.098520 | 0.021012 |
| | $u(x_{zert})$ / % | 0.000126 | 0.000094 | 0.000315 | 0.000006 |
| | $u_{\text{rel}}(x_{\text{zert}})$ | 4.0E-05 | 9.0E-05 | 1.5E-04 | 2.9E-04 |
| | $U_{\text{rel}}(x_{\text{zert}})$ | 8.0E-05 | 1.8E-04 | 3.0E-04 | 5.7E-04 |
| 8069-210614 | $x_{\text{Hersteller}}$ / % | 2.998175 | 1.000759 | 2.002137 | 0.020014 |
| | $u(x_{Hersteller})$ / % | 0.000120 | 0.000095 | 0.000320 | 0.000005 |
| | $u_{\text{rel}}(x_{\text{Hersteller}})$ | 4.0E-05 | 9.5E-05 | 1.6E-04 | 2.7E-04 |
| | $U_{\text{rel}}(x_{\text{Hersteller}})$ | 8.0E-05 | 1.9E-04 | 3.2E-04 | 5.4E-04 |

In a measurement campaign prior to the investigation of the sample to validate the prepared mixtures, the calibration gases (two “bracket gases” 8036-210614 and 8092-210614 and a “zero” sample 8069-210614 that resembles the targeted composition) were found to be consistent [for details see file VAL-G241].

The purity analysis of the initial pure gases was based on the information provided by the supplier or on the results of determination of impurities in pure gases using an analysis method developed at BAM. As the analyte concentrations in the automotive gas are rather high, blanks of the initial gases were not significantly contributing to values and uncertainty.

## A.8 Measurement outline

For a measurement sequence, the two calibration gases (C1 = 8036 & C2 = 8092) and the sample (S = 8069 or ML 6817) were connected to the GC. Using a stream selector valve, each calibration gas was sampled three times, the sample gas five times to the GC in the following consecutive order: C1–S–C2–S–C1–S–C2–S–C1–S–C2. When the stream is flowing through the sampling loop, four injections were made from each stream before the stream selector valve switched to the next stream in the sequence. The first injection of each stream was discarded, only the last three were used for data evaluation. The complete sequence runs over a period of four hours with the Maxum GC and of 22 hours with the Thermo GC, respectively.
Using the Maxum GC, one measurement campaign consisting of three sequences was conducted. Using the Thermo GC, two measurement campaigns were conducted. Each campaign was

executed on different days and the assembly was flushed and mounted (dismounted) to the analyzer at the start.

The calibration follows the two-point calibration with bracketing (TPC) protocol as basically described in ISO 12963. The practical implementation in this study is briefly described and exemplarily illustrated below with numbers for an arbitrary measurement of propane {Code783_EURAMET_K3_Thermo_5, Ausw_MAX_1, 4. Kurvenwert}. All other data (stored in EXCEL spreadsheets) are also available upon request.

From the three recorded measurements for each gas, the mean value (MW) and standard deviation (Stdev) (understood as uncertainty of type A) and relative standard deviation (urel) are calculated for the observed signal intensities. In this case, the signal refers to the integrated peak area of propane.

| | | |
|---|---|---|
| 3,2 | MW | 2.1958 |
| | Stdev | 0.0018 |
| | urel | 8.2E-04 |
| 2,4 | MW | 2.0870 |
| | Stdev | 0.0011 |
| | urel | 5.1E-04 |
| 1,3 | MW | 1.9880 |
| | Stdev | 0.0011 |
| | urel | 5.7E-04 |

Together with the gas composition (from gravimetry) with uncertainties taken as type B of the calibration gases, i.e.,

| | | |
|---|---|---|
| C1 | $x_{\text{zert}}$ / % | 0.019002 |
| | $u(x_{zert})$ / % | 0.000005 |
| 8036-210614 | $u_{\text{rel}}(x_{\text{zert}})$ | 2.7E-04 |

| | | |
|---|---|---|
| C2 | $x_{\text{zert}}$ / % | 0.021012 |
| | $u(x_{zert})$ / % | 0.000006 |
| 8092-210614 | $u_{\text{rel}}(x_{\text{zert}})$ | 2.9E-04 |

a bracketing calculation is performed to obtain the amount-of-substance fraction (in our evaluation worksheet denoted as “Kurvenwert”) for the sample S, the corresponding uncertainty is calculated according to the general rules of uncertainty propagation. The obtained values are:

| | |
|---|---|
| $m$ | 106.7 |
| $b$ | 0.0 |
| Kurvenwert / % | 0.019947 |
| $u$(Kurvenwert) / % | 0.000014 |
| $u_{\text{rel}}$(Kurvenwert) | 7.1E-04 |
| (X3-X1) | 0.0020 |
| (Y3-Y1) | 0 |
| (Y3-Y2) | 0 |
| (Y2-Y1) | 0 |
| (dX2/dY2)^2 * u(Y2)^2 | 1.30E-10 |
| | 64% |

| | |
|---|---|
| (dX2/dY3)^2 * u(Y3)^2 | 4.54E-11 |
| | 23% |
| (dX2/dY1)^2 * u(Y1)^2 | 1.13E-11 |
| | 6% |
| (dX2/dX1)^2 * u(X1)^2 | 7.39E-12 |
| | 4% |
| (dX2/dX3)^2 * u(X3)^2 | 7.93E-12 |
| | 4% |
| sum | 2.02E-10 |

As can be seen from these numbers, the uncertainty is dominated from the measurement statistics of the three gases (i.e., 64 % + 23 % + 6 %), the proportion of the three values vary about randomly between the five different sets in a measurement campaign. The uncertainty from the calibration gases has an influence of < 25 %, often < 5 % on the combined uncertainty of the amount of substance fraction.

From an evaluation of the measurement sequence, in total five bracketing combinations are possible. (Correlation from using C2,1; C2,2; C1,2 and C1,3 twice in the calculation is not considered.) The values and corresponding uncertainties obtained are:

| | |
|---|---|
| Kurvenwert 1 / % | 0.020017 |
| $u$(Kurvenwert) / % | 0.000018 |
| Kurvenwert 2 / % | 0.019947 |
| $u$(Kurvenwert) / % | 0.000014 |
| Kurvenwert 3 / % | 0.019972 |
| $u$(Kurvenwert) / % | 0.000011 |
| Kurvenwert 4 / % | 0.019960 |
| $u$(Kurvenwert) / % | 0.000015 |
| Kurvenwert 5 / % | 0.019983 |
| $u$(Kurvenwert) / % | 0.000015 |

The values from the measurement sequence are sufficiently compatible, i.e., they agree within their uncertainty. The five individual results (amount-of-substance fractions of propane) are pooled to:

| | |
|---|---|
| Kurvenwert / % | 0.019976 |
| $u$(Kurvenwert) / % | 0.000015 |
| $u_{\mathrm{rel}}$(Kurvenwert) | 7.4E-04 |

Since a measurement campaign consists of usually three full sequences (A1, A2, A3), the results (amount-of-substance fractions of propane) for each sequence are:

| | |
|---|---|
| $x_{\mathrm{A1}}$ / % | 0.019976 |
| $u(x_{\mathrm{A1}})$ / % | 0.000015 |
| $u_{\mathrm{rel}}(x_{\mathrm{A1}})$ | 7.4E-04 |
| | |
| $x_{\mathrm{A2}}$ / % | 0.019991 |
| $u(x_{\mathrm{A2}})$ / % | 0.000019 |
| $u_{\mathrm{rel}}(x_{\mathrm{A2}})$ | 9.4E-04 |
| | |
| $x_{\mathrm{A3}}$ / % | 0.019991 |
| $u(x_{\mathrm{A3}})$ / % | 0.000015 |

| | |
|---|---|
| $u_{rel}(x_{A3})$ | 7.4E-04 |

All values from the measurement sequences are compatible, i.e., they agree within their uncertainty. The three individual results are pooled to the final result of a measurement campaign:

| | |
|---|---|
| $x_{BAM\_MW}$ / % | 0.019986 |
| $u(x_{BAM\_MW})$ / % | 0.000016 |
| $u_{rel}(x_{BAM\_MW})$ | 8.1E-04 |
| $U_{rel}(x_{BAM\_MW})$ | 1.6E-03 |
| $u^2(x_{BAM\_MW})$ | 2.629E-10 |

Note that square root of *n* is not used in any of these calculations.

## A.9 Considered sources of uncertainty

The results and uncertainties given here include the uncertainty of the composition of the calibration gases, the uncertainty from the measurement statistics (i.e., consecutive portions of three injections), the uncertainty propagation for the calibration approach, the bias within a measurement campaign over the period of time, and finally from combining the different individual measurement campaigns. Main source of uncertainty is the imprecision of the TCD and FID used.

## A.10 Raw data:

2021-07-01 (for more details see \Code783_Euramet_K3)
2021-08-06 (for more details see \Code783_Euramet_K3\Thermo_4a)
2021-08-12 (for more details see \Code783_Euramet_K3\Thermo_5)

## A.11 Results from the measurement campaigns

From the direct measurement the results of all compounds (note that the results were not normalized) are:

| Maxum | Oxygen | Carbon monoxide | Carbon dioxide | Propane |
|---|---|---|---|---|
| $x_{zert}$ / % | 2.9713 | 1.0134 | 1.9925 | 0.0200 |
| $u(x_{zert})$ / % | 0.0008 | 0.0024 | 0.0025 | 0.0004 |
| $u_{rel}(x_{zert})$ | 2.6E-04 | 2.4E-03 | 1.3E-03 | 1.8E-02 |
| $U_{rel}(x_{zert})$ | 5.2E-04 | 4.8E-03 | 2.5E-03 | 3.6E-02 |

| Thermo4a | Oxygen | Carbon monoxide | Carbon dioxide | Propane |
|---|---|---|---|---|
| $x_{zert}$ / % | 2.9718 | 1.0140 | 1.9953 | 0.019966 |
| $u(x_{zert})$ / % | 0.0028 | 0.0007 | 0.0013 | 0.000015 |
| $u_{rel}(x_{zert})$ | 9.3E-04 | 6.8E-04 | 6.4E-04 | 7.6E-04 |
| $U_{rel}(x_{zert})$ | 1.9E-03 | 1.4E-03 | 1.3E-03 | 1.5E-03 |

| Thermo5 | Oxygen | Carbon monoxide | Carbon dioxide | Propane |
|---|---|---|---|---|
| $x_{zert}$ / % | 2.9748 | 1.0149 | 1.9972 | 0.019986 |
| $u(x_{zert})$ / % | 0.0023 | 0.0007 | 0.0012 | 0.000016 |

| | | | | |
|---|---|---|---|---|
| $u_{\mathrm{rel}}(x_{\mathrm{zert}})$ | 7.9E-04 | 6.9E-04 | 6.2E-04 | 8.1E-04 |
| $U_{\mathrm{rel}}(x_{\mathrm{zert}})$ | 1.6E-03 | 1.4E-03 | 1.2E-03 | 1.6E-03 |

The results from the two campaigns with the Thermo analyzer are consistent ($k$ < 1.1) and pooled to:

| Thermo all | Oxygen | Carbon monoxide | Carbon dioxide | Propane |
|---|---|---|---|---|
| $x_{\mathrm{zert}}$ / % | 2.973 | 1.0145 | 1.9963 | 0.019976 |
| $u(x_{zert})$ / % | 0.003 | 0.0007 | 0.0013 | 0.000016 |
| $u_{\mathrm{rel}}(x_{\mathrm{zert}})$ | 8.6E-04 | 6.9E-04 | 6.3E-04 | 7.8E-04 |
| $U_{\mathrm{rel}}(x_{\mathrm{zert}})$ | 1.7E-03 | 1.4E-03 | 1.3E-03 | 1.6E-03 |

The values from Thermo and the Maxum campaign are also consistent ($k$ < 1.3).

## A.12 Consolidated results

| consolidated | Oxygen | Carbon monoxide | Carbon dioxide | Propane |
|---|---|---|---|---|
| $x_{\mathrm{zert}}$ / % | 2.9733 | 1.0145 | 1.9963 | 0.019976 |
| $u(x_{zert})$ / % | 0.0045 | 0.0015 | 0.0030 | 0.000040 |
| $u_{\mathrm{rel}}(x_{\mathrm{zert}})$ | 1.5E-03 | 1.5E-03 | 1.5E-03 | 2.0E-03 |
| $U_{\mathrm{rel}}(x_{\mathrm{zert}})$ | 3.0E-03 | 3.0E-03 | 3.0E-03 | 4.0E-03 |

Given is in the last row the expanded relative measurement uncertainty $U = u_c \cdot k$ with $k = 2$ according to the ISO/BIPM Guide to the Expression of Uncertainty in Measurement.

## A.13 Responsibility

The calibration gases have been prepared by the filling team consisting of Claudia Boissière and Peer Wichmann under the supervision of Dr. Dirk Tuma. The measurements using the Maxum II process GC have been performed by Jeannette Pelchen, measurements using the Thermo analytical GC have been performed by Dr. Dirk Tuma. Strategy, reporting, and calculations have been performed by Dr. Heinrich Kipphardt. Advice was given by Dr. Michael Maiwald.
The overall technical responsibility for the measurement result is with Dr. Heinrich Kipphardt.

Berlin, 2021-09-03 Heinrich Kipphardt FB 1.4

## A.14 Appendix: Purity Tables with typical examples

| | | | | |
|---|---|---|---|---|
| Material | Nitrogen | 99.99991 | 0.00003 | 3.3E-07 |
| gas quality | 6.0 | | | |
| supplier | Linde | | | |
| batch | 276311-21144639 | | | |
| | Impurities | 0.00010 | 0.00003 | 3.4E-01 |
| | | | | |
| | Sum | 100.00000 | | |

| Index | compound | $M$ / g/mol | $u(M)$ / g/mol | vq | $x$ / % | $u(x)$ / % | $u_\mathrm{r}(x)$ |
|---|---|---|---|---|---|---|---|
| 1 | Nitrogen | 28.01 | 0.00 | | 99.99991 | 0.00003 | 3.3E-07 |
| 2 | Argon | 39.95 | 0.00 | | 0.00005 | 0.00003 | 5.8E-01 |
| 3 | Oxygen | 16.00 | 0.00 | | 0.00000 | 0.00000 | 5.8E-01 |
| 4 | Carbon dioxide | 44.01 | 0.01 | | 0.00001 | 0.00000 | 5.8E-01 |
| 5 | Carbon monoxide | 28.01 | 0.01 | | 0.00000 | 0.00000 | 5.8E-01 |
| 6 | Methane | 16.04 | 0.01 | | 0.00000 | 0.00000 | 5.8E-01 |
| 17 | Hydrogen | 1.01 | 0.00 | | 0.00000 | 0.00000 | 5.8E-01 |
| 31 | Moisture | 18.01 | 0.00 | | 0.00003 | 0.00001 | 5.8E-01 |
| 36 | UNKNOWN | 80.00 | 20.00 | | 0.00001 | 0.00000 | 5.8E-01 |
| 37 | 2-Butine | 54.09 | 0.01 | | | | |

| | | | | |
|---|---|---|---|---|
| Material | Oxygen | 99.99989 | 0.00004 | 3.6E-07 |
| gas quality | 6.0 | | | |
| supplier | Linde | | | |
| batch | 276311-20326434 | | | |
| | Impurities | 0.00012 | 0.00004 | 3.1E-01 |
| | | | | |
| | Sum | 100.00000 | | |

| Index | compound | $M$ / g/mol | $u(M)$ / g/mol | vq | $x$ / % | $u(x)$ / % | $u_\mathrm{r}(x)$ |
|---|---|---|---|---|---|---|---|
| 1 | Nitrogen | 28.01 | 0.00 | | 0.00003 | 0.00001 | 5.8E-01 |
| 2 | Argon | 39.95 | 0.00 | | 0.00005 | 0.00003 | 5.8E-01 |
| 3 | Oxygen | 16.00 | 0.00 | | 99.99989 | 0.00004 | 3.6E-07 |
| 4 | Carbondioxide | 44.01 | 0.01 | | 0.00001 | 0.00000 | 5.8E-01 |
| 5 | Carbon monoxide | 28.01 | 0.01 | | 0.00001 | 0.00000 | 5.8E-01 |
| 9 | Propane | 44.10 | 0.01 | | 0.00001 | 0.00000 | 5.8E-01 |
| 31 | Moisture | 18.01 | 0.00 | | 0.00003 | 0.00001 | 5.8E-01 |

| | | | | |
|---|---|---|---|---|
| Material | Carbon dioxide | 99.99971 | 0.00009 | 8.9E-07 |
| gas quality | 5.5 | | | |
| supplier | Air Liquide | | | |
| batch | | | | |
| | Impurities | 0.00029 | 0.00009 | 3.1E-01 |
| | | | | |
| | Sum | 100.00000 | | |

| Index | compound | $M$ / g/mol | $u(M)$ / g/mol | vq | $x$ / % | $u(x)$ / % | $u_\mathrm{r}(x)$ |
|---|---|---|---|---|---|---|---|
| 1 | Nitrogen | 28.01 | 0.00 | | 0.00010 | 0.00006 | 5.8E-01 |
| 3 | Oxygen | 16.00 | 0.00 | | 0.00005 | 0.00003 | 5.8E-01 |
| 4 | Carbon dioxide | 44.01 | 0.01 | | 99.99971 | 0.00009 | 8.9E-07 |
| 5 | Carbon monoxide | 28.01 | 0.01 | | 0.00003 | 0.00002 | 5.8E-01 |
| 22 | NO | 30.01 | 0.10 | | 0.00001 | 0.00000 | 5.8E-01 |
| 31 | Moisture | 18.01 | 0.00 | | 0.00010 | 0.00006 | 5.8E-01 |
| 36 | unknown | 80.00 | 20.00 | | 0.00001 | 0.00000 | 5.8E-01 |

| | | | | |
|---|---|---|---|---|
| Material | Carbon monoxide | 99.99929 | 0.00021 | 2.1E-06 |
| gas quality | 4.7 | | | |
| supplier | Linde | | | |
| batch | 276311-20642382 (24125) | | | |
| | Impurities | 0.00071 | 0.00021 | 2.9E-01 |
| | | | | |
| | Sum | 100.00000 | | |

| Index | compound | $M$ / g/mol | $u(M)$ / g/mol | vq | $x$ / % | $u(x)$ / % | $u_\mathrm{r}(x)$ |
|---|---|---|---|---|---|---|---|
| 1 | Nitrogen | 28.01 | 0.00 | | 0.00020 | 0.00012 | 5.8E-01 |
| 2 | Argon | 39.95 | 0.00 | | 0.00010 | 0.00006 | 5.8E-01 |
| 3 | Oxygen | 16.00 | 0.00 | | 0.00001 | 0.00001 | 5.8E-01 |
| 5 | Carbon monoxide | 28.01 | 0.01 | | 99.99929 | 0.00021 | 2.1E-06 |
| 9 | Propane | 44.10 | 0.01 | | 0.00010 | 0.00006 | 5.8E-01 |
| 17 | Hydrogen | 1.01 | 0.00 | | 0.00005 | 0.00003 | 5.8E-01 |
| 31 | Moisture | 18.01 | 0.00 | | 0.00025 | 0.00014 | 5.8E-01 |

| | | | | |
|---|---|---|---|---|
| Material | Propane | 99.97175 | 0.01198 | 1.2E-04 |
| gas quality | 3.5 | | | |
| supplier | Gerling | | | |
| batch | 25E | | | |
| | Impurities | 0.02825 | 0.01198 | 4.2E-01 |
| | | | | |
| | Sum | 100.00000 | | |

| Index | compound | $M$ / g/mol | $u(M)$ / g/mol | vq | $x$ / % | $u(x)$ / % | $u_\mathrm{r}(x)$ |
|---|---|---|---|---|---|---|---|
| 1 | Nitrogen | 28.01 | 0.00 | | 0.00200 | 0.00116 | 5.8E-01 |
| 3 | Oxygen | 16.00 | 0.00 | | 0.00050 | 0.00029 | 5.8E-01 |
| 4 | Carbon dioxide | 44.01 | 0.01 | | 0.00050 | 0.00029 | 5.8E-01 |
| 9 | Propane | 44.10 | 0.01 | | 99.97175 | 0.01198 | 1.2E-04 |
| 10 | Propene | 42.08 | 0.01 | | 0.00500 | 0.00289 | 5.8E-01 |

# Annex B Measurement report of CEM

## B.1 Results

Cylinder number: 8500E

**Measurement #1**

| **Component** | **Date (dd/mm/yy)** | **Result (cmol/mol)** | **Standard deviation (% relative)** | **number of replicates** |
|---|---|---|---|---|
| Oxygen | 21/07/2021 | 3.0356 | 0.09 | 6 |
| Carbon dioxide | 05/08/2021 | 2.0272 | 0.18 | 6 |
| Propane | 16/07/2021 | 0.020225 | 0.36 | 6 |
| Carbon monoxide | 13/08/2021 | 0.9927 | 0.12 | 6 |

**Measurement #2**

| **Component** | **Date (dd/mm/yy)** | **Result (cmol/mol)** | **Standard deviation (% relative)** | **number of replicates** |
|---|---|---|---|---|
| Oxygen | 06/08/2021 | 3.0080 | 0.11 | 6 |
| Carbon dioxide | 11/08/2021 | 2.0073 | 0.13 | 6 |
| Propane | 20/07/2021 | 0.019897 | 0.49 | 6 |
| Carbon monoxide | 16/08/2021 | 0.9964 | 0.11 | 6 |

**Measurement #3**

| **Component** | **Date (dd/mm/yy)** | **Result (cmol/mol)** | **Standard deviation (% relative)** | **number of replicates** |
|---|---|---|---|---|
| Oxygen | 09/08/2021 | 3.0401 | 0.07 | 6 |
| Carbon dioxide | 12/08/2021 | 2.0136 | 0.16 | 6 |
| Propane | 22/07/2021 | 0.01990 | 0.54 | 6 |
| Carbon monoxide | 17/08/2021 | 0.9960 | 0.12 | 6 |

**Results**

| **Component** | **Result (cmol/mol)** | **Expanded uncertainty (cmol/mol)** | **Coverage factor** |
|---|---|---|---|
| Oxygen | 3.028 | 0.021 | 2 |
| Carbon dioxide | 2.016 | 0.013 | 2 |
| Propane | 0.02001 | 0.00029 | 2 |
| Carbon monoxide | 0.9962 | 0.0046 | 2 |

## B.2 Calibration standards

Method of preparation: Two sets of primary standard gas mixtures (PSMs) were prepared using the gravimetric method according to ISO 6142-1:2015 [1]. All PSMs were prepared in nitrogen balance. The standard uncertainty relies on the uncertainty of the gravimetric preparation method and the purity data of the parent gases. Occasionally, other available PSMs were used in some of the analysis.

Weighing data:

- A first batch of six PSMs of propane (nominally amount fraction of 30 µmol/mol to 350 µmol/mol) and oxygen (nominally amount fraction of 0.45 cmol/mol to 12 cmol/mol) in nitrogen was prepared by first adding pre-mixtures of propane in nitrogen (nominally amount fraction of 900 µmol/mol to 4 cmol/mol) and then nitrogen and oxygen from pure sources.

**Table 1: PSMs of propane and oxygen in nitrogen balance.**

| **Cylinder** | Component | Assigned value, $x_i$ (cmol/mol) | Expanded uncertainty, $U_i$ (cmol/mol) | Coverage factor $k$ |
|---|---|---|---|---|
| **MRP100177** | Oxygen | 0.4551 | 0.0019 | 2 |
| | Propane | 0.003018 | 0.000025 | 2 |
| **MRP100171** | Oxygen | 9.5049 | 0.0016 | 2 |
| | Propane | 0.005035 | 0.000074 | 2 |
| **MRP548527** | Oxygen | 4.8045 | 0.0018 | 2 |
| | Propane | 0.01003 | 0.00011 | 2 |
| **MRP100170** | Oxygen | 9.6320 | 0.0016 | 2 |
| | Propane | 0.02019 | 0.00014 | 2 |
| **MRP601155** | Oxygen | 9.5342 | 0.0024 | 2 |
| | Propane | 0.03151 | 0.00021 | 2 |
| **MRP392354** | Oxygen | 12.2114 | 0.0020 | 2 |
| | Propane | 0.03499 | 0.00023 | 2 |

- A second batch of three PSMs of carbon dioxide (nominally amount fraction of 2 cmol/mol to 5 cmol/mol), carbon monoxide (nominally amount fraction of 0.5 cmol/mol to 2 cmol/mol), and oxygen (nominally amount fraction of 2.8 cmol/mol to 3.2 cmol/mol) in nitrogen balance was prepared. Pre-mixtures of carbon monoxide in nitrogen (nominally amount fraction of 5 cmol/mol and 6 cmol/mol) were added in two of the three mixtures. Carbon dioxide, carbon monoxide, oxygen and nitrogen were then added from pure sources.

**Table 2: PSMs of carbon dioxide, carbon monoxide and oxygen in nitrogen balance.**

| **Cylinder** | Component | Assigned value, $x_i$ (cmol/mol) | Expanded uncertainty, $U_i$ (cmol/mol) | Coverage factor $k$ |
|---|---|---|---|---|
| **MRP502452** | Oxygen | 2.8184 | 0.0036 | 2 |
| | Carbon monoxide | 0.5083 | 0.0012 | 2 |
| | Carbon dioxide | 1.9869 | 0.0013 | 2 |
| **MRP302441** | Oxygen | 3.0355 | 0.0035 | 2 |
| | Carbon monoxide | 1.2286 | 0.0012 | 2 |
| | Carbon dioxide | 3.2970 | 0.0026 | 2 |
| **MRP502447** | Oxygen | 3.2458 | 0.0051 | 2 |
| | Carbon monoxide | 2.7699 | 0.0047 | 2 |
| | Carbon dioxide | 4.9065 | 0.0026 | 2 |

- PSMs occasionally used: carbon dioxide (nominally amount fraction of 5 cmol/mol and 17 cmol/mol), and carbon monoxide (nominally amount fraction of 0.5 cmol/mol), in nitrogen balance.

**Table 3: PSMs of carbon dioxide, carbon monoxide in nitrogen balance.**

| **Cylinder** | Component | Assigned value, $x_i$ (cmol/mol) | Expanded uncertainty, $U_i$ (cmol/mol) | Coverage factor $k$ |
|---|---|---|---|---|
| **MRP602434** | Carbon dioxide | 5.0023 | 0,0011 | 2 |
| **MRP166321** | Carbon dioxide | 17.0015 | 0.0011 | 2 |
| **MRP306300** | Carbon monoxide | 0.5129 | 0.0010 | 2 |

**Purity tables (composition) of the parent gases:**

| | **Nitrogen 6.0 (LINDE)** | | | **Carbon dioxide N48 (AIR LIQUIDE)** | | | **Oxygen ULTRAPLUS 6X (PRAXAIR)** | |
|---|---|---|---|---|---|---|---|---|
| COMPONENT | $x_i$ (mmol/mol) | $u_i$ (mmol/mol) | COMPONENT | $x_i$ (mmol/mol) | $u_i$ (mmol/mol) | COMPONENT | $x_i$ (mmol/mol) | $u_i$ (mmol/mol) |
| Water | 0.25 | 0.14 | Oxygen | 1 | 0.58 | Carbon dioxide | 0.05 | 0.029 |
| Oxygen | 0.25 | 0.14 | Hydrocarbons | 1 | 0.58 | Carbon monoxide | 0.10 | 0.058 |
| Carbon monoxide | 0.05 | 0.029 | Hydrogen | 0.25 | 0.14 | Hydrocarbons | 0.03 | 0.014 |
| Carbon dioxide | 0.05 | 0.029 | Water | 1.5 | 0.87 | Argon | 0.50 | 0.29 |
| Hydrocarbons | 0.05 | 0.029 | | | | Nitrogen | 0.50 | 0.29 |
| | | | | | | Water | 0.25 | 0.14 |
| **Nitrogen** | **999999.35** | **0.21** | **Carbon dioxide** | **999996.2** | **1.2** | **Oxygen** | **999998.58** | **0.44** |

**Table 4: Purity tables of pure gases.**

| | **Carbon monoxide N47 (NIPPON GASES)** | | | **Propane N35 (AIR LIQUIDE)** | |
|---|---|---|---|---|---|
| COMPONENT | $x_i$ (mmol/mol) | $u_i$ (mmol/mol) | COMPONENT | $x_i$ (mmol/mol) | $u_i$ (mmol/mol) |
| Argon | 1 | 0.58 | Propene | 100 | 58 |
| Carbon dioxide | 0.5 | 0.29 | Hydrocarbons | 100 | 58 |
| Oxygen | 0.5 | 0.29 | Nitrogen | 20 | 12 |
| Nitrogen | 10 | 5.8 | Hydrogen | 20 | 12 |
| Water | 0.5 | 0.29 | Oxygen | 5 | 3 |
| Hydrogen | 10 | 5.8 | Carbon dioxide | 2 | 1 |
| Hydrocarbons | 0.5 | 0.29 | Water | 2 | 1 |
| **Carbon monoxide** | **999977** | **8** | **Propane** | **999750** | **83** |

Verification measures:

- The PSM were validated against CEM's calibration standards or against each other, using gas chromatography with thermal conductivity detector (micro-GC-TCD).
- The levels of water, methane, carbon monoxide and carbon dioxide in high purity nitrogen used as gas balance were checked by Cavity ring-down spectroscopy (CRDS). Results showed concentration of these compounds well below the specifications given by manufacturer.

## B.3 Instrumentation

The analyses were performed in a micro gas chromatograph Agilent 3000A with thermal conductivity detector (micro-GC-TCD). Helium 5.6 (Nippon Gases) is used as carrier gas. The micro-GC is equipped with 2 channels:

- Channel A, with a PLOT-U (3 m x 0.30 mm x 30 µm) pre-column and a Molsieve 5A column (10 m x 0.30 mm x 30 µm) and a backflush injector type of 1 µL.
- Channel B, with a OV-1 (length: 8 m; thick: 2.0 µm) with fixed injector type.

A single analytical method is programmed to analyse oxygen in channel A and propane and carbon dioxide in channel B. A different method is used to analyse carbon monoxide using only channel A. The runtime of both methods is close to 60 s each.

After rolling the cylinders, the sample and the PSMs are connected to pressure regulators. A set of four 5-ways-valves are connected to the sampling rig and used for connecting the sample cylinder and the standards with the analyser. This rig is used to purge before the analysis of each cylinder.

## B.4 Calibration method and value assignment

PSMs and sample cylinder are analysed individually in increasing order of concentration. A minimum of 40 injections per cylinder are performed meanwhile a minimum of 4 injections of pure nitrogen (6.0 LINDE) were done between cylinders. Only the 6 last analytical signals are used to calculations.

The analysis are performed under repeatability conditions during at least three days. Three results are selected for each component. The calibration curve, results of analysis and uncertainties associated were determined using the methodology of ISO 6143 [2]. The assigned values for components concentration is the average of the three individual values obtained.

| Component | Measurement method | Type of calibration curve |
|---|---|---|
| Oxygen | GC/TCD | 3 points, linear<br>3 points, linear<br>3 points, linear |
| Carbon dioxide | GC/TCD | 3 points, linear<br>3 points, linear<br>3 points, linear |
| Propane | GC/TCD | 3 points, linear<br>5 points, quadratic<br>3 points, linear |
| Carbon monoxide | GC/TCD | 3 points, linear<br>3 points, linear<br>3 points, linear |

Table 5: Measurement method and type of calibration curve used.

## B.5 Uncertainty evaluation

The expression for combined standard uncertainty ($u_c$) includes the quadratic sum of individual standard uncertainties as obtained according to ISO 6143 from each measurement and the standard deviation of the mean from average the three results:

$$u_\mathrm{c} = \sqrt{\frac{1}{3}(u_1^2 + u_2^2 + u_3^2) + (\frac{s}{\sqrt{3}})^2}$$

The expanded uncertainty ($U$) was obtained by multiplying the combined uncertainty with a coverage factor of k = 2.

$$U = k \cdot u_c$$

## 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", ISO Geneva, 2015.

[2] International Organization for Standardization, “ISO 6143 – Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures”, ISO Geneva, 2001.

# Annex C Measurement report of LNE

## C.1 Calibration standards

### C.1.1 Method of preparation

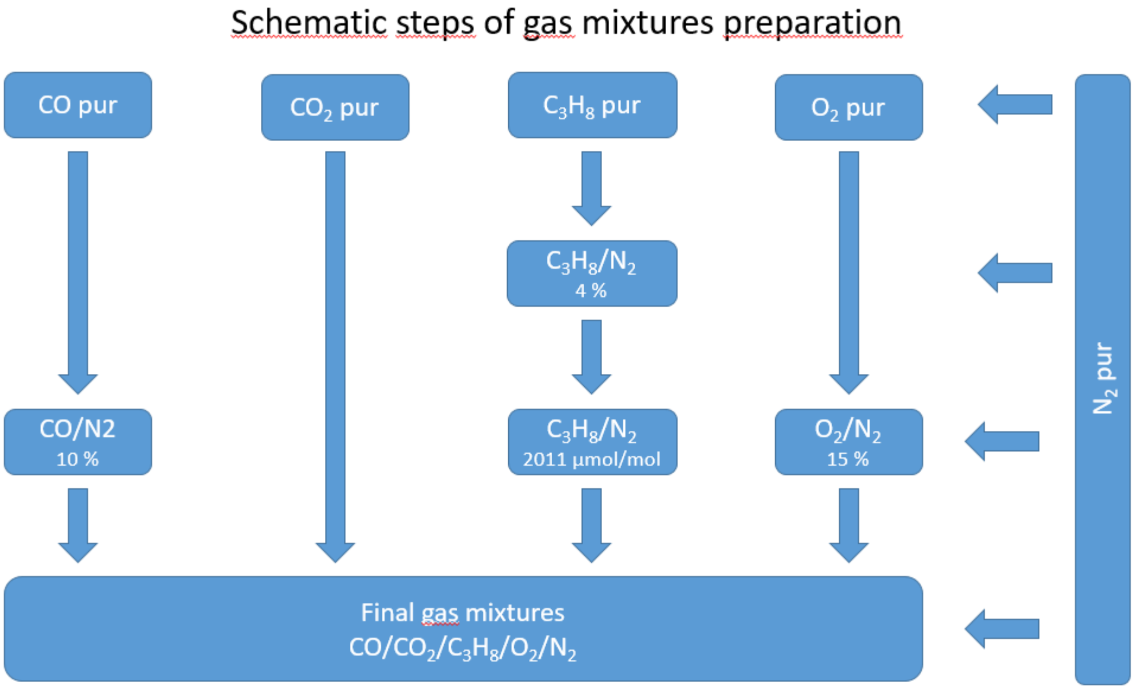
The standard gas mixtures were prepared according to the ISO 6142 standard.

Gas cylinders were evacuated using a turbo vacuum pump and weighed using a Mettler AX32004 mass comparator with a 0.1 mg resolution.

For propane, two premix gas mixtures in nitrogen were produced at amount fractions of 4 % and 0.2 %.

For CO and $O_2$, one premix gas mixture in nitrogen was produced respectively at amount fractions of 10% and 15%.

The final standard gas mixtures were produced by gravimetric dilution of the different premix gas mixtures and pure $CO_2$ in nitrogen as shown below.



### C.1.2 Weighing data and amount fractions of Gazmot 0033

```
––––––––––––––     Gazmot 0033                ––––––––––––––––

Component           µmol/mol                   uncertainty   % u/c
----------------------------------------------------------
N2                  939180.4701                7.63198477    0.001
O2                  29922.71076                2.11616911    0.007
CO2                 20413.95936                7.50705393    0.037
CO                  10277.19254                1.41425695    0.014
propane             205.4284253                0.05279044    0.026
H2O                 0.06342333                 0.02057347    32.438
Ar                  0.05138667                 0.02966840    57.736
methane             0.04538974                 0.01477692    32.556
H2                  0.03932743                 0.01012582    25.747
CnHm                0.03082531                 0.01326367    43.028
propene             0.02054798                 0.01186222    57.729


INPUTS
======

File                Mass (g)                   u/c (g)
--------------------------------------
Pur\CO2pur009.tx    37.46552                   0.01400
melanges\co_n2_02   119.9104                   0.01400
melanges\o2_n2_02   237.8485                   0.01500
melanges\c3h8_n2    119.4520                   0.01600
G_d_f\N2_Bip_plus   672.2678                   0.02100




––––––––––––––      Pur\CO2pur009.txt          ––––––––––––––––

Component           µmol/mol                   uncertainty
---------------------------------------------------
CO2                 0.9999922500               0.0000026021
H2O                 0.0000015000               0.0000008660
O2                  0.0000010000               0.0000005774
methane             0.0000010000               0.0000005774
H2                  0.0000002500               0.0000001443
N2                  0.0000040000               0.0000023094


–––––––––––         Gas mixture\co_n2_0077.txt ––––––––––––
```

| Component | µmol/mol | uncertainty |
|---|---|---|
| $N_2$ | 0.8998755361 | 0.0000093232 |
| CO | 0.1001233929 | 0.0000093025 |
| Ar | 0.0000005006 | 0.0000002890 |
| $H_2O$ | 0.0000001592 | 0.0000000869 |
| $O_2$ | 0.0000001547 | 0.0000000867 |
| $C_nH_m$ | 0.0000001001 | 0.0000000578 |
| $H_2$ | 0.0000000726 | 0.0000000317 |
| $CO_2$ | 0.0000000613 | 0.0000000296 |
| methane | 0.0000000225 | 0.0000000130 |

——————— Gas mixture\o2_n2_0030.txt ———————

| Component | µmol/mol | uncertainty |
|---|---|---|
| $N_2$ | 0.8498931366 | 0.0000071596 |
| $O_2$ | 0.1501067912 | 0.0000071557 |
| $H_2O$ | 0.0000000460 | 0.0000000223 |
| methane | 0.0000000288 | 0.0000000130 |
| $H_2$ | 0.0000000288 | 0.0000000130 |
| $CO_2$ | 0.0000000181 | 0.0000000075 |
| CO | 0.0000000111 | 0.0000000061 |

—————— Gas mixture\c3h8_n2_0036.txt ——————

| Component | µmol/mol | uncertainty |
|---|---|---|
| $N_2$ | 0.9979880776 | 0.0000005075 |
| propane | 0.0020113698 | 0.0000004550 |
| propene | 0.0000002012 | 0.0000001161 |
| $C_nH_m$ | 0.0000002012 | 0.0000001161 |
| $H_2$ | 0.0000000652 | 0.0000000270 |
| methane | 0.0000000249 | 0.0000000137 |
| $CO_2$ | 0.0000000175 | 0.0000000074 |
| $O_2$ | 0.0000000150 | 0.0000000064 |
| $H_2O$ | 0.0000000150 | 0.0000000062 |
| CO | 0.0000000125 | 0.0000000068 |

——————— G_d_f\N2_Bip_plus.txt ———————

| Component | µmol/mol | uncertainty |
|---|---|---|
| $N_2$ | 0.9999999100 | 0.0000000237 |
| $H_2O$ | 0.0000000100 | 0.0000000058 |
| $O_2$ | 0.0000000050 | 0.0000000029 |
| CO | 0.0000000125 | 0.0000000072 |
| $CO_2$ | 0.0000000125 | 0.0000000072 |
| methane | 0.0000000250 | 0.0000000144 |
| H2 | 0.0000000250 | 0.0000000144 |

### C.1.3 Analytical validation of the preparation of the standard gas mixture Gazmot 0033

The standard gas mixture Gazmot 0033 was compared to other gas mixtures to validate the gravimetric preparation. The standard gas mixture was analysed ten times in repeatability conditions. The average amount fraction and the standard deviation of the five last injections were calculated.

The results are used to calculate the gravimetric uncertainties according to the ISO 6142-1 standard.

$$u_{prep} = \frac{1}{2}\sqrt{u_{gravi}^2 + u_{stab}^2 + u_{analy}^2 + (prep - analy)^2}$$

The gravimetric gas mixture is validated if:

$$\left|x_{analy} - x_{gravi}\right| < 2 \times \sqrt{u_{prep}^2 + u_{analy}^2}$$

**Validation of the gravimetric preparation of the Gazmot 0033 standard gas mixture; all the data are given in µmol/mol**

| Compounds | $x_{gravi}$ | $u_{gravi}$ | $u_{stab}$ | $U_{prep}$ k=2 | $x_{analy}$ | $u_{analy}$ | Validation |
|---|---|---|---|---|---|---|---|
| CO | 10277.2 | 1.5 | 0.15% | 41.6 | 10251 | 28.57 | Yes |
| $CO_2$ | 20414.0 | 7.5 | 0.05% | 101.1 | 20496 | 57.69 | Yes |
| $C_3H_8$ | 205.428 | 0.053 | 0.05% | 0.50 | 205.27 | 0.46 | Yes |
| $O_2$ | 29922.71 | 2.12 | 0.00% | 184.3 | 29993.9 | 170.00 | Yes |

## C.2 Instrumentation

The automotive exhaust gas mixtures were analysed by gas chromatography on a AGILENT instrument equipped with a 250 µl sample loop, a PDHID detector and a FID with methanizer.

Oxygen was eluted with a 50 m, 0.53 mm 5A Molsieve capillary column coupled to the PDHID detector. The oven was regulated at 30°C during 6 min and then the temperature rose to 100°C at 20°C/min during 5 min.

$CO$, $CO_2$ and $C_3H_8$ were eluted on a 30 m, 0.53 mm PLOTQ capillary column coupled to the FID detector with a methanizer. The oven was regulated at 40°C during 4.5 min and then the temperature rose to 130°C at 40°C/min during 2 min.

## C.3 Calibration method and value assignment

The gas chromatograph was calibrated at a single point close to the amount fraction of the gas sample according to the sequence "standard gas mixture Gazmot 0033/gas sample N°8457E from VSL/ standard gas mixture Gazmot 0033" with 10 runs for each gas (only the last five runs were used for the calculation).

The amount fraction of the gas sample was determined as follows:

$$\boldsymbol{x = 2 \times \frac{S_{sample} \times x_{gravi}}{S_{gravi1} + S_{gravi2}}} \qquad \textbf{(Eq.1)}$$

where

$S_{sample}$ : Average of the last 5 chromatographic areas of the compound peaks for the gas sample N°8457E

$X_{gravi}$ : Amount fraction of the standard gas mixture Gazmot 0033

$S_{gravi1}$ : Average of the last 5 chromatographic areas of the compound peaks for the standard gas mixture Gazmot 0033 before the injection of the gas sample N°8457E

$S_{gravi2}$ : Average of the last 5 chromatographic areas of the compound peaks for the standard gas mixture Gazmot 0033 after the injection of the gas sample N°8457E

The procedure is repeated three times on 3 different days.

The final amount fraction is the average of the three determinations obtained on the 3 different days.

## C.4 Uncertainty evaluation

The uncertainty evaluation is established by combining the uncertainty on the amount fractions of the standard gas mixture and the repeatability and reproducibility standard deviations of the measurements; they are calculated according to the law of propagation of uncertainty (Eq.2).

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 \times u^2(x_i) + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \left(\frac{\partial f}{\partial x_i}\right)\left(\frac{\partial f}{\partial x_j}\right) u(x_i, x_j) \qquad \text{(Eq. 1)}$$

The table 4 shows an example for the determination of the CO amount fraction and the associated expanded uncertainty on the first day of the measurements (16/09/2021).

**Uncertainty budget on the CO amount fraction for cylinder 8457E determined on the first day (16/09/2021)**

| Variable | Units | Value | u(Xi) | C(Xi) | C(Xi).u(Xi) | Weight% |
|---|---|---|---|---|---|---|
| $x_{gravi}$ | cmol/mol | 1.0277 | 0.00208 | 0.984807 | 0.002048 | 55.56% |
| $S_{gravi1}$ | | 7160 | 10 | -0.000071 | -0.000670 | 5.95% |
| $S_{sample}$ | | 7027 | 11 | 0.0001440 | 0.0015490 | 31.77% |
| $S_{gravi2}$ | | 7111 | 10 | -0.000071 | -0.000712 | 6.71% |

| **C_CO** | **cmol/mol** | **1.0121** | **0.0027** | **(k = 1)** |
|---|---|---|---|---|

The final uncertainty is the quadratic sum of the maximal uncertainty calculated for the three determinations and the standard deviation of the three determinations.

$$u = \sqrt{u_c^2 + std_{repro}^2}$$

With:

$u_c$ Maximal uncertainty calculated for the three measurements

$Std_{repro}$ Standard deviation of the three determinations of the amount fractions under reproducibility conditions

# Annex D Measurement report of BFKH

## D.1 Calibration standards

### D.1.1 Overview

| Cylinder Identification Number | 0153A | | 0157A | | D521804 | |
|---|---|---|---|---|---|---|
| Component | x<br>ppm$^{*}$ | Expanded Measurement Uncertainty<br>U (k=2)<br>ppm | x<br>ppm | Expanded Measurement Uncertainty<br>U (k=2)<br>ppm | x<br>ppm | Expanded Measurement Uncertainty<br>U (k=2)<br>ppm |
| Oxygen | 30123.47 | 6.0 | 30085.46 | 6.0 | 30061.31 | 6.0 |
| Carbon dioxide | 20003.28 | 3.6 | 19973.27 | 3.6 | 20002.18 | 3.6 |
| Propane | 200.81 | 0.10 | 200.98 | 0.10 | 200.90 | 0.10 |
| Carbon monoxide | 10073.27 | 1.9 | 10049.57 | 1.9 | 10026.77 | 1.9 |
| Water | 1.54 | 1.8 | 1.54 | 1.8 | 1.54 | 1.8 |
| Methane | 0.10 | 0.11 | 0.10 | 0.11 | 0.10 | 0.11 |
| Argon | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 |

$^{*}$1 ppm = 1 µmol mol$^{-1}$

### D.1.2 Method of preparation of the standard

5 mixtures were prepared before:

| | Cylinder No | Composition | Component | g | Component | g |
|---|---|---|---|---|---|---|
| 1. | OMH231 | 30.091678 % $O_2$-$N_2$ | $O_2$ 5.0 | 193.7311 | $N_2$ 5.0 | 394.0107 |
| 2. | OMH279 | 21.414597 % $CO_2$-$N_2$ | $CO_2$ 4.8 | 192.8283 | $N_2$ 5.0 | 450.4207 |
| 3. | OMH222 | 4.07337 % $C_3H_8$-$N_2$ | $C_3H_8$ 3.5 | 35.5720 | $N_2$ 5.0 | 539.8303 |
| 4. | OMH217 | 0.211177 % $C_3H_8$-$N_2$ | 4.07337 % $C_3H_8$-$N_2$ | 30.3193 | $N_2$ 5.0 | 534.1420 |
| 5. | A8629 | 9.986464 % CO-$N_2$ | CO 4.7 | 118.1035 | $N_2$ 5.0 | 1064.6446 |

### D.1.3 Weighing data of preparation of the standard:

Standard 1.

| Step | Component | g |
|---|---|---|
| 1. | Mixture 1 | 123.4550 |
| 2. | Mixture 2 | 123.9795 |
| 3. | Mixture 4 | 112.5984 |
| 4. | Mixture 5 | 119.2918 |

| | | |
|---|---|---|
| 5. | $N_2$ 5.0 | 722.0410 |

Standard 2.

| Step | Component | g |
|---|---|---|
| 1. | Mixture 1 | 123.1902 |
| 2. | Mixture 2 | 123.6840 |
| 3. | Mixture 4 | 112.5941 |
| 4. | Mixture 5 | 118.9059 |
| 5. | $N_2$ 5.0 | 721.9026 |

Standard 3.

| Step | Component | g |
|---|---|---|
| 1. | Mixture 1 | 122.9387 |
| 2. | Mixture 2 | 123.7095 |
| 3. | Mixture 4 | 112.4083 |
| 4. | Mixture 5 | 118.4891 |
| 5. | $N_2$ 5.0 | 721.2588 |

Parent gases:

| Gas | Quality | Supplier |
|---|---|---|
| Nitrogen | 99.999 | Messer |
| Oxygen | 99.999 | Messer |
| Carbon dioxide | 99.998 | Siad |
| Propane | 99.95 | Messer |
| Carbon monoxide | 99.997 | Siad |

**Purity table of pure Oxygen:**

| Component | Method | Mole fraction (mol/mol) | Uncertainty (mol/mol) |
|---|---|---|---|
| $O_2$ | specifications | 0.99998675 | 0.0000153 |
| $N_2$ | specifications | 0.00001000 | 0.0000115 |
| $H_2O$ | specifications | 0.00000250 | 0.0000029 |
| $CH_4$ | specifications | 0.00000025 | 0.00000029 |
| CO | specifications | 0.00000025 | 0.00000029 |
| $CO_2$ | specifications | 0.00000025 | 0.00000029 |

**Purity table of pure $CO_2$: (88434)**

| Component | Method | Mole fraction (mol/mol) | Uncertainty (mol/mol) |
|---|---|---|---|
| $CO_2$ | specifications | 0.999990 | 0.000012 |
| $N_2$ | specifications | 0.0000050 | 0.0000058 |
| $H_2O$ | specifications | 0.0000025 | 0.0000029 |
| $CH_4$ | specifications | 0.0000010 | 0.0000012 |
| $O_2$ | specifications | 0.0000010 | 0.0000012 |
| CO | specifications | 0.0000005 | 0.00000058 |

**Purity table of pure $C_3H_8$:**

| Component | Method | Mole fraction (mol/mol) | Uncertainty (mol/mol) |
|---|---|---|---|
| $C_3H_8$ | measured | 0.9997825 | 0.000100 |

| | | | |
|---|---|---|---|
| $N_2$ | measured | 0.000030 | 0.000010 |
| $H_2O$ | specifications | 0.0000025 | 0.0000029 |
| $CH_4$ | measured | 0.000060 | 0.000010 |
| $O_2$ | specifications | 0.000005 | 0.0000058 |
| $CO_2$ | measured | 0.000120 | 0.000010 |

**Purity table of pure CO:**

| Component | Method | Mole fraction (mol/mol) | Uncertainty (mol/mol) |
|---|---|---|---|
| CO | specifications | 0.9999895 | 0.000012 |
| $N_2$ | specifications | 0.0000025 | 0.0000029 |
| $H_2O$ | specifications | 0.0000015 | 0.0000017 |
| $H_2$ | specifications | 0.0000005 | 0.00000058 |
| $CH_4$ | specifications | 0.000001 | 0.0000012 |
| $O_2$ | specifications | 0.0000015 | 0.0000017 |
| Ar | specifications | 0.0000035 | 0.0000041 |

**Purity table of pure nitrogen:**

| Component | Method | Mole fraction (mol/mol) | Uncertainty (mol/mol) |
|---|---|---|---|
| $N_2$ | specifications | 0.99999745 | 0.0000029 |
| $O_2$ | specifications | 0.000001 | 0.00000115 |
| $H_2O$ | specifications | 0.0000015 | 0.00000173 |
| $CH_4$ | specifications | 0.00000005 | 0.000000058 |

Verification measures confirmed the gravimetric method validity, their results were within the stated uncertainty of the standard in case of each components.

## D.2 Instrumentation

### D.2.1 Measurement of Carbon dioxide and Propane

HP 6890 GC-TCD/FID with two parallel columns:

to TCD: Restek Haysep A 8.8 m x 0.75 mm Sulfinert SST, Pressure in 10 bar He,

to FID: Restek Porapak PS 4.4 m x0.75 mm Sulfinert SST, Pressure in 4.5 bar He.

Isotherm method at 180 $^0$C.

### D.2.2 Measurement of Carbon monoxide and Oxygen

HP 7890 GC-TCD/FID with two parallel columns:

to TCD: Restek PCK 5A Mole Sieve 80/100 2m 1.00 mm ID

to FID: Restek PCK PP-PS 100/120 4.4 m 0.75 MMID 0.95

Isotherm method at 70 $^0$C.

## D.3 Calibration method and value assignment

The results came from two independent measurements.

1. Measurement of Carbon dioxide and Propane with HP 6890 GC-TCD/FID with two parallel columns.

   The sample injections were in case of the standard and the sample during the same run with 3.5 min different, and sample exchange were every 30 min. After the excluding the outliers, the area data were used for the calculation.

2. Measurement of Carbon monoxide and Oxygen (and Propane) with HP 7890 GC-TCD/FID with two parallel columns.

   The sample injections were in case of the standard and the sample during the same run with 4 min different, and sample exchange were every 60 min. After the excluding the outliers, the area data were used for the calculation.

## D.4 Uncertainty evaluation

The standard uncertainty of $x_i$ component can be expressed as

$$u^2(x_i) = u^2_{xi,meas} + u^2_{sti} + u^2_{sti,meas} \quad (1)$$

$$U\,(x_i) = k \times u(x_i) \quad (2)$$

| | |
|---|---|
| $x_i$ | amount-of-substance fraction of gas i component |
| $u_{xi,meas}$ | uncertainty of measurements of gas i component |
| $u_{sti}$ | uncertainty of calibration standard value of i component |
| $u_{sti,meas}$ | uncertainty of measurements of calibration standard i component |
| $U_{i,x}$ | stated uncertainty of laboratory, at 95 % level of confidence (cmol/mol) |
| $k$ | assigned coverage factor for degree of equivalence |

## D.5 Results

**The table shows the detailed results in case of measurement.**

| Component | $x_i$ | $u_{xi,meas}$ | $u_{sti}$ | $u_{sti,meas}$ | $k$ | $U(x_i)$ | $U(x_i)$ |
|---|---|---|---|---|---|---|---|
| | % | rel | rel | rel | | rel | % |
| Oxygen | 3.0032 | 0.00019 | 0.00010 | 0.00036 | 2 | 0.00084 | 0.0025 |
| Carbon dioxide | 1.9832 | 0.0003 | 0.00009 | 0.0009 | 2 | 0.0019 | 0.0038 |
| Propane | 0.020060 | 0.0014 | 0.00025 | 0.0016 | 2 | 0.0043 | 0.000086 |
| Carbon monoxide | 1.0021 | 0.00121 | 0.00010 | 0.00090 | 2 | 0.00302 | 0.0030 |

| Component | $x_i$ | $u_{xi,meas}$ | $u_{sti}$ | $u_{sti,meas}$ | $k$ | $U(x_i)$ | $U(x_i)$ |
|---|---|---|---|---|---|---|---|
| | % | rel | rel | rel | | rel | % |
| Oxygen | 3.0015 | 0.00095 | 0.00010 | 0.00048 | 2 | 0.00214 | 0.0064 |

| Component | $x_\mathrm{i}$ | $u_\mathrm{xi,meas}$ | $u_\mathrm{sti}$ | $u_\mathrm{sti,meas}$ | $k$ | $U(x_i)$ | $U(x_i)$ |
|---|---|---|---|---|---|---|---|
| | % | rel | rel | rel | | rel | % |
| Carbon dioxide | 1.9781 | 0.0008 | 0.00009 | 0.0005 | 2 | 0.0019 | 0.0037 |
| Propane | 0.020037 | 0.0007 | 0.00025 | 0.0013 | 2 | 0.0030 | 0.000060 |
| Carbon monoxide | 1.0024 | 0.00135 | 0.00010 | 0.0008 | 2 | 0.00314 | 0.0032 |

| Component | $x_\mathrm{i}$ | $u_\mathrm{xi,meas}$ | $u_\mathrm{sti}$ | $u_\mathrm{sti,meas}$ | $k$ | $U(x_i)$ | $U(x_i)$ |
|---|---|---|---|---|---|---|---|
| | % | rel | rel | rel | | rel | % |
| Oxygen | 3.0032 | 0.00030 | 0.00010 | 0.00065 | 2 | 0.00145 | 0.0043 |
| Carbon dioxide | 1.9852 | 0.0007 | 0.00009 | 0.0013 | 2 | 0.00296 | 0.0059 |
| Propane | 0.020097 | 0.0010 | 0.00025 | 0.0010 | 2 | 0.00287 | 0.000058 |
| Carbon monoxide | 1.0012 | 0.00193 | 0.00010 | 0.00110 | 2 | 0.00445 | 0.0045 |

| Component | $x_\mathrm{i}$ | $u_\mathrm{xi,meas}$ | $u_\mathrm{sti}$ | $u_\mathrm{sti,meas}$ | $k$ | $U(x_i)$ | $U(x_i)$ |
|---|---|---|---|---|---|---|---|
| | % | rel | rel | rel | | rel | % |
| Oxygen | 3.0022 | 0.00135 | 0.00010 | 0.00126 | 2 | 0.00370 | 0.0111 |
| Carbon dioxide | 1.9862 | 0.0005 | 0.00009 | 0.0005 | 2 | 0.00143 | 0.0028 |
| Propane | 0.020038 | 0.0006 | 0.00025 | 0.0013 | 2 | 0.00291 | 0.000058 |
| Carbon monoxide | 1.0015 | 0.00148 | 0.00010 | 0.00237 | 2 | 0.00559 | 0.0056 |

| Component | $x_\mathrm{i}$ | $u_\mathrm{xi,meas}$ | $u_\mathrm{sti}$ | $u_\mathrm{sti,meas}$ | $k$ | $U(x_i)$ | $U(x_i)$ |
|---|---|---|---|---|---|---|---|
| | % | rel | rel | rel | | rel | % |
| Oxygen | 3.0052 | 0.00024 | 0.00010 | 0.00027 | 2 | 0.00075 | 0.0023 |
| Carbon dioxide | 1.9828 | 0.0005 | 0.00009 | 0.0008 | 2 | 0.00190 | 0.0038 |
| Propane | 0.020026 | 0.0007 | 0.00025 | 0.0006 | 2 | 0.00191 | 0.000038 |
| Carbon monoxide | 1.0033 | 0.00063 | 0.00010 | 0.00060 | 2 | 0.00175 | 0.0018 |

**Summary of all measurements**

| Component | *Result* | $k$ | *Expanded uncertainty* $U(x_i)$ |
|---|---|---|---|
| | % | | % |
| Oxygen | 3.0031 | 2 | 0.0028 |

| | | | |
|---|---|---|---|
| Carbon dioxide | 1.9831 | 2 | 0.0018 |
| Propane | 0.020052 | 2 | 0.000028 |
| Carbon monoxide | 1.0021 | 2 | 0.0017 |

The submitted value of the component came from the average of the five measurements. The uncertainty of this value calculated from the root of sum of the independent uncertainty's square by divided 5.

## References

CCQM key comparison CCQM-K3 of measurements of CO, $CO_2$, and $C_3H_8$ in $N_2$ , É. Deák - **A van der Veen and all, Metrologia, Volume 39, Number 1,** 2002 ***Metrologia*** 39 121

# Annex E Measurement report of GUM

## E.1 Calibration standards

Composition of calibration standards:

| Cylinder number | Component | Assigned value mol/mol | Standard uncertainty mol/mol |
|---|---|---|---|
| D752078_2 | $CO_2$ | 0.020135 | 0.000033 |
| | $C_3H_8$ | 0.0001001 | 0.0000002 |
| | CO | 0.005054 | 0.000006 |
| | $O_2$ | 0.010107 | 0.000007 |
| | $N_2$ | balance | |

| Cylinder number | Component | Assigned value mol/mol | Standard uncertainty mol/mol |
|---|---|---|---|
| D752091_2 | $CO_2$ | 0.034476 | 0.000034 |
| | $C_3H_8$ | 0.0001997 | 0.0000003 |
| | CO | 0.012639 | 0.000011 |
| | $O_2$ | 0.027914 | 0.000046 |
| | $N_2$ | balance | |

| Cylinder number | Component | Assigned value mol/mol | Standard uncertainty mol/mol |
|---|---|---|---|
| D752094_2 | $CO_2$ | 0.050020 | 0.000035 |
| | $C_3H_8$ | 0.0003014 | 0.0000006 |
| | CO | 0.020104 | 0.000012 |
| | $O_2$ | 0.042508 | 0.000047 |
| | $N_2$ | balance | |

Standards were prepared (by Central Office of Measures) by gravimetric method according to ISO 6142 from separate premixtures. The premixtures were prepared by using: propane 3.5, carbon dioxide 4.5, carbon monoxide 4.7, oxygen 5.5 and nitrogen 6.0 The minimal weighed samples are 20 g. The minimal weighed sample of nitrogen is 150g. The cylinders were evacuated on turbo molecular pump, filled up an weighted on the verification balance. All the standards were prepared in aluminum (with coated layers) cylinders. The standards were (and still are) under metrological control.

## E.2 Instrumentation

The measurements were repeated 9 times for the sample and the standards by gas chromatograph Thermo Trace 1300 with TCD detector and FID detector with capillary column. The cylinders (standards and sample) were in the same room for the whole time also during the measurements (temperature stabilization) and the mixtures were mixed up before the measurements. Samples were transferred to the instrument via the reducing valve and the automatic input pressure stabilization system.

## E.3 Calibration method and value assignment

The measurements were made by using standards: D752078_2, D752091_2, D752094_2 by multi point calibration according to ISO 6143.

## E.4 Uncertainty evaluation

The final uncertainty, consists of the following components:

- the uncertainty of standard preparation calculated according to ISO 6142
- the standard deviation of the measurement

Resolution of the chromatograph is negligible.

# Annex F Measurement report of SMU

Cylinder number: **8449E**

## F.1 Calibration standards

All calibration standards were made gravimetrically according ISO 6142-1:2015 and verified against SMU Primary standard gas mixtures in accordance to ISO 6143:2001. Impurities (hydrocarbons, oxygen, nitrogen, CO, $CO_2$) in parent gases were analysed on GC and FTIR. Each parent gas has its purity table with composition from purity measurements and manufacturer specifications.

The result values for parent gases and premixtures are given in following purity tables:

**Table 1 CO Messer**

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) |
|---|---|---|
| Ar | 0.0000035 | 0.0000010 |
| $CO_2$ | 0.00000052 | 0.00000015 |
| $N_2$ | 0.000045 | 0.000013 |
| $O_2$ | 0.0000025 | 0.0000007 |
| $H_2$ | 0.00000050 | 0.00000014 |
| $H_2O$ | 0.00000387 | 0.00000045 |
| Methane | 0.00000010 | 0.00000003 |
| **CO** | **0.999944** | **0.000013** |

**Table 2 $CO_2$ Messer**

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) |
|---|---|---|
| CO | 0.00000028 | 0.000000010 |
| $H_2O$ | 0.00000100 | 0.00000029 |
| $N_2$ | 0.000151 | 0.000041 |
| $O_2$ | 0.0000297 | 0.0000085 |
| Methane | 0.00000025 | 0.00000007 |
| **$CO_2$** | **0.999817** | **0.000042** |

**Table 3 $O_2$ BIP**

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) |
|---|---|---|
| CO | 0.00000024 | 0.000000013 |
| $CO_2$ | 0.000000050 | 0.000000010 |
| $N_2$ | 0.00001499 | 0.00000081 |
| $H_2O$ | 0.00000100 | 0.00000029 |
| Methane | 0.00000010 | 0.000000029 |
| **$O_2$** | **0.99998312** | **0.00000087** |

**Table 4 $N_2$ BIP Plus**

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) |
|---|---|---|
| CO | 0.0000000050 | 0.000000000025 |
| $CO_2$ | 0.00000050 | 0.000000087 |
| $H_2$ | 0.000000025 | 0.0000000072 |
| $O_2$ | 0.000000011 | 0.0000000042 |
| $H_2O$ | 0.000000010 | 0.0000000029 |
| Methane | 0.000000090 | 0.000000026 |
| **$N_2$** | **0.999999355** | **0.000000092** |

**Table 5 Propane Messer**

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) |
|---|---|---|
| $O_2$ | 0.000138 | 0.000010 |
| $CO_2$ | 0.0000025 | 0.0000007 |
| $N_2$ | 0.0002385 | 0.0000301 |
| $H_2O$ | 0.0000050 | 0.0000014 |
| Methane | 0.0000022 | 0.0000010 |
| Ethylene | 0.0000093 | 0.0000023 |
| Ethane | 0.0000537 | 0.0000026 |
| iso-butane | 0.0000518 | 0.0000019 |
| Butane | 0.00001057 | 0.00000043 |
| 1-butene | 0.00000608 | 0.00000028 |
| Hexane | 0.00000103 | 0.00000014 |

| | | |
|---|---|---|
| **Propane** | **0.999481** | **0.000032** |

**Table 6 CO premixture 0015F_12**

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) |
|---|---|---|
| Argon | 0.00000070 | 0.00000020 |
| Methane | 0.000000092 | 0.000000022 |
| $CO_2$ | 0.000000615 | 0.000000089 |
| $H_2$ | 0.000000121 | 0.000000030 |
| $H_2O$ | 0.000000786 | 0.000000090 |
| $N_2$ | 0.7986653 | 0.0000039 |
| $O_2$ | 0.00000051 | 0.00000015 |
| **CO** | **0.2013319** | **0.0000053** |

**Table 7 Propane premixture 0722E_7**

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) |
|---|---|---|
| Methane | 0.000000101 | 0.000000024 |
| CO | 0.0000000044 | 0.00000000002 |
| $CO_2$ | 0.000000648 | 0.000000095 |
| Hydrogen | 0.000000025 | 0.000000007 |
| Water | 0.000000035 | 0.000000008 |
| Nitrogen | 0.99496838 | 0.00000033 |
| Oxygen | 0.000000702 | 0.000000051 |
| Ethane | 0.000000270 | 0.000000013 |
| iso-butane | 0.000000261 | 0.000000010 |
| Butane | 0.000000053 | 0.000000002 |
| Hexane | 0.000000005 | 0.000000001 |
| Ethylene | 0.000000047 | 0.000000012 |
| 1-butene | 0.000000031 | 0.000000001 |
| **Propane** | **0.00502944** | **0.00000025** |

**Table 8 Propane premixture 0721E_6**

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) |
|---|---|---|
| Methane | 0.000000106 | 0.000000025 |
| CO | 0.0000000044 | 0.00000000002 |
| $CO_2$ | 0.000000653 | 0.000000095 |
| Hydrogen | 0.000000025 | 0.000000007 |
| Water | 0.000000047 | 0.000000011 |
| Nitrogen | 0.99250248 | 0.00000048 |
| Oxygen | 0.000001043 | 0.000000076 |
| Ethane | 0.000000403 | 0.000000020 |
| iso-butane | 0.000000389 | 0.000000014 |
| Butane | 0.000000079 | 0.000000003 |
| Hexane | 0.000000008 | 0.000000001 |
| Ethylene | 0.000000069 | 0.000000017 |

| | | |
|---|---|---|
| 1-butene | 0.000000046 | 0.000000002 |
| **Propane** | **0.00749465** | **0.00000037** |

**Table 9 Propane premixture 0012F_4**

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) |
|---|---|---|
| Methane | 0.000000111 | 0.000000028 |
| CO | 0.0000000049 | 0.00000000002 |
| $CO_2$ | 0.000000524 | 0.000000087 |
| Hydrogen | 0.000000025 | 0.000000007 |
| Water | 0.000000060 | 0.000000015 |
| Nitrogen | 0.9900301 | 0.0000013 |
| Oxygen | 0.00000139 | 0.00000010 |
| Ethane | 0.000000535 | 0.000000026 |
| iso-butane | 0.000000517 | 0.000000019 |
| Butane | 0.000000105 | 0.000000004 |
| Hexane | 0.000000010 | 0.000000001 |
| Ethylene | 0.000000092 | 0.000000023 |
| 1-butene | 0.000000061 | 0.000000003 |
| **Propane** | **0.0099665** | **0.0000013** |

Preparation of 3 Primary standard gas mixtures containing automotive gases with oxygen was carried out gravimetrically in 5 steps:

1. Propane in $N_2$, one of the three premixtures 0722E_7, 0721E_6, 0012F_4,
2. CO in $N_2$, premixture 00015F_12, or pure CO,
3. pure $CO_2$,
4. pure $O_2$,
5. pure $N_2$.

All mixtures were prepared in aluminium cylinders, V= 5 dm$^3$. Inner surface of the cylinder was Aculife IV. Before preparation, the cylinder was evacuated at least 15 hours using dry evacuation system. The final value of vacuum was approximately 6x$10^{-5}$ Pa.

The mass of added amount of parent mixture was determined by the difference of the cylinder masses before and after filling (line **m** in following tables). Weighting of evacuated or filled cylinder were executed on automatic SMU balance system. Filled cylinder mass was not determined absolutely, but as a difference (6 repetitions) between filled cylinder mass and reference cylinder mass. Mass scale reading for loaded cylinder (line **r** in following tables) is value obtained from loaded built-in weights (line **M** in following tables) and from arithmetic mean of the differences.

For the calculations of the gravimetric composition with associated uncertainties, validated spreadsheet xlISO6142 v1.11 was used based on the models described in ISO 6142-1:2015 and ISO 19229.

Weighing data of 3 Primary standard mixtures are shown below. The values of the added mass in the tables are in [g].

**Table 10 0024F_6 16.03.2021**

| | | 0012F_4 | CO | $O_2$ | $CO_2$ | $N_2$ |
|---|---|---|---|---|---|---|
| | Vacuum | SMU | Messer | Bip Plus | Messer | Bip Plus |
| Difference [1] | 53.652 | 8.004 | 17.965 | 42.737 | -0.324 | 26.134 |
| Difference [2] | 53.653 | 8.004 | 17.965 | 42.736 | -0.324 | 26.135 |
| Difference [3] | 53.653 | 8.004 | 17.964 | 42.736 | -0.325 | 26.135 |
| Difference [4] | 53.653 | 8.003 | 17.964 | 42.736 | -0.325 | 26.136 |
| Difference [5] | 53.653 | 8.003 | 17.965 | 42.736 | -0.324 | 26.136 |
| Difference [6] | 53.653 | 8.003 | 17.965 | 42.737 | -0.324 | 26.136 |
| M | 0 | 53.5482 | 53.5482 | 53.5482 | 114.5305 | 571.9389 |

| | | | | | | |
|---|---|---|---|---|---|---|
| r | 53.6526 | 61.5518 | 71.5128 | 96.2848 | 114.2069 | 598.0859 |
| u(rept) | 0.0004 | 0.0003 | 0.0002 | 0.0003 | 0.0002 | 0.0006 |
| u(res) | 0.0003 | 0.0003 | 0.0003 | 0.0003 | 0.0003 | 0.0003 |
| u(M) | 0.0000 | 0.0003 | 0.0003 | 0.0003 | 0.0003 | 0.0008 |
| u(r) | 0.0005 | 0.0005 | 0.0005 | 0.0005 | 0.0005 | 0.0036 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **m** | - | **7.8992** | **9.9609** | **24.7720** | **17.9221** | **483.8791** |
| **u(m)** | - | **0.0007** | **0.0007** | **0.0007** | **0.0007** | **0.0051** |
| | - | 0.0089% | 0.0069% | 0.0028% | 0.0041% | 0.0011% |

**Table 11 0059F_7 01.06.2021**

| | | 0722E_7 | 0015F_12 | $CO_2$ | $O_2$ | $N_2$ |
|---|---|---|---|---|---|---|
| | Vacuum | SMU | SMU | Messer | Bip Plus | Bip Plus |
| Difference [1] | 3.303 | 26.584 | 1.960 | 19.052 | 39.497 | 12.226 |
| Difference [2] | 3.301 | 26.585 | 1.961 | 19.052 | 39.497 | 12.227 |
| Difference [3] | 3.303 | 26.585 | 1.961 | 19.052 | 39.498 | 12.227 |
| Difference [4] | 3.305 | 26.585 | 1.961 | 19.053 | 39.498 | 12.227 |
| Difference [5] | 3.305 | 26.585 | 1.960 | 19.053 | 39.498 | 12.227 |
| Difference [6] | 3.305 | 26.585 | 1.961 | 19.053 | 39.498 | 12.226 |
| M | 0 | 0 | 53.5482 | 53.5482 | 53.5482 | 571.9389 |

| | | | | | | |
|---|---|---|---|---|---|---|
| r | 3.3035 | 26.5854 | 55.5094 | 72.6007 | 93.0462 | 584.1773 |
| u(rept) | 0.0010 | 0.0003 | 0.0002 | 0.0005 | 0.0003 | 0.0002 |
| u(res) | 0.0003 | 0.0003 | 0.0003 | 0.0003 | 0.0003 | 0.0003 |
| u(M) | 0.0000 | 0.0000 | 0.0003 | 0.0003 | 0.0003 | 0.0008 |
| u(r) | 0.0010 | 0.0004 | 0.0005 | 0.0006 | 0.0005 | 0.0037 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **m** | - | **23.2819** | **28.9240** | **17.0913** | **20.4455** | **491.1311** |
| **u(m)** | - | **0.0011** | **0.0007** | **0.0008** | **0.0008** | **0.0052** |
| | - | 0.0047% | 0.0024% | 0.0048% | 0.0041% | 0.0011% |

**Table 12 0726E_7 24.06.2021**

| | | 0721E_6 | CO | CO$_2$ | O$_2$ | N$_2$ |
|---|---|---|---|---|---|---|
| | Vacuum | SMU | Messer | Messer | Bip Plus | Bip Plus |
| Difference [1] | -16.113 | 3.249 | 14.727 | -1.790 | -29.255 | 26.556 |
| Difference [2] | -16.112 | 3.250 | 14.727 | -1.789 | -29.255 | 26.556 |
| Difference [3] | -16.110 | 3.251 | 14.728 | -1.788 | -29.254 | 26.557 |
| Difference [4] | -16.109 | 3.251 | 14.729 | -1.788 | -29.254 | 26.558 |
| Difference [5] | -16.108 | 3.252 | 14.729 | -1.788 | -29.254 | 26.559 |
| Difference [6] | -16.108 | 3.253 | 14.729 | -1.788 | -29.254 | 26.560 |
| M | 0 | 0 | 0 | 53.5482 | 114.5305 | 571.9389 |

| | | | | | | |
|---|---|---|---|---|---|---|
| r | -16.1099 | 3.2511 | 14.7283 | 51.7604 | 85.2770 | 598.5088 |
| u(rept) | 0.0013 | 0.0008 | 0.0006 | 0.0006 | 0.0005 | 0.0009 |
| u(res) | 0.0003 | 0.0003 | 0.0003 | 0.0003 | 0.0003 | 0.0003 |
| u(M) | 0.0000 | 0.0000 | 0.0000 | 0.0003 | 0.0003 | 0.0008 |
| u(r) | 0.0013 | 0.0009 | 0.0007 | 0.0007 | 0.0007 | 0.0040 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **m** | - | **19.3610** | **11.4771** | **37.0321** | **33.5166** | **513.2318** |
| **u(m)** | - | **0.0016** | **0.0011** | **0.0010** | **0.0010** | **0.0055** |
| | - | 0.0083% | 0.0095% | 0.0027% | 0.0031% | 0.0011% |

For the verification of Primary standard mixtures GC method in accordance to ISO 6143:2001was used calibration with SMU standard. All of the target components corresponded to the validation criteria. Neither stability changes were assumed for automotive gas mixtures. To the validated PRM´s were assigned values of amount fraction of target component $k$ (derived from the process of gravimetric preparation) and associated combined standard uncertainty calculated in accordance to the following formula (ISO 6142-1:2015):

$$u_{cert,x,k} = \frac{1}{2}\sqrt{u^2\left(x_{k,grav}\right) + u^2\left(x_{k,ver}\right) + \left(x_{k,grav} - x_{k,ver}\right)^2}$$

Composition of calibration mixtures used in this comparison is shown in following table.

**Table 13 SMU Primary calibration standards**

| Cylinder number | Component | x<br>(mol/mol) | $U_{cert}$ (k=2)<br>(mol/mol) | $U_{cert.rel}$ (k=2)<br>(%) |
|---|---|---|---|---|
| 0059F_7 | Carbon monoxide | 0.010180 | 0.000010 | 0.10 |
|  | Carbon dioxide | 0.019016 | 0.000020 | 0.11 |
|  | Oxygen | 0.031290 | 0.000084 | 0.27 |
|  | Propane | 0.00020410 | 0.00000026 | 0.13 |
| 0024F_6 | Carbon monoxide | 0.018627 | 0.000036 | 0.19 |
|  | Carbon dioxide | 0.021330 | 0.000030 | 0.14 |
|  | Oxygen | 0.040552 | 0.000060 | 0.15 |
|  | Propane | 0.00014637 | 0.00000032 | 0.22 |
| 0726E_7 | Carbon monoxide | 0.019229 | 0.000020 | 0.10 |
|  | Carbon dioxide | 0.039487 | 0.000040 | 0.10 |
|  | Oxygen | 0.049158 | 0.000080 | 0.16 |
|  | Propane | 0.00024205 | 0.00000030 | 0.12 |

## F.2 Instrumentation

### GC method

For this key comparison, following equipment of Slovak national standard of amount fraction in gaseous phase was used for the verification of calibration standards and for analytical measurement of unknown sample:

**Table 14 Equipment for automotive gas analysis**

| Equipment | Specifications |
|---|---|
| GC Agilent 7890A |  |
| Columns set | Plot Q,<br>Molsieve |
| Detectors | TCD, FID |
| electric or pneumatic valves | for dosing, shut-off for measured gas mixture |
| PC | control software for measurement on GC which records chromatograms to the PC |
| valve for gas mixture selection | 1 output and min. 10 inputs, controlled from PC |
| distribution of gas (pipes, connections) | stainless steel, dimensions and threads 1/4‘,1/8‘ Swagelok |
| regulations of outlet pressure | outlet pressure 2x$10^2$ kPa, stainless steel membrane input DIN-1, output 1/8‘ Swagelok |
| lines of pipes | stainless steel or FEP |
| measuring system of temperature, pressure and relative humidity of ambient air during measurement | resolution of: temperature: less than 0.05°C,<br>pressure: less than 0.1 kPa, humidity: less than 0.2% |

### Analytical method GC settings

GC method parameters for automotive gas analysis are shown in the following tables:

**Table 15 GC Settings**

| GC | L; cm$^3$ | Oven temperature; °C | Total time; min | Inlet flow cm$^3$/min |
|---|---|---|---|---|
| Agilent 7890A | 1.0 | 10-220 | 13.83 | 20.4 |

**Table 16 *Gas flows***

| Gas | Flow ml/min |
|---|---|
| Carrier gas He | 20.4 |
| Make up $N_2$ | 10 |
| Make up He | 5 |
| Hydrogen | 40 |
| Air | 300 |

Detectors:

| | |
|---|---|
| TCD | $O_2$, $CO_2$, CO |
| FID | Propane |

## F.3 Calibration method and value assignment

GC measurement method with several automated runs was used. All runs in first, third, fifth measurement sequence had rising amount fraction. Second, fourth and sixth were processed in reverse order. From each run was made one calibration curve. 3 point linear model of analytical curve was used. No corrections were used.

Data were subjected to the B_least program (weighted least square regression). Inputs to the B_least were: values of measured signals (peak areas) with their standard uncertainties and amount fractions certified values of calibration gas mixtures with their standard uncertainties.

Uncertainty of instrument response consisted from figure characterized roughly immediate repeatability and from signal drift estimated. B-least program for each run produced sample mole fraction with its standard uncertainty. From all runs results = average of amount fractions in one sequence were standard deviation found $u_1(\bar{x}_i)$ and from runs results uncertainties the mean (through squares) was found $u_2(\bar{x}_i)$. These 2 figures were combined to give standard uncertainty $u_{an}(\bar{x}_i)$ for one sequence. Following formulas were used for the uncertainty calculations:

$$u_1(\bar{x}_i) = 1.3 * \sqrt{\frac{\sum_{j=1}^{n} (x_j - \bar{x}_i)^2}{n*(n-1)}}$$

$$u_2(\bar{x}_i) = \sqrt{\frac{\sum_{j=1}^{n} u(x_j)^2}{n^2}}$$

$$u_{an}(\bar{x}_i) = \sqrt{u_1(\bar{x}_i)^2 + u_2(\bar{x}_i)^2}$$

$$\bar{x}_i = \frac{\sum_{j=1}^{n} x_j}{n}$$

$n$- number of measuring runs

Final result of amount fraction was average value from 5 day results. Associated type A standard uncertainties were calculated as a standard deviation. The results are shown in the table 17.

**Table 17 Measurement results with associated standard uncertainty type-A**

| **Comp.** | **1. meas. (mol/mol)** | **2. meas. (mol/mol)** | **3. meas. (mol/mol)** | **4. meas. (mol/mol)** | **5. meas. (mol/mol)** | $\bar{x}$ **(mol/mol)** | $u_A$ **(mol/mol)** |
|---|---|---|---|---|---|---|---|
| CO | 0.0100097 | 0.0100091 | 0.0100066 | 0.0100134 | 0.0100032 | 0.0100084 | 0.0000017 |
| $CO_2$ | 0.0200365 | 0.0200286 | 0.0200278 | 0.0200270 | 0.0200157 | 0.0200271 | 0.0000033 |
| Propane | 0.000199213 | 0.000199048 | 0.000199010 | 0.000199047 | 0.000198960 | 0.000199056 | 0.000000043 |
| Oxygen | 0.0301203 | 0.0301172 | 0.0301168 | 0.0301080 | 0.0300935 | 0.0301112 | 0.0000049 |

Standard uncertainty type B was calculated as a combined value from maximum value from 5 day analysis uncertainties and uncertainty of primary standard calibration gas (0059F_7). Results are shown in the table 18.

**Table 18 Type-B uncertainty evaluation results**

| Component | $u_{an}$ 1. meas. (mol/mol) | $u_{an}$ 2.meas. (mol/mol) | $u_{an}$ 3. meas. (mol/mol) | $u_{an}$ 4. meas. (mol/mol) | $u_{an}$ 5. meas. (mol/mol) |
|---|---|---|---|---|---|
| CO | 0.000014 | 0.000013 | 0.0000059 | 0.0000095 | 0.000010 |
| $CO_2$ | 0.000021 | 0.000028 | 0.0000080 | 0.000017 | 0.000015 |
| Propane | 0.00000027 | 0.00000018 | 0.00000011 | 0.00000013 | 0.00000017 |
| Oxygen | 0.000042 | 0.000051 | 0.000023 | 0.000031 | 0.000029 |

| Component | $u_{an.max}$ (mol/mol) | $u_{cert}$ (mol/mol) | $u_B$ (mol/mol) |
|---|---|---|---|
| CO | 0.000014 | 0.000005 | 0.000015 |
| $CO_2$ | 0.000028 | 0.000010 | 0.000030 |
| Propane | 0.00000027 | 0.00000013 | 0.00000030 |
| Oxygen | 0.000051 | 0.000042 | 0.000066 |

Total standard uncertainty was evaluated by following formula:

$$u(\bar{x}) = \sqrt{u_A^2 + u_B^2}$$

Expanded uncertainty (k=2) of final result:

$$U(\bar{x}) = 2 * u(\bar{x})$$

**Table 19** ***Results***

| Component | Fraction (cmol/mol) | Expanded uncertainty (cmol/mol) | Coverage factor |
|---|---|---|---|
| Oxygen | 3.011 | 0.013 | 2 |
| $CO_2$ | 2.0027 | 0.0060 | 2 |
| Propane | 0.019906 | 0.000061 | 2 |
| CO | 1.0008 | 0.0030 | 2 |

**References**

| | |
|---|---|
| ISO 6142-1:2015 | Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures. |
| ISO 6143:2001 | Gas analysis– Comparison methods for determining and checking the composition of calibration gas mixtures. |
| ISO 14912:2003 | Gas analysis – Conversion of gas mixture composition data |

# Annex G Measurement report of METAS

## G.1 $C_3H_8$:

### G.1.1 Calibration standards

| | |
|---|---|
| Reference 1: Cylinder No. NPL 1420 | METAS value (100.19 ± 0.40) µmol/mol |
| Reference 2: Cylinder No. Carbagas A1W24E9 | METAS value (99.52 ± 0.40) µmol/mol |
| Reference 3: Cylinder No. Messer D358312 | METAS value (100.40 ± 0.40) µmol/mol |
| Reference 4: Cylinder No. PanGas 75631100061351 | METAS value (300.2 ± 1.2) µmol/mol |
| Reference 5: Cylinder No. Messer 80786 | METAS value (299.5 ± 1.2) µmol/mol |
| Reference 6: Cylinder No. PanGas 75631110845534 | METAS value (601.1 ± 2.4) µmol/mol |
| Reference 7: Cylinder No. Messer 6728F | METAS value (597.6 ± 2.4) µmol/mol |

### G.1.2 Instrumentation

A fully automatic pressure controlled Gas-Chromatograph with FID (Orthodyne S.A., Belgium) was used with an autosampler (Swagelok IGC-III, all gas lines are electropolished and pneumatically controlled).

Sample Handling: The sample flow through the sample loop of the injector is controlled at 60 ml/min @ 0 °C/1013 hPa, the pressure of the sample flow after the sample loop is also controlled at 1000 hPa absolute.

### G.1.3 Calibration method and value assignment

The transfer standard has been compared against seven standard mixtures. These mixtures were cylinders out of the set of national reference gas mixtures for $C_3H_8$ in nitrogen in the range between 100 µmol/mol to 600 µmol/mol $C_3H_8$.

The area results (responses) of known mixtures and the unknown mixture have been evaluated using the bracketing technique with a linear regression according to ISO standard 6143 using the B-Least software.

## G.2 CO:

### G.2.1 Calibration standards

| | |
|---|---|
| Reference 1: Cylinder No. Messer 80507 | METAS value (0.29927 ± 0.0012) cmol/mol |
| Reference 2: Cylinder No. PanGas 220117 | METAS value (0.29941 ± 0.0012) cmol/mol |
| Reference 3: Cylinder No. Messer 680 | METAS value (0.8004 ± 0.0032) cmol/mol |
| Reference 4: Cylinder No. PanGas 101357 | METAS value (0.8005 ± 0.0032) cmol/mol |
| Reference 5: Cylinder No. VSL D248683 | METAS value (0.8003 ± 0.0032) cmol/mol |
| Reference 6: Cylinder No. Messer 24889 | METAS value (1.5039 ± 0.0060) cmol/mol |
| Reference 7: Cylinder No. Carbagas A1EFUN2 | METAS value (1.5003 ± 0.0060) cmol/mol |
| Reference 8: Cylinder No. Carbagas A1DNG69 | METAS value (3.005 ± 0.012) cmol/mol |
| Reference 9: Cylinder No. PanGas 221510 | METAS value (3.008 ± 0.012) cmol/mol |

### G.2.2 Instrumentation

A fully automatic pressure controlled Gas-Chromatograph with methaniser and FID (Orthodyne S.A., Belgium) was used with an autosampler (Swagelok IGC-III, all gas lines are electropolished and pneumatically controlled).

Sample Handling: The sample flow through the sample loop of the injector is controlled at 60 ml/min @ 0 °C/1013 hPa, the pressure of the sample flow after the sample loop is also controlled at 1000 hPa absolute.

### G.2.3 Calibration method and value assignment

The transfer standard has been compared against nine standard mixtures. These mixtures were cylinders out of the set of national reference gas mixtures for CO in nitrogen in the range between 0.3 cmol/mol to 3.0 cmol/mol CO.

The area results (responses) of known mixtures and the unknown mixture have been evaluated using the bracketing technique with a linear regression according to ISO standard 6143 using the B-Least software.

## G.3 $O_2$:

### G.3.1 Calibration standards

| | |
|---|---|
| Reference 1: Cylinder No. Messer D053973 | METAS value (2.500 ± 0.010) cmol/mol |
| Reference 2: Cylinder No. PanGas 175920 | METAS value (2.497 ± 0.010) cmol/mol |
| Reference 3: Cylinder No. VSL D247747 | METAS value (2.503 ± 0.010) cmol/mol |
| Reference 4: Cylinder No. Messer 81263 | METAS value (5.006 ± 0.020) cmol/mol |
| Reference 5: Cylinder No. Messer D492909 | METAS value (4.992 ± 0.020) cmol/mol |

### G.3.2 Instrumentation

A paramagnetic measurement system (SIEMENS Oxymat 6E) was used with an autosampler (Swagelok IGC-III, all gas lines are electropolished and pneumatically controlled).

Sample Handling: The sample flow through the sample cell is controlled by a massflow controller at 400 ml/min @ 0 °C/1013 hPa.

### G.3.3 Calibration method and value assignment

The transfer standard has been compared against five standard mixtures. These mixtures were cylinders out of the set of national reference gas mixtures for $O_2$ in nitrogen in the range between 2.5 cmol/mol to 5.0 cmol/mol $O_2$.

The signals (responses) of known mixtures and the unknown mixture have been evaluated using the bracketing technique with a linear regression according to ISO standard 6143 using the B-Least software.

## G.4 $CO_2$:

### G.4.1 Calibration standards

| | |
|---|---|
| Reference 1: Cylinder No. Messer D055005 | METAS value (9.013 ± 0.032) cmol/mol |
| Reference 2: Cylinder No. NPL 1485 | METAS value (9.984 ± 0.035) cmol/mol |
| Reference 3: Cylinder No. PanGas 104777 | METAS value (11.008 ± 0.039) cmol/mol |

The premixtures were diluted with purified nitrogen (liquid nitrogen quality 99.999%, Purifier: SAES-Getter MonoTorr, $CO_2$ < 10 nmol/mol), using a METAS-calibrated massflow controller system for the flow measurements.

### G.4.2 Instrumentation

A fully automatic pressure controlled Gas-Chromatograph with Methaniser and FID (Orthodyne S.A., Belgium) was used with an autosampler (Swagelok IGC-III, all gas lines are electropolished and pneumatically controlled).

Sample Handling: The sample flow through the sample loop of the injector is controlled at 80 ml/min @ 0 °C/1013 hPa, the pressure of the sample flow after the sample loop is also controlled at 1000 hPa absolute.

### G.4.3 Calibration method and value assignment

The transfer standard has been compared against six mixtures by means of a fully automatic pressure controlled GC with methaniser and FID. The mixtures have been prepared by dilution of three gravimetric premixtures with nitrogen. The binary gravimetric premixtures were cylinders out of the set of national reference gas mixtures for $CO_2$ in nitrogen in the range between 9 cmol/mol to 11 cmol/mol.

A preliminary analysis of the transfer standard revealed an approximate amount of substance fraction of 2 cmol/mol. The calibration points for referencing the transfer standard readings have therefore been adapted. Two different dilutions have been produced for each cylinder. The area results (responses) of known calculated mixtures and the unknown mixture have been evaluated.

Detailed uncertainty budget:

The uncertainty estimation has been done using GUM Workbench Pro V. 2.4.1.406.

## G.5 Example uncertainty evaluation

**List of Quantities:**

| Quantity | Unit | Definition |
|---|---|---|
| $Anz_{A1}$ | au | first reference gas mixture: indicated measuring signal |
| $Anz_{A2}$ | au | second reference gas mixture: indicated measuring signal |
| $Anz_{A3}$ | au | third reference gas mixture: indicated measuring signal |
| $Anz_{A4}$ | au | fourth reference gas mixture: indicated measuring signal |
| $Anz_{A5}$ | au | fifth reference gas mixture: indicated measuring signal |
| $Anz_{A6}$ | au | sixth reference gas mixture: indicated measuring signal |
| AnzRes | au | DUT: indicated measuring signal |
| a | au | Axis intercept of the calibration line |
| b | au/(cmol/mol) | Slope of the calibration line |

| Quantity | Unit | Definition |
|---|---|---|
| p | au*cmol/mol | numerator for slope |
| q | $(cmol/mol)^2$ | denominator for slope |
| $Q_{MFC1n1}$ | ml/min@STP | first reference gas mixture: flow of the first gas mixture standard |
| $Q_{MFC1n2}$ | ml/min@STP | second reference gas mixture: flow of the first gas mixture standard |
| $Q_{MFC1n3}$ | ml/min@STP | third reference gas mixture: flow of the second gas mixture standard |
| $Q_{MFC1n4}$ | ml/min@STP | fourth reference gas mixture: flow of the second gas mixture standard |
| $Q_{MFC1n5}$ | ml/min@STP | fifth reference gas mixture: flow of the third gas mixture standard |
| $Q_{MFC1n6}$ | ml/min@STP | sixth reference gas mixture: flow of the third gas mixture standard |
| $Q_{MFC2n1}$ | ml/min@STP | first reference gas mixture: nitrogen flow |
| $Q_{MFC2n2}$ | ml/min@STP | second reference gas mixture: nitrogen flow |
| $Q_{MFC2n3}$ | ml/min@STP | third reference gas mixture: nitrogen flow |
| $Q_{MFC2n4}$ | ml/min@STP | fourth reference gas mixture: nitrogen flow |
| $Q_{MFC2n5}$ | ml/min@STP | fifth reference gas mixture: nitrogen flow |
| $Q_{MFC2n6}$ | ml/min@STP | sixth reference gas mixture: nitrogen flow |
| $X_{Ref1}$ | cmol/mol | first gas mixture standard: amount fraction |
| $X_{Ref2}$ | cmol/mol | second gas mixture standard: amount fraction |
| $X_{Ref3}$ | cmol/mol | third gas mixture standard: amount fraction |
| $X_{N}$ | cmol/mol | nitrogen: residual CO2 (amount fraction) |
| $X_{A1}$ | cmol/mol | first reference gas mixture: amount fraction in final mixture |
| $X_{A2}$ | cmol/mol | second reference gas mixture: amount fraction in final mixture |
| $X_{A3}$ | cmol/mol | third reference gas mixture: amount fraction in final mixture |
| $X_{A4}$ | cmol/mol | fourth reference gas mixture: amount fraction in final mixture |
| $X_{A5}$ | cmol/mol | fifth reference gas mixture: amount fraction in final mixture |
| $X_{A6}$ | cmol/mol | sixth reference gas mixture: amount fraction in final mixture |
| $X_{meanA}$ | cmol/mol | mean CO2 amount fraction of the reference gas mixtures |
| $Anz_{meanA}$ | au | mean indicated measuring signal of the reference gas mixtures |
| XCO2Res | cmol/mol | DUT: amount fraction |

## Uncertainty Budget:

**XCO2Res: DUT: amount fraction**

| Quantity | Value | Standard Uncert. (rel.) | df | Sens.-Coeff. | Uncert.-Contrib. | Corr.-Coeff. | Index |
|---|---|---|---|---|---|---|---|
| $Anz_{A1}$ | $13.03382 \cdot 10^{6}$ au | 0.033 % | 4 | $-22 \cdot 10^{-9}$ | $-93 \cdot 10^{-6}$ cmol/mol | -0.0266 | 0.0 % |
| $Anz_{A2}$ | $14.41982 \cdot 10^{6}$ au | 0.025 % | 4 | $-26 \cdot 10^{-9}$ | $-95 \cdot 10^{-6}$ cmol/mol | -0.0272 | 0.0 % |
| $Anz_{A3}$ | $12.98667 \cdot 10^{6}$ au | 0.016 % | 4 | $-22 \cdot 10^{-9}$ | $-45 \cdot 10^{-6}$ cmol/mol | -0.0128 | 0.0 % |
| $Anz_{A4}$ | $14.38665 \cdot 10^{6}$ au | 0.009 % | 4 | $-26 \cdot 10^{-9}$ | $-34 \cdot 10^{-6}$ cmol/mol | $-9.7 \cdot 10^{-3}$ | 0.0 % |
| $Anz_{A5}$ | $13.03161 \cdot 10^{6}$ au | 0.022 % | 4 | $-22 \cdot 10^{-9}$ | $-61 \cdot 10^{-6}$ cmol/mol | -0.0174 | 0.0 % |

| Quantity | Value | Standard Uncert. (rel.) | df | Sens.-Coeff. | Uncert.-Contrib. | Corr.-Coeff. | Index |
|---|---|---|---|---|---|---|---|
| $Anz_{A6}$ | $14.40962\cdot10^{6}$ au | 0.030 % | 4 | $-26\cdot10^{-9}$ | $-110\cdot10^{-6}$ cmol/mol | -0.0322 | 0.1 % |
| AnzRes | $13.77692\cdot10^{6}$ au | 0.019 % | 4 | $140\cdot10^{-9}$ | $380\cdot10^{-6}$ cmol/mol | 0.1083 | 1.2 % |
| a | $-194\cdot10^{3}$ au | 68 % | 130 | | | | |
| b | $6.9689\cdot10^{6}$ au/(cmol/mol) | 0.97 % | 140 | | | | |
| p | $414.93\cdot10^{3}$ au*cmol/mol | 0.97 % | 140 | | | | |
| q | 0.05954 $(\text{cmol/mol})^{2}$ | 1.9 % | 130 | | | | |
| $Q_{MFC1n1}$ | 16.8890 ml/min@STP | 0.25 % | 100 | 0.013 | $570\cdot10^{-6}$ cmol/mol | 0.2146 | 3.5 % |
| $Q_{MFC1n2}$ | 18.6670 ml/min@STP | 0.25 % | 100 | 0.016 | $740\cdot10^{-6}$ cmol/mol | 0.2243 | 4.7 % |
| $Q_{MFC1n3}$ | 15.2000 ml/min@STP | 0.25 % | 100 | 0.015 | $580\cdot10^{-6}$ cmol/mol | 0.2153 | 3.5 % |
| $Q_{MFC1n4}$ | 16.8000 ml/min@STP | 0.25 % | 100 | 0.018 | $750\cdot10^{-6}$ cmol/mol | 0.2252 | 4.8 % |
| $Q_{MFC1n5}$ | 13.8180 ml/min@STP | 0.25 % | 100 | 0.017 | $590\cdot10^{-6}$ cmol/mol | 0.2162 | 3.7 % |
| $Q_{MFC1n6}$ | 15.2730 ml/min@STP | 0.25 % | 100 | 0.020 | $780\cdot10^{-6}$ cmol/mol | 0.2266 | 5.0 % |
| $Q_{MFC2n1}$ | 63.328 ml/min@STP | 0.20 % | 100 | $-3.6\cdot10^{-3}$ | $-450\cdot10^{-6}$ cmol/mol | 0.1565 | -2.0 % |
| $Q_{MFC2n2}$ | 61.566 ml/min@STP | 0.20 % | 100 | $-4.8\cdot10^{-3}$ | $-590\cdot10^{-6}$ cmol/mol | 0.1488 | -2.5 % |
| $Q_{MFC2n3}$ | 65.001 ml/min@STP | 0.20 % | 100 | $-3.6\cdot10^{-3}$ | $-460\cdot10^{-6}$ cmol/mol | 0.1560 | -2.1 % |
| $Q_{MFC2n4}$ | 63.416 ml/min@STP | 0.20 % | 100 | $-4.7\cdot10^{-3}$ | $-600\cdot10^{-6}$ cmol/mol | 0.1481 | -2.5 % |
| $Q_{MFC2n5}$ | 66.370 ml/min@STP | 0.20 % | 100 | $-3.6\cdot10^{-3}$ | $-470\cdot10^{-6}$ cmol/mol | 0.1553 | -2.1 % |
| $Q_{MFC2n6}$ | 64.929 ml/min@STP | 0.20 % | 100 | $-4.8\cdot10^{-3}$ | $-620\cdot10^{-6}$ cmol/mol | 0.1470 | -2.6 % |
| $X_{Ref1}$ | 9.0130 cmol/mol | 0.20 % | 100 | 0.074 | $1.3\cdot10^{-3}$ cmol/mol | 0.7626 | 29.1 % |
| $X_{Ref2}$ | 9.9840 cmol/mol | 0.20 % | 100 | 0.067 | $1.3\cdot10^{-3}$ cmol/mol | 0.7610 | 28.8 % |
| $X_{Ref3}$ | 11.0080 cmol/mol | 0.20 % | 100 | 0.061 | $1.3\cdot10^{-3}$ cmol/mol | 0.7625 | 29.1 % |
| $X_{N}$ | $200.0\cdot10^{-6}$ cmol/mol | 41 % | $\infty$ | 0.80 | $65\cdot10^{-6}$ cmol/mol | 0.0186 | 0.0 % |
| $X_{A1}$ | 1.89777 cmol/mol | 0.23 % | 160 | | | | |
| $X_{A2}$ | 2.09712 cmol/mol | 0.23 % | 160 | | | | |
| $X_{A3}$ | 1.89237 cmol/mol | 0.23 % | 170 | | | | |
| $X_{A4}$ | 2.09115 cmol/mol | 0.23 % | 160 | | | | |

| Quantity | Value | Standard Uncert. (rel.) | df | Sens.-Coeff. | Uncert.-Contrib. | Corr.-Coeff. | Index |
|---|---|---|---|---|---|---|---|
| $X_{A5}$ | 1.89706 cmol/mol | 0.24 % | 170 | | | | |
| $X_{A6}$ | 2.09643 cmol/mol | 0.23 % | 170 | | | | |
| $X_{meanA}$ | 1.99532 cmol/mol | 0.17 % | 190 | | | | |
| $Anz_{meanA}$ | $13.71137 \cdot 10^{6}$ au | 0.01 % | 17 | | | | |
| XCO2Res | 2.00472 cmol/mol | 0.17 % | 190 | | | | |

**Result:**

| Quantity | Value | Expanded Uncertainty | Coverage factor | Coverage |
|---|---|---|---|---|
| XCO2Res | 2.0047 cmol/mol | 0.35 % (relative) | 2.00 | 95% (t-table 95.45%) |

# Annex H Measurement report of UME

Cylinder code : D751979

## H.1 Calibration standards

Primary reference gas mixtures of automotive exhaust gases mixtures, used in calibrations are given in Table 1. They were prepared individually in accordance with ISO 6142-1:2015 [1] at UME and were verified. Several pre-mixtures were individually prepared from pure components; these pre-mixtures were diluted to prepare three reference gas standards for automotive exhaust gases mixtures. The pure gases used for the preparation of gas mixtures are given in Table 2. The uncertainties of reference gas mixtures were determined by combining the standard uncertainties of weighing, purity and molecular masses for all components.

**Table 1. List of primary reference gas mixtures**

| Item | Prepared By | Cylinder Number | Component | Mole Fraction (cmol/mol) | Uncertainty (k=1) (cmol/mol) |
|---|---|---|---|---|---|
| 1 | UME | PSM499770 | Oxygen | 2.8146 | 0.0007 |
| | | | Carbon dioxide | 1.8777 | 0.0005 |
| | | | Propane | 0.019243 | 0.000005 |
| | | | Carbon monoxide | 0.8944 | 0.0001 |
| | | | Nitrogen | Balance | |
| 2 | UME | PSM499763 | Oxygen | 2.9696 | 0.0007 |
| | | | Carbon dioxide | 2.0209 | 0.0005 |
| | | | Propane | 0.019980 | 0.000005 |
| | | | Carbon monoxide | 0.9997 | 0.0001 |
| | | | Nitrogen | Balance | |
| 3 | UME | PSM298280 | Oxygen | 3.2498 | 0.0007 |
| | | | Carbon dioxide | 2.0636 | 0.0005 |
| | | | Propane | 0.021053 | 0.000005 |
| | | | Carbon monoxide | 1.1001 | 0.0001 |
| | | | Nitrogen | Balance | |

**Table 2. List of pure gases**

| Component | Suppliers | Grade | Origin |
|---|---|---|---|
| Nitrogen | Linde | 6.0 | Turkey |
| Oxygen | Linde | 5.0 | Germany |
| Carbon dioxide | Linde | 5.5 | Turkey |
| Propane | Air Liquide | 3.5 | Germany |
| Carbon monoxide | Hat Group | 4.7 | Germany |

## H.2 Instrumentation

The automotive exhaust gases mixtures were analyzed on an Agilent 6890N gas chromatography instrument equipped with FID and TCD, split/splitless injector, gas injection valve, including GC ChemStation software (Rev. B. 04.03-SP2 [108]) to collect and process data. Carbon monoxide, carbon dioxide and propane in the mixtures were analyzed on Agilent 6890N gas chromatography with FID using Helium as carrier gas. Oxygen in the mixtures was also analyzed on Agilent 6890N gas chromatography with TCD using Argon as carrier gas. The conditions for the analyses are given below:

*a) Conditions for Agilent 6890N (for CO, $CO_2$ and $C_3H_8$)*

<u>Oven</u>

Equilibration Time : 0.30 min
Initial Temperature : On 50°C
Max Temperature : 300°C
Oven Program : On
#1 then 100 °C/min to 100 °C for 2.5 min
Run Time : 13 min

<u>Front SS Inlet He</u>

Mode : Split
Heater : On 150 °C
Pressure : On 18.77 psi
Total Flow : On 210.0 mL/min
Split Ratio : 25:1
Split Flow : 199.6 mL/min
Gas Type : Helium

<u>Column #1</u>

Agilent PLOTQ+ Molesieve + Agilent 19095P-Q04+PerkinNR210040
Max Temperature : 270°C
Nominal length : 60.0 m
Nominal diameter : 530.00 um
Nominal film thickness : 50.00 um
Mode : Constant flow
Initial flow : 8.0 mL/min
Nominal init pressure : 18.78 psi
Average velocity : 58 cm/sec
Inlet : Front Inlet
Outlet : Back Detector

Outlet pressure : Ambient

### Front Detector FID

Heater : On 250 °C
$H_2$ Flow : On 40.0 mL/min
Air Flow : On 400 mL/min
Makeup Flow : Off 45.0 mL/min
Makeup Gas Type : Helium
Flame : On
Electrometer : On
Data rate : 20 Hz

### Back Detector TCD

Heater : Off 250 °C
Reference Flow : Off 15 mL/min
Makeup Flow : Off 8 mL/min
Makeup Gas Type : Helium
Filament : Off
Negative Polarity : Off

*b) Conditions for Agilent 6890N (for $O_2$)*

### Oven

Equilibration Time : 0.30 min
Initial Temperature : On 50°C
Max Temperature : 300°C
Oven Program : On
Initial Time : 5.5 min
#1 then 25 °C/min to 150 °C for 1.0 min
Run Time : 10.5 min

### Front SS Inlet He

Mode : Split
Heater : On 150 °C
Pressure : On 20.8 psi
Total Flow : On 17.8 mL/min
Split Ratio : 1:1
Split Flow : 7.9 mL/min
Gas Type : Argon methane 5%

### Column #1

Agilent PLOTQ+ Molesieve + Agilent 19095P-Q04+PerkinNR210040
Max Temperature : 270°C
Nominal length : 60.0 m
Nominal diameter : 530.00 um
Nominal film thickness : 50.00 um
Mode : Constant flow
Initial flow : 7.9 mL/min
Nominal init pressure : 20.81 psi
Average velocity : 55 cm/sec
Inlet : Front Inlet
Outlet : Back Detector
Outlet pressure : Ambient

Front Detector FID
Heater : Off 250 °C
$H_2$ Flow : Off 40.0 mL/min
Air Flow : Off 400 mL/min
Makeup Flow : Off 45.0 mL/min
Makeup Gas Type : Helium
Flame : Off
Electrometer : Off

Back Detector TCD
Heater : On 250 °C
Reference Flow : On 15 mL/min
Makeup Flow : On 8 mL/min
Makeup Gas Type : Helium
Filament : On
Negative Polarity : On
Data rate : 5Hz

## H.3 Calibration method and value assignment

After the arrival of the cylinder from coordinator, it was stored in the laboratory at least 24 hours prior to analyses. Reference gas mixtures were also stored in the same laboratory during all measurements. Sample and the calibration standards were equipped with pressure reducers and connected to computer programmed multiposition valve gas sampling box. They were flushed at least 3 times before the first measurement. The pressures of sample and reference gases were controlled by an electronic pressure controller at 150 mbar.

The data was collected using ChemStation software. Each sample in the sequence was injected 9 times, and the first two injections in each case were discarded as they were considered as flushing of sample loop. The responses were averaged. The software “CurveFit” was utilized to determine the fitting data for the calibrations. The value for goodness of fit in each measurement was found to be less than 2 in each case for linear function.

The assigned value was calculated by averaging the results of four independent sets of measurements.

## H.4 Uncertainty evaluation

The measurement uncertainty of sample was determined according to ISO 6143:2001 [2], using the CurveFit software.

The largest uncertainty of the four sets of measurements for each component was taken as the standard uncertainty in the sample for the corresponding component.

The expanded uncertainty was determined by multiplying the standard uncertainty by a coverage factor of 2 with a confidence interval of 95%.

**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”

# Annex I Measurement report of CMI

## I.1 Calibration standards

All mixtures were prepared in aluminium cylinders, V= 5 $dm^3$. Before preparation, the cylinder was evacuated at least 12 hours using dry evacuation system. The mass of added amount was determined by the difference of the cylinder masses before and after filling. Weighting of evacuated or filled cylinder were executed on automatic balance system "Kalipro 15". During automatic weighting, the filled cylinder mass was not determined absolutely, but as a difference between filled cylinder mass and reference cylinder mass.

| RM number: | | D036624 |
|---|---|---|
| | $x_i$ | $U_{(xi)}$ |
| compounds: | ($10^{-2}$ mol/mol) | |
| propane | 0.73 | 1.80 |
| CO | 0.079 | 0.001 |
| CO2 | 0.018 | 0.001 |
| Oxygen | 0.03 | 0.001 |

| RM number: | | D036625 |
|---|---|---|
| | $x_i$ | $U_{(xi)}$ |
| compounds: | ($10^{-2}$ mol/mol) | |
| propane | 390.51 | 1.83 |
| CO | 2.0046 | 0.001 |
| CO2 | 5.0653 | 0.001 |
| Oxygen | 4.0038 | 0.001 |

| RM number: | | D036641 |
|---|---|---|
| | $x_i$ | $U_{(xi)}$ |
| compounds: | ($10^{-2}$ mol/mol) | |
| propane | 102.76 | 1.76 |
| CO | 0.5003 | 0.001 |
| CO2 | 2.0815 | 0.001 |
| Oxygen | 1.0044 | 0.001 |

| RM number: | | 20427 |
|---|---|---|
| | $x_i$ | $U_{(xi)}$ |
| compounds: | ($10^{-2}$ mol/mol) | |
| propane | 178.12 | 1.81 |
| CO | 1.007 | 0.001 |
| CO2 | 3.0214 | 0.001 |
| Oxygen | 2.0108 | 0.001 |

## I.2 Instrumentation

Dani Master (gas chromatograph with 2x TCD and FID)

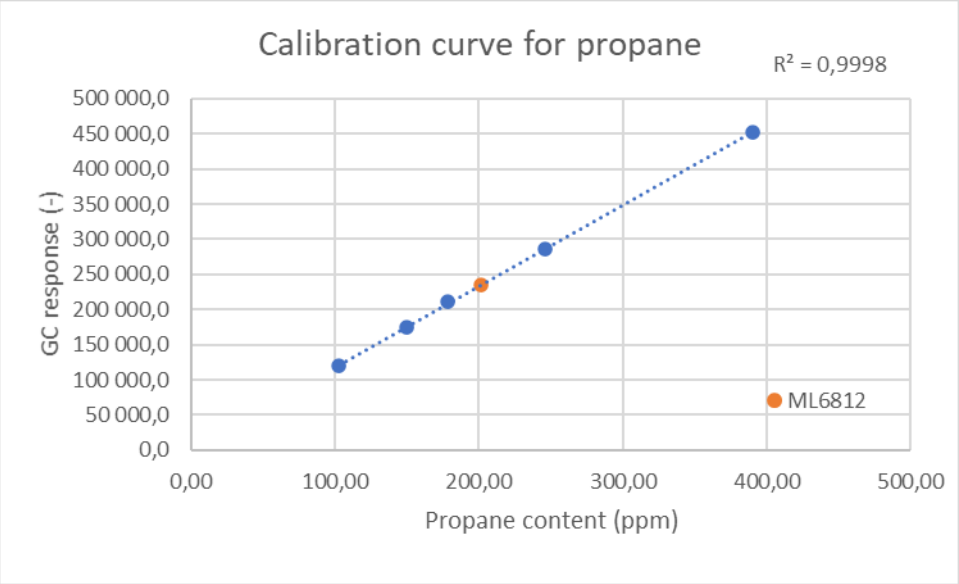
- Owen temperature: 60°C, isothermal,

| Carrier gas: | sample loop: | Detector: | |
|---|---|---|---|
| hydrogen | 1ml | FID | MTX-1 60m x 0,53mm |
| helium | 1ml | TCD | HS-Q 80/100 3m x 1/16" x 1,0 mm |
| | | | MS5A 80/100 3m x 1/16" x 1,0 mm |

## I.3 Calibration method and value assignment

GC measurement method with automated runs was used. Four-point linear model of analytical curve was used.

Four calibration mixtures were prepared for building of the linear calibration curve. For the verification the GC method was used. All of target components corresponded to the validation criteria. The values of mole fraction of target component were assigned to the validated PRM´s (derived from the process of gravimetric preparation).



## I.4 Uncertainty evaluation:

$$u_a = Rel.\,std.\,dev\ (\%) = \sqrt{\frac{\sum_{j=1}^{n}(x_j - x_i)^2}{N.(N-1)}} * 100$$

$$u_{RM}(x_i) = \sqrt{\sum_{j=1}^{m} {u_{RM}}_j^{\,2}}$$

$$u_c(x_i) = \sqrt{u_a(x_i)^2 + u_b(x_i)^2}$$

$$U_{c(xi)} = k \cdot u_{c(xi)}$$

Where:

$u_a$ - uncertainty from measurement
$u_{RM(xi)}$ - uncertainty reference materials
$u_{xi}$ - standard uncertainty compounds $x_i$
$U_{xi}$ - extended standard uncertainty compounds $x_i$
k - coverage factor,
$x_i$ - molar fraction of component i
N - number of measurements

## References:

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