

Calibration and measurement capabilities for propane in nitrogen and synthetic air[†]

Adriaan M.H. van der Veen, Heleen Meuzelaar, and J. Wouter van der Hout

VSL, Dutch Metrology Institute, Thijsseweg 11, 2629 JA Delft, the Netherlands

22 September 2020

Abstract

In 2016, the Gas Analysis Working Group of the Consultative Committee on Amount of substance (GAWG) introduced an extrapolation scheme to be used for translating the measurement uncertainty reported in a key comparison to a measurement capability. This extrapolation scheme has a tipping point at $10 \mu\text{mol mol}^{-1}$. Below this amount fraction level, the expanded uncertainty is assumed to be independent of the amount fraction, and above the relative expanded uncertainty is assumed to constant. So, a relative expanded uncertainty of 1.0% at $10 \mu\text{mol mol}^{-1}$ translates to an expanded uncertainty of 1.0% at 0.1 mol mol^{-1} , and into a relative expanded uncertainty of 10% at $1.0 \mu\text{mol mol}^{-1}$.

This work revisits the calibration and measurement capabilities (CMCs) for propane in nitrogen and synthetic air and outlines the calculations necessary for a customised extrapolation scheme. Key inputs include the measurements performed to support the national measurement standards, the stability studies run on representative gas mixtures to understand their long-term behaviour and last but not least, the uncertainty calculations performed in the participation in key or other international comparisons. Meta-analysis is used to determine a reproducibility component of uncertainty, which is combined with the standard uncertainty calculated in accordance with ISO 6143.

The re-evaluation of the long-term stability study data for calibration gas mixtures of propane in nitrogen shows that there is good agreement between the expanded uncertainty calculated from these data and the expanded uncertainties submitted in four international comparisons. It is shown that the relationship between the amount fraction and the expanded uncertainty can be satisfactorily be described by a straight line when taking the logarithm on both axes to get an acceptable distribution of the data points along the axes. The proposed extrapolation scheme outperforms the scheme proposed by the GAWG.

Contents

1 Introduction and rationale

[†]Filed as report S-CH.20.34

31	2 GAWG extrapolation scheme	4
32	3 Calculation of CMCs	4
33	4 Results and discussion	6
34	4.1 Propane in nitrogen	6
35	4.2 Propane in synthetic air	11
36	5 Interpolation scheme for CMCs	15
37	5.1 Propane in nitrogen	15
38	5.2 Propane in synthetic air	15
39	6 Conclusions	15

40 **Notice**

41 This report cancels and replaces report S-CH.17.16.

42 **Comments**

43 "CMCs are reviewed according to GAWG, KCWG and CIPM documents entitled ""CCQM-
44 GAWG strategy for comparisons and CMC claims"", ""Guidelines for the CCQM KCWG on
45 the Review of CCQM CMCs for Inclusion in Appendix C of the CIPM MRA"" and CIPM-
46 MRA-D-04. All of the documents can be downloaded from the BIPM website. If this CMC is
47 reviewed according to CIPM-MRA-D-04, only CCQM-K120 can be used to support this CMC.
48 I think that it is too strict that only Key and Suppl. comparisons can be used as evidences,
49 and that other kinds of evidences can support CMCs if the evidences cover all the relevant
50 metrological aspects to support claims appropriately.

51 As mentioned above, the report "Calibration and measurement capabilities for propane"
52 including the interpolation scheme is not sufficient to support this CMC, or the report can't
53 be the evidence for this CMC. The result of CCQM-K111 does not also support uncertainty
54 of 0.2 % at 1 umol/mol.

55 VSL claimed that the result for 6 ppm standard gases with 0.08% uncertainty (k=1) can be
56 evidence for this CMC. I don't think uncertainty estimation is not enough because the un-
57 certainty of 0.08% includes only tau and sigma. Even if result of the uncertainty estimation
58 (u=0.08%) could be used as an evidence for this CMC, uncertainty at 1 umol/mol should
59 be larger than 0.96% (=0.08 * 2 * 6)."

1 Introduction and rationale

Laboratories and national metrology institutes (NMIs) are required to participate in interlaboratory comparisons to demonstrate their competence [1]. For NMIs, this requirement is laid down in the Mutual Recognition Arrangement of the International Committee on Weights and Measures [2]. Even if such a participation leads to a “satisfactory” performance [3], there remains the question how the result submitted should be viewed over the interval for which a calibration and measurement capability (CMC) is requested. These intervals can be very wide, and the expanded uncertainty of the submitted result may not be representative for the entire interval.

Looking at how expanded uncertainty should be evaluated, for the quantity of interest a measurement model should be formulated [4, 5] and the input quantities should be evaluated in such a fashion that the standard uncertainty computed for the output quantity is valid for the intervals of values contemplated for the input quantities. This is an ideal situation, and not all NMIs state such a measurement model, let alone evaluate the input quantities over the relevant intervals. It is important to emphasise that such requirements are not posed on participants in key comparisons [2, 6] or proficiency tests [7]. Alternatively, the expanded uncertainty of a CMC can be related to results in a key comparison if a measurand is assessed at different levels [8]. In gas analysis, there are examples of such key comparisons, including the first one [9] and the key comparisons on natural gas composition [9, 10, 11, 12].

In 2016, the Gas Analysis Working Group of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (GAWG) introduced an extrapolation scheme to be used for translating the measurement uncertainty reported in a key comparison to a calibration and measurement capability (CMC) [13]. This extrapolation scheme has a tipping point at $10 \mu\text{mol mol}^{-1}$. Below this amount fraction level, the expanded uncertainty is extrapolated absolute, and above relative. So, a relative expanded uncertainty of 1.0 % at $10 \mu\text{mol mol}^{-1}$ translates to an expanded uncertainty of 1.0 % at 0.1 mol mol^{-1} , and into a relative expanded uncertainty of 10 % at $1.0 \mu\text{mol mol}^{-1}$.

The introduction of this extrapolation scheme for calibration and measurement capabilities (CMCs) had some unfortunate side effects for VSL, especially for the services related to $\mu\text{mol mol}^{-1}$ - and %-levels of propane, carbon monoxide, carbon dioxide and methane. The claimed calibration and measurement capabilities for these services had to be increased for no other reason than that the extrapolation scheme [13] predicted something different from what can be justified on the basis of, e.g., the multipoint calibration of the analyser and propagating the uncertainty from gas mixture preparation [14, 15] and analysis [16], among other uncertainty sources.

For the measurement standards and related calibration and reference material services, there is another issue. The use of expanded uncertainties reported during the last three ‘track A’ key comparisons (assessing the ‘core capabilities’ of a national metrology institute [13]) provided $U_{\text{rel}}(x_0) = 0.07\%$ at amount fraction $x_0 = 10 \mu\text{mol mol}^{-1}$, a CMC that is not supported by direct evidence involving this group of measurement standards, such as the calculation of the measurement uncertainty using a calibration function or the evaluation of relevant long-term stability study data.

The decision was taken to revisit the data collected over the years concerning the status of the

98 national measurement standards (in most cases suites of Primary Standard gas Mixtures, PSMs) and
99 related measurement and preparative facilities and to develop for all groups of measurement standards
100 a customised extrapolation scheme that relates the expanded uncertainty for calibrations and reference
101 materials to the amount fractions for the entire range for which services are provided. A model for
102 calculating CMCs is presented, as well as an extrapolation scheme.

103 2 GAWG extrapolation scheme

The amount fraction range described in the GAWG Strategy [13] for a component runs in principle from the purity analysis up to 50 % The tipping point in the extrapolation scheme is at an amount fraction $x_0 = 10 \mu\text{mol mol}^{-1}$. For smaller amount fractions, the expanded uncertainty is assumed to be the same as for x_0 , and for greater amount fractions, the relative expanded uncertainty is assumed to be constant, viz., [13]

$$\begin{aligned} U(x) &= \frac{U(x_0)}{x_0} \cdot x && \text{for } x > x_0 \\ U(x) &= U(x_0) && \text{for } x \leq x_0 \end{aligned} \quad (1)$$

104 According to the same strategy document, calibration and measurement capabilities can be supported
105 in two different ways by key comparisons [13]:

- 106 1. a dedicated key comparison (track A or track C)
 - 107 2. for selected components and ranges, the combination of the last three track A key comparisons
- 108 Where possible, VSL seeks to support its CMCs though the default scheme, i.e., using dedicated key
109 comparisons. The flexible scheme, involving the last three track A key comparisons, is used in excep-
110 tional cases. In 2017, VSL was requested to resubmit their CMCs based on the performance in the last
111 three track A key comparisons. The pooling of the past three participations in track A key comparisons
112 gave a relative expanded uncertainty of 0.09 % at $x_0 = 10 \mu\text{mol mol}^{-1}$.

113 3 Calculation of CMCs

114 The basis for CMCs for this component is given in the measurement reports of key comparisons [17, 18].
115 The relative standard uncertainty from gravimetric gas mixture preparation is typically between 0.01 %
116 to 0.03 %, where the smallest uncertainties are associated with amount fraction in the percentage range,
117 and the largest with the parts-per-million range. Whereas these amount fractions and associated uncer-
118 tainties are at the basis the hierarchy of national measurement standards [19], they play a subordinate
119 role. It is important to bear in mind that for certified reference materials, ISO 6142-1 [14] is used,
120 which requires the standard uncertainty from gravimetric gas mixture preparation to be combined with
121 the verification uncertainty. This combination is carried out in accordance with ISO 6142 [20], which
122 implies that usually a slightly larger standard uncertainty is computed.

123 Hence, the CMCs for calibrations and for certified reference materials can be established on the same
124 footing, namely by considering the verification uncertainty only. ISO 6143 [16] requires evaluating the
125 uncertainty of the responses under reproducibility conditions, which is usually not done. Instead, the
126 long-term behaviour of primary standard gas mixtures (PSMs) has been considered, and based on the
127 verification data, the reproducibility of the entire system (gas mixture preparation and verification) has
128 been evaluated.

129 In the first stage, the data from monitoring selected PSMs has been evaluated using a mixed-effects
130 models as is customary in the evaluation of stability studies in reference material production [21, 22, 23]

$$y_i = \mu + At_i + B_i + \varepsilon_i \quad (2)$$

131 where y_i denotes the amount fraction of the i^{th} data point, μ the expected value at time 0, A the degra-
132 dation rate, t_i the time of the i^{th} data point, B_i the bias in data point i , and the random measurement
133 error ε_i . The mixed effects model in equation (2) is an extension of the simple mixed effects model for
134 stability study in reference material production [22, 23]. The term B_i enables accounting for an excess
135 variance [24] due to a reproducibility effect in the stability study measurements. For stable gas mixtures,
136 $A = 0$ and the model in equation (2) reduces to a random effects model as known from between-bottle
137 homogeneity studies [25] and meta-analysis [24], i.e.,

$$y_i = \mu + B_i + \varepsilon_i \quad (3)$$

138 This random effects model has been used for the re-evaluation of the CMCs for propane in nitrogen and
139 air.

140 In the following, the excess variance $\tau^2 = \text{var}(B_i)$ and the variance computed from the i^{th} measure-
141 ment $\sigma^2 = \text{var}(\varepsilon_i)$. The latter variance is the verification uncertainty and computed using the procedure
142 of ISO 6143 [16] and is known in ISO 6142-1 as “verification uncertainty”. The uncertainty contribu-
143 tion τ is a reproducibility component, to address the fact that the σ as computed is obtained under
144 repeatability conditions. For evaluating the long-term stability study data, the variance computed for
145 the last measurement is used in the subsequent meta-analysis. If there would be an improvement in the
146 performance of the measurement method, then this would result in an understatement of the standard
147 uncertainty of older measurements. Consequently, the value obtained for τ would be larger. For the
148 data for propane, the assumption that σ did not change during the stability study is justified, for there
149 have not been any meaningful improvements in the instrumentation and methods used.

150 The data from the gas mixtures used for long-term stability monitoring have been used. At regular
151 time intervals, these gas mixtures are analysed using a suite of Primary Standard gas Mixtures (PSMs).
152 The data of the stability study is then assessed for a trend [22]. If no trend is observed, the data is
153 then fitted to the DerSimonian-Laird model to assess whether there is an excess variance. This excess

154 variance is a reproducibility component, and calculated as [26]

$$\tau^2 = \frac{\sum_i w_i (y_i - \bar{y})^2 - (a - 1)}{\sum_i w_i - \sum_i w_i^2 / \sum_i w_i} \quad (4)$$

155 where $w_i = 1/s_i^2$, s_i denotes the within-group standard deviation, a the number of groups, and $\bar{y} =$
156 $\sum_i w_i \bar{y}_i / \sum_i w_i$. Similar to traditional ANOVA, in meta-analysis $\tau^2 = 0$ when the result of equation (4)
157 is negative.

158 The calibration and measurement capability is then calculated as

$$U(x) = k \sqrt{\tau^2 + \sigma^2} \quad (5)$$

159 where σ denotes the standard uncertainty computed in accordance with ISO 6143, k the coverage factor
160 and U the CMC. This computation is made for several amount fractions across the entire range for which
161 measurement standards of C_3H_8 in nitrogen and synthetic air are maintained. As stated previously, the
162 standard uncertainty associated with the amount fraction due to gravimetric gas mixture preparation is
163 small enough to be ignored.

164 4 Results and discussion

165 4.1 Propane in nitrogen

166 The first subrange of propane in nitrogen is the range of amount fractions from 0.5 % to 6.0 %. These
167 analyses are performed using a gas chromatograph with thermal conductivity detector (GC-TCD). The
168 calibration function is a second-order polynomial. Figure 1 shows the calibration data (top left), the
169 calibration function (bottom left), and the residuals in both directions (right-hand side). All residuals
170 meet the criteria of ISO 6143.

171 The datasets obtained for the other C_3H_8 subranges in nitrogen, i.e., 400 $\mu\text{mol mol}^{-1}$ to 2000 $\mu\text{mol mol}^{-1}$,
172 100 $\mu\text{mol mol}^{-1}$ to 1000 $\mu\text{mol mol}^{-1}$, 10 $\mu\text{mol mol}^{-1}$ to 100 $\mu\text{mol mol}^{-1}$, and 1 $\mu\text{mol mol}^{-1}$ to 10 $\mu\text{mol mol}^{-1}$,
173 are measured using a gas chromatograph with flame ionization detector (GC-FID). The calibration func-
174 tions for all of these amount fraction ranges are also quadratic and show full consistency with the criteria
175 of ISO 6143 for the residuals (see figures 2, 3, 4, and 5, respectively). In these figures, also the expanded
176 uncertainty from the gravimetric gas mixture preparation are depicted.

177 The results of the meta-analysis on the long-term stability study data are shown in table 1, while
178 the results of the international comparisons are summarised in table 2.

179 The relationship between the amount fraction and the standard uncertainty is visualised in fig-
180 ure 6. In the figures, also the results from CCQM-K3 [27], Euramet.QM-S4 [28], CCQM-K111 [17] and
181 Euramet.QM-S1 [29] are included. It is important to note that (1) the results in these comparisons were
182 consistent, and (2) the calculated standard uncertainty matches well with the standard uncertainties
183 summarised in table 1.

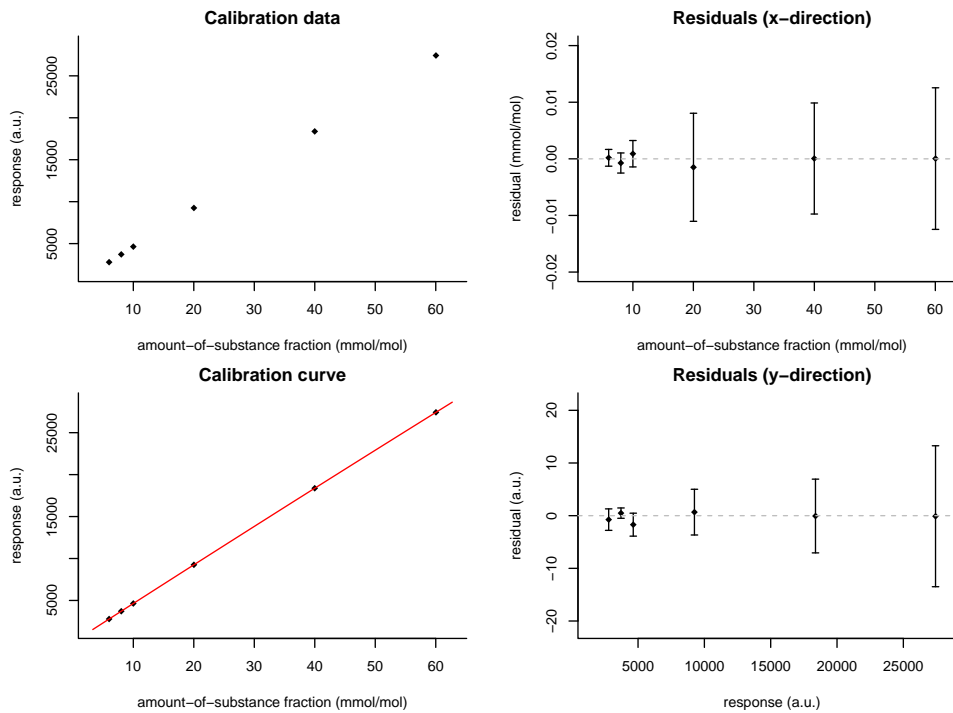


Figure 1: Calibration data, function and residuals for propane in nitrogen on a gas chromatograph with thermal conductivity detector (GC-TCD) calibrated in accordance with ISO 6143 [16]. The uncertainty bars represent 95 % coverage intervals.

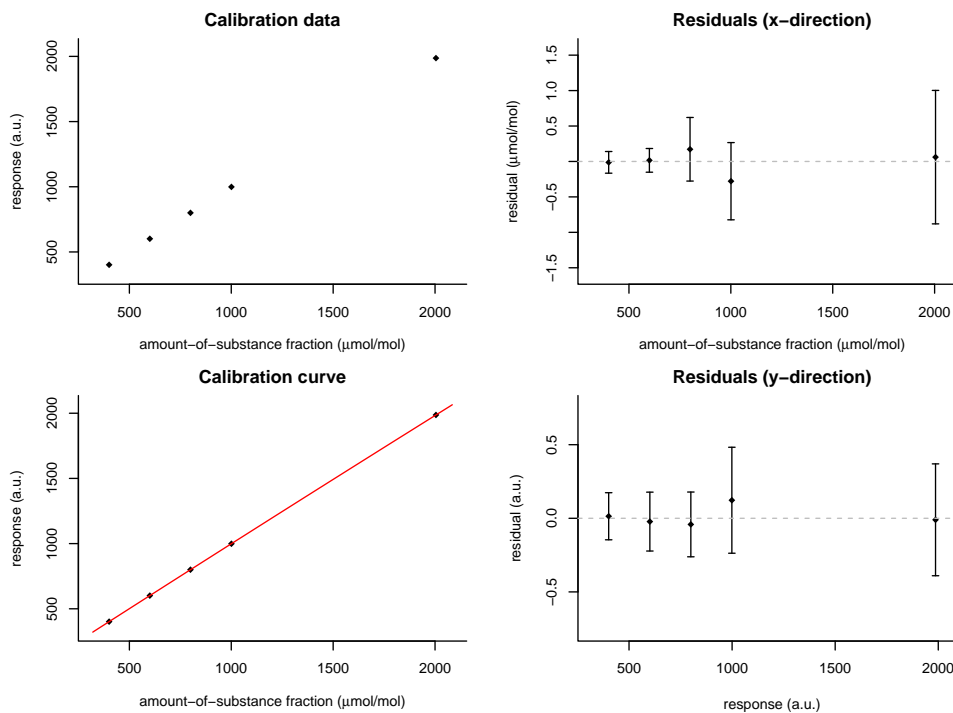


Figure 2: Calibration data, function and residuals for propane in nitrogen on a gas chromatograph with flame ionization detector (GC-FID) calibrated in accordance with ISO 6143 [16]. The uncertainty bars represent 95 % coverage intervals.

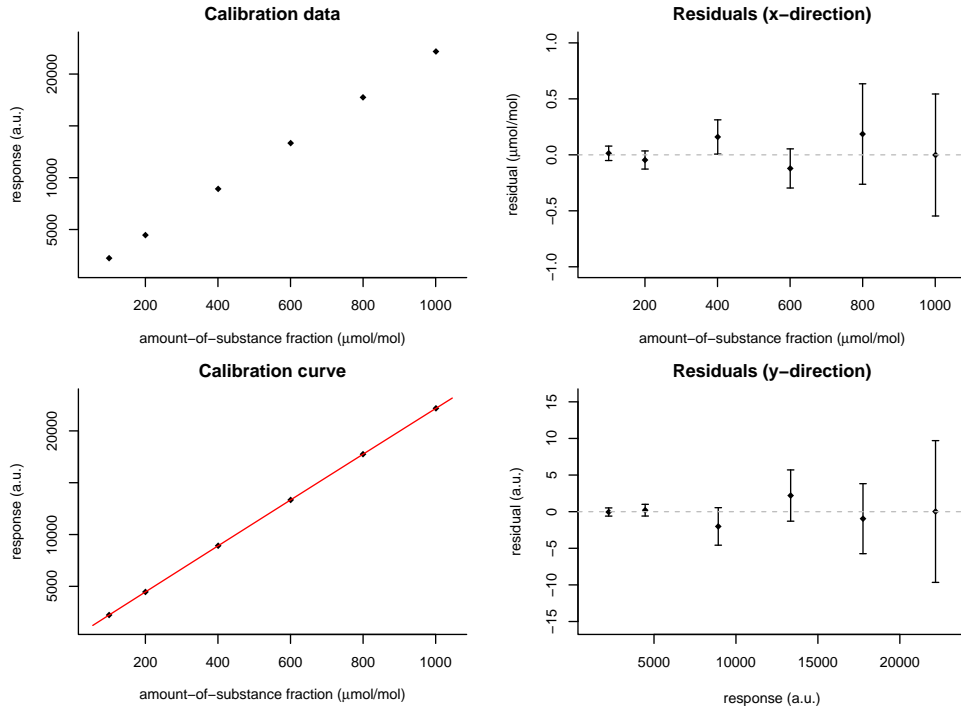


Figure 3: Calibration data, function and residuals for propane in nitrogen on a gas chromatograph with flame ionization detector (GC-FID) calibrated in accordance with ISO 6143 [16]. The uncertainty bars represent 95 % coverage intervals.

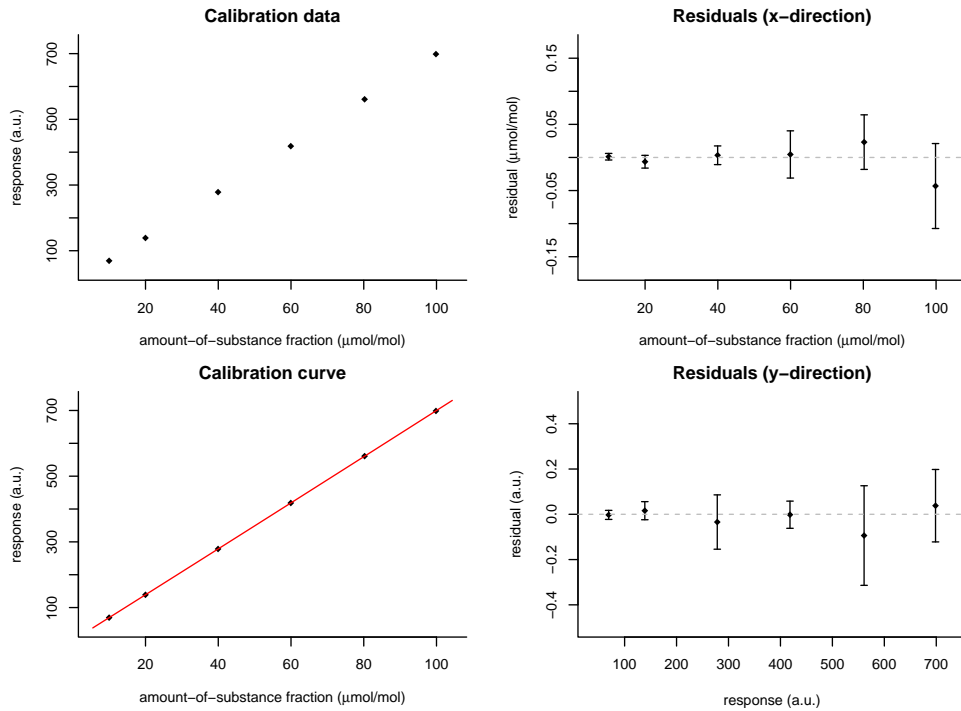


Figure 4: Calibration data, function and residuals for propane in nitrogen on a gas chromatograph with flame ionization detector (GC-FID) calibrated in accordance with ISO 6143 [16]. The uncertainty bars represent 95 % coverage intervals.

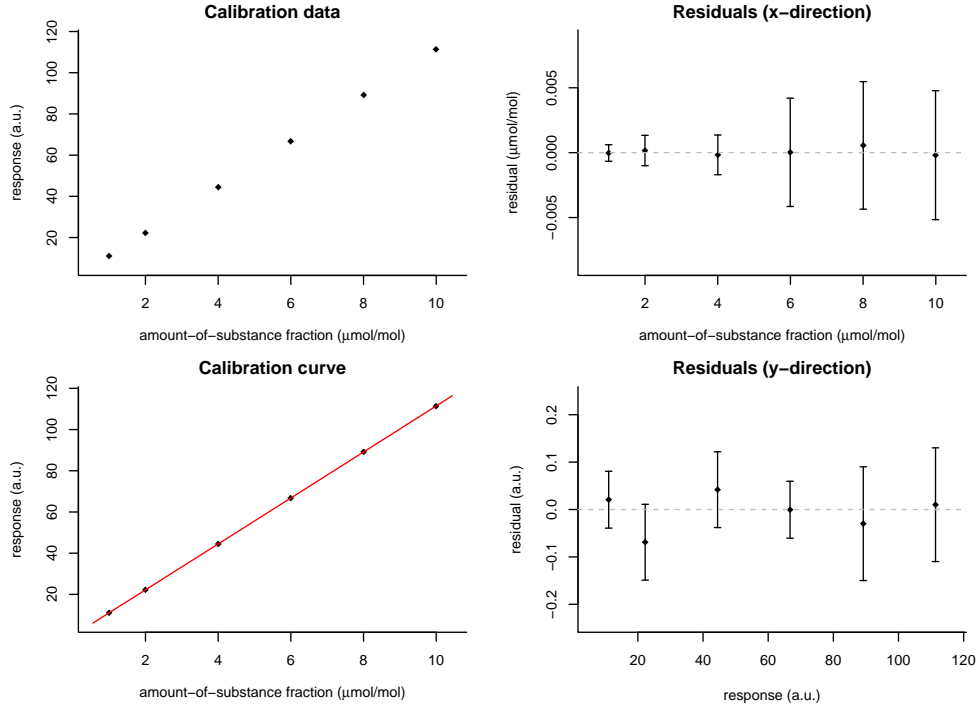


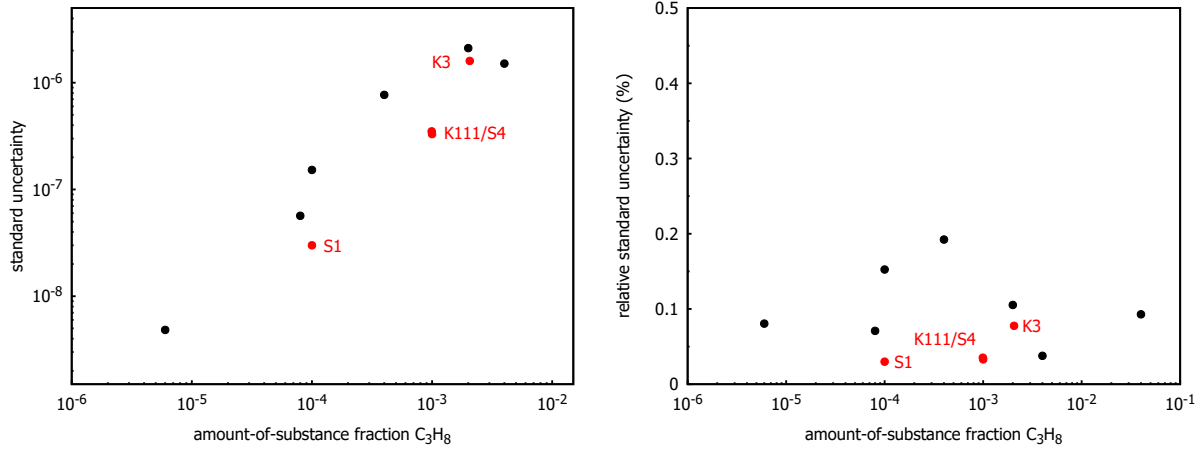
Figure 5: Calibration data, function and residuals for propane in nitrogen on a gas chromatograph with flame ionization detector (GC-FID) calibrated in accordance with ISO 6143 [16]. The uncertainty bars represent 95 % coverage intervals.

Table 1: Results from the meta-analysis performed on the calibration gas mixtures used to assess the long-term behaviour of propane in nitrogen mixtures. τ denotes the coefficient of variation between-groups, and σ that within-groups. x_0 denotes the amount fraction propane, as computed using ISO 6142-1.

Mixture	x_0	τ	σ	$\sqrt{\tau^2 + \sigma^2}$
VSL204667	4.00×10^{-2}	0.09 %	0.02 %	0.09 %
VSL117417	4.00×10^{-3}	0.01 %	0.04 %	0.04 %
VSL228555	2.00×10^{-3}	0.10 %	0.03 %	0.11 %
VSL104656	4.00×10^{-4}	0.19 %	0.03 %	0.19 %
PRM238552	1.00×10^{-4}	0.15 %	0.04 %	0.15 %
VSL307414	8.00×10^{-5}	0.06 %	0.04 %	0.07 %
VSL307401	6.00×10^{-6}	0.07 %	0.04 %	0.08 %

Table 2: Reported expanded uncertainty (including verification) in CCQM and Euramet comparisons; all results were consistent with the assigned value.

Project	x mol mol ⁻¹	$U(x)$ mol mol ⁻¹	$U_{\text{rel}}(x)$
CCQM-K3	2.06×10^{-3}	3.2×10^{-6}	0.16 %
Euramet.QM-S4	1.00×10^{-3}	6.6×10^{-7}	0.07 %
CCQM-K111	9.93×10^{-4}	7.0×10^{-7}	0.07 %
Euramet.QM-S1	1.00×10^{-4}	6.0×10^{-8}	0.06 %



(a) Standard uncertainty as a function of the amount fraction C_3H_8 in nitrogen. (b) Coefficient of variation as a function of the amount fraction C_3H_8 in nitrogen.

Figure 6: CMCs as a function of the fraction C_3H_8 in nitrogen.

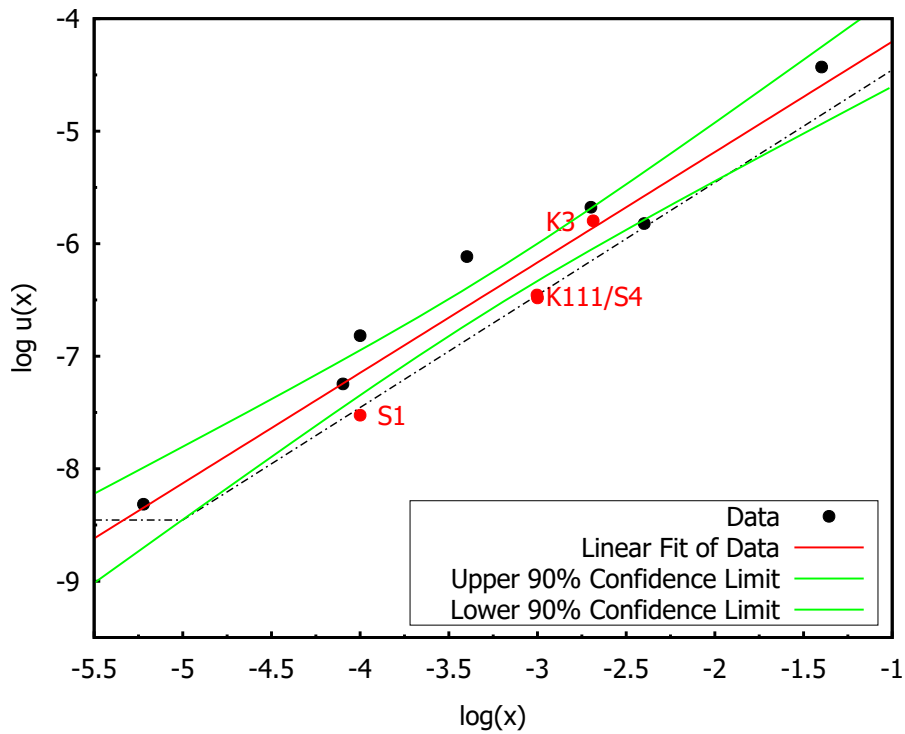


Figure 7: Regression of the standard uncertainty as a function of the amount fraction C_3H_8 in nitrogen. The dotted lines indicate the extrapolation scheme from the GAWG.

184 From figure 6a, it can be seen that in first approximation the data can be described by a model of
185 the kind

$$\log u = a_1 \log x + a_0 \quad (6)$$

186 where a_1 denotes the slope and a_0 the intercept. Comparing this model with equation (1), it has the
187 same shape for $x \geq x_0$ if the slope is set $a_1 = 1$, and for $x < x_0$ if $a_1 = 0$.

188 4.2 Propane in synthetic air

189 The analyses performed for the C_3H_8 subranges in synthetic air, i.e., $800 \mu\text{mol mol}^{-1}$ to $4000 \mu\text{mol mol}^{-1}$,
190 $20 \mu\text{mol mol}^{-1}$ to $600 \mu\text{mol mol}^{-1}$, and $1 \mu\text{mol mol}^{-1}$ to $80 \mu\text{mol mol}^{-1}$, are obtained using a gas chro-
191 matograph with flame ionization detector (GC-FID).

192 The first subrange is the range of amount fractions from 800 to $4000 \mu\text{mol mol}^{-1}$. The calibration
193 function is a second-order polynomial. Figure 8 shows the calibration data (top left), the calibration
194 function (bottom left), and the residuals in both directions (right-hand side). All residuals meet the
195 criteria of ISO 6143. In the figure, also the expanded uncertainty associated with the gravimetric gas
196 mixture preparation is shown.

197 The calibration function for the amount fraction range from 20 to $600 \mu\text{mol mol}^{-1}$ is also quadratic
198 (see figure 9). All residuals are meeting the criteria of ISO 6143, save the x-residuals at $40 \mu\text{mol mol}^{-1}$,
199 $80 \mu\text{mol mol}^{-1}$ and $100 \mu\text{mol mol}^{-1}$. Previous measurements in the same range showed full consistency
200 with the criteria of ISO 6143 for the residuals. In the figure, also the expanded uncertainty associated
201 with the gravimetric gas mixture preparation is shown.

202 The calibration function for the amount fraction C_3H_8 range from 1 to $80 \mu\text{mol mol}^{-1}$ is also quadratic
203 (see figure 10). All residuals meet the criteria of ISO 6143. In the figure, also the expanded uncertainty
204 associated with the gravimetric gas mixture preparation is shown.

205 The results of the meta-analysis on the long-term stability study data are shown in table 3. Note that
206 due to the lack of data from propane in synthetic air mixtures used for long-term stability monitoring,
207 the between-group standard deviations are calculated from the long-term stability data of the propane in
208 nitrogen mixtures. The results of the international comparisons Euramet.QM-S4 [28] and Euramet.QM-
209 S1 [29] are summarised in table 2.

210 The relationship between the amount fraction and the standard uncertainty is visualised in figure 11.
211 In the figures, also the results from Euramet.QM-S4 [28] and Euramet.QM-S1 [29] are included. Again,
212 it is important to note that (1) the results in these comparisons were consistent, and (2) the calculated
213 standard uncertainty matches well with the standard uncertainties summarised in table 3.

214 From figure 11a, it can be seen that in first approximation the data can be described by a model
215 of the kind as described by equation 6. Fitting the data using ordinary least squares (OLS) [30] yields
216 for $a_1 = 0.995$ (see figure 12). In the figure, the 90% coverage interval is also given. Two points lie
217 slightly outside the interval. The model gives a reasonable description of the data.

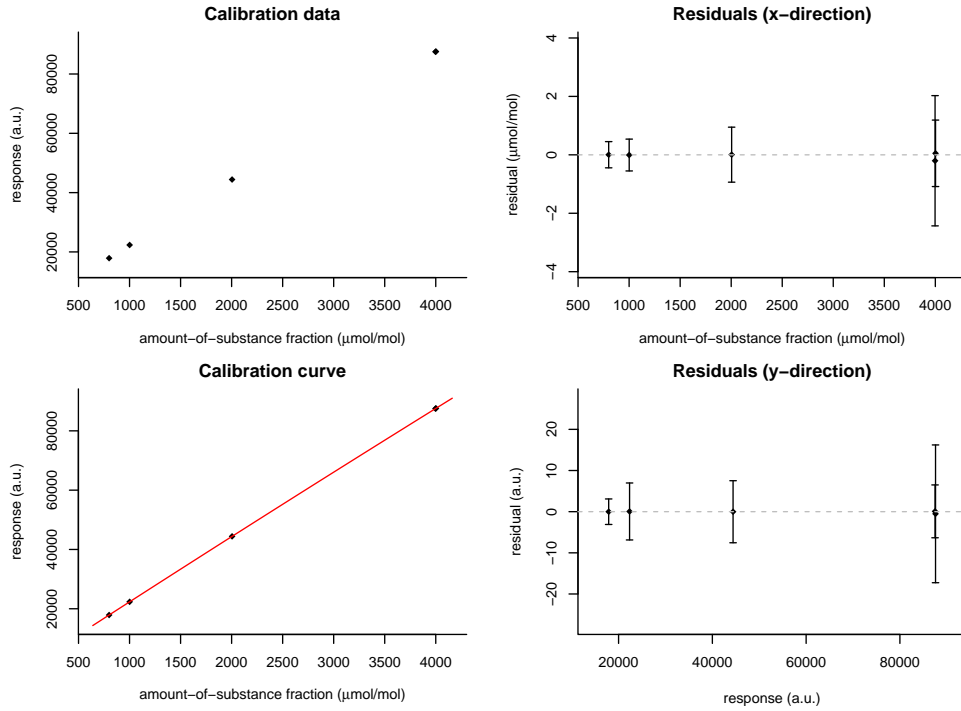


Figure 8: Calibration data, function and residuals for propane in synthetic air on a gas chromatograph with flame ionization detector (GC-FID) calibrated in accordance with ISO 6143 [16]. The uncertainty bars represent 95 % coverage intervals.

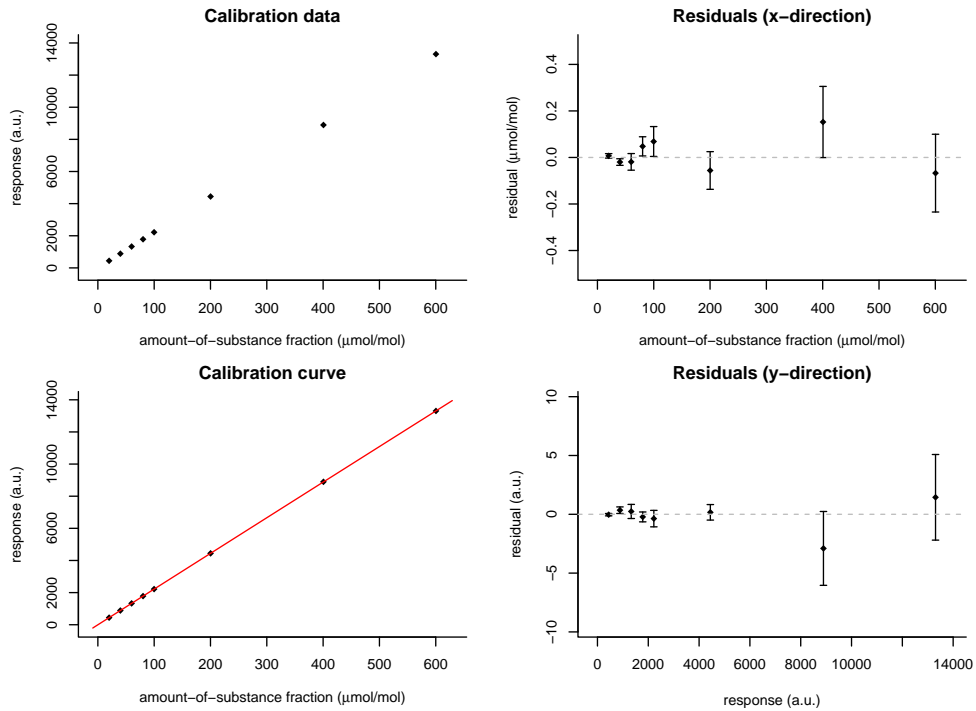


Figure 9: Calibration data, function and residuals for propane in synthetic air on a gas chromatograph with flame ionization detector (GC-FID) calibrated in accordance with ISO 6143 [16]. The uncertainty bars represent 95 % coverage intervals.

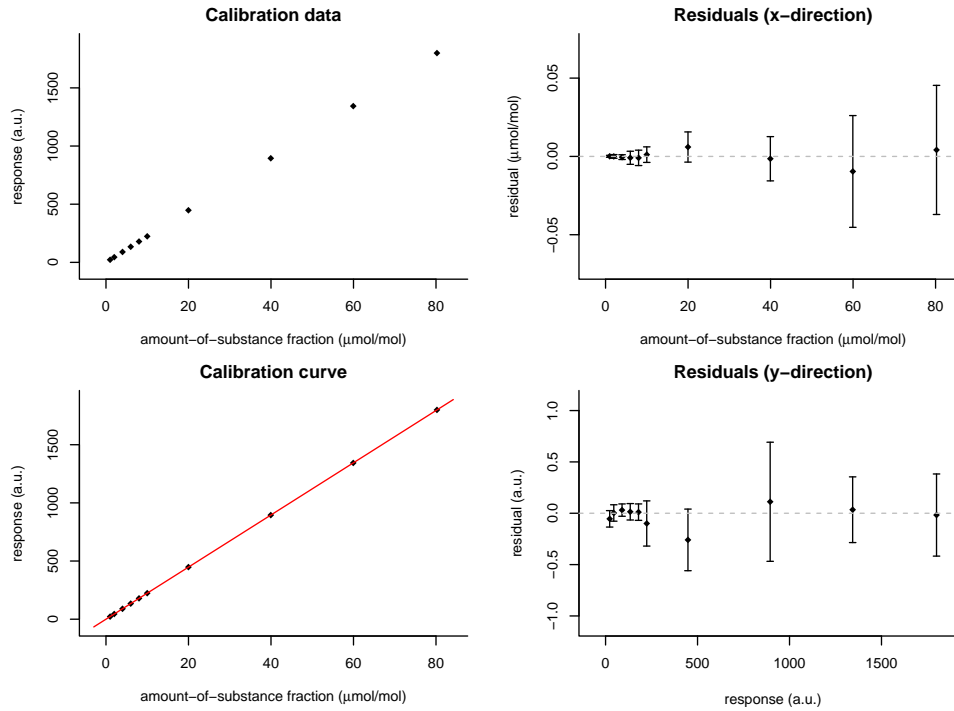
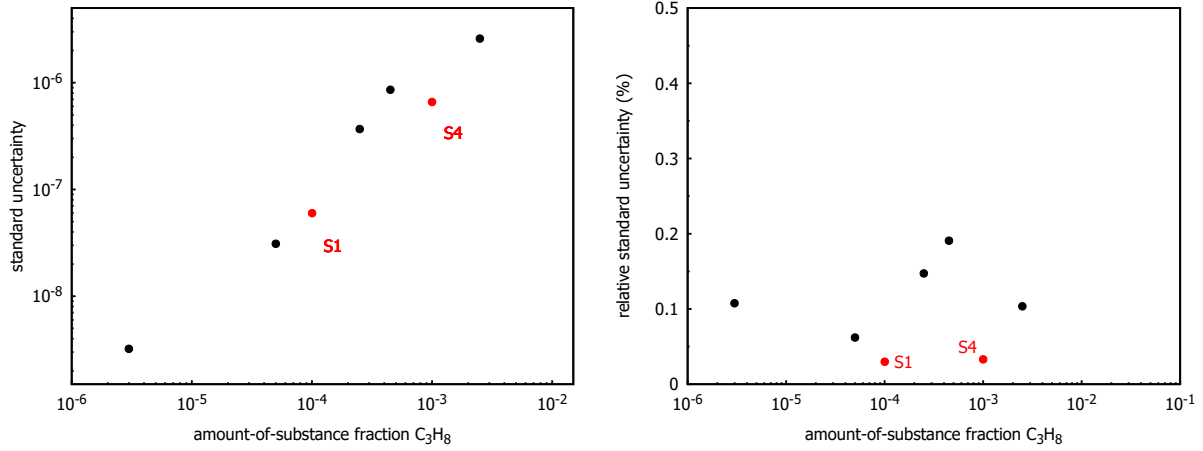


Figure 10: Calibration data, function and residuals for propane in synthetic air on a gas chromatograph with flame ionization detector (GC-FID) calibrated in accordance with ISO 6143 [16]. The uncertainty bars represent 95 % coverage intervals.

Table 3: Results from the meta-analysis performed on the calibration gas mixtures used to assess the long-term behaviour of propane in synthetic air mixtures. τ denotes the coefficient of variation between-groups, and σ that within-groups. Note that the calculation of τ is based on the long-term stability data of propane in nitrogen mixtures. x_0 denotes the amount fraction propane, as computed using ISO 6142-1.

Mixture ^a	x_0	σ	$\sqrt{\tau^2 + \sigma^2}$
PRM144624	2.50×10^{-3}	0.02 %	0.10 %
PRM149344	4.50×10^{-4}	0.02 %	0.19 %
PRM238554	2.50×10^{-4}	0.02 %	0.15 %
PRM238560	5.00×10^{-5}	0.02 %	0.06 %
PRM249133	2.99×10^{-6}	0.08 %	0.11 %

^apropane in synthetic air mixtures



(a) Standard uncertainty as a function of the amount fraction C₃H₈ in synthetic air. (b) Coefficient of variation as a function of the amount fraction C₃H₈ in synthetic air.

Figure 11: CMCs as a function of the fraction C₃H₈ in synthetic air.

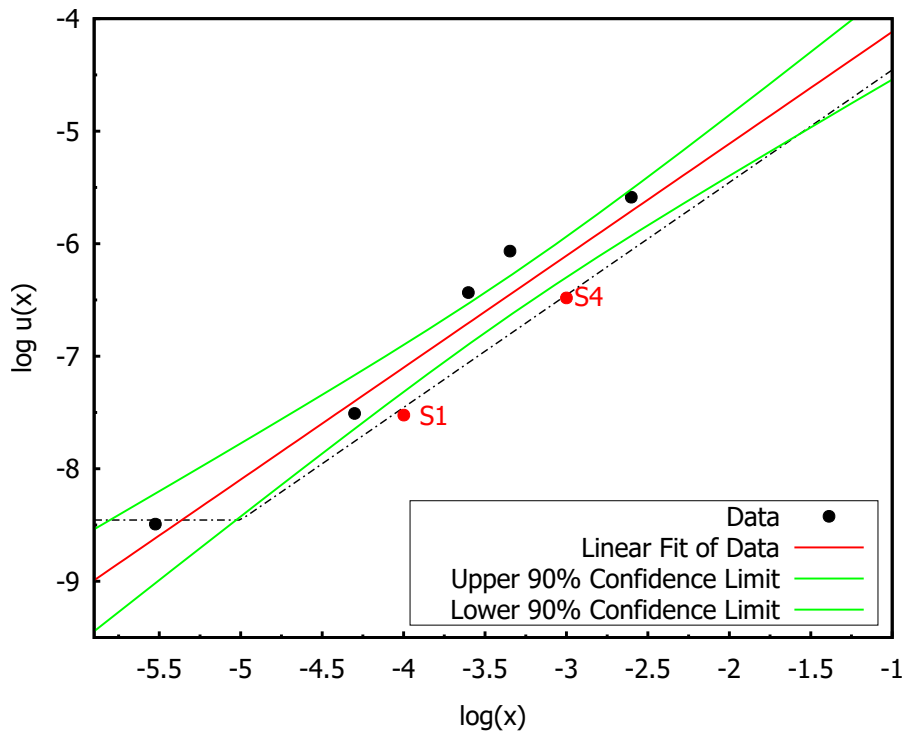


Figure 12: Regression of the standard uncertainty as a function of the amount fraction C₃H₈ in synthetic air. The dotted lines indicate the extrapolation scheme from the GAWG.

218 5 Interpolation scheme for CMCs

219 5.1 Propane in nitrogen

220 The current CMCs for propane in nitrogen range from 0.9% → 0.09% for amount fractions C₃H₈ from
221 1 μmol mol⁻¹ to 1%. Based on the calculations as presented, this relationship becomes

$$\log u = -3.223 + 0.981 \log x \quad (7)$$

222 which means a relative expanded uncertainty of 0.16% at 1 μmol mol⁻¹ to 0.13% at 1%.

223 5.2 Propane in synthetic air

224 The old CMC for propane in synthetic air was from 0.9% → 0.09% for amount fractions C₃H₈ from
225 1 μmol mol⁻¹ to 1%. Based on the calculations as presented, this relationship becomes

$$\log u = -3.123 + 0.995 \log x \quad (8)$$

226 which means a relative expanded uncertainty of 0.16% at 1 μmol mol⁻¹ to 0.15% at 1%. The expanded
227 uncertainties are slightly larger in air than in nitrogen.

228 6 Conclusions

229 The approach developed for relating the expanded uncertainty of the analysis of propane in nitrogen and
230 propane in synthetic air to the amount fraction provides satisfactory results. The use of meta-analysis
231 is helpful in characterising the dispersion due to, a combination of, reproducibility of the measurement
232 method, effects of cylinder walls and regulators. The standard deviation τ from the DerSimonian-
233 Laird model is combined with the standard uncertainty computed from the multipoint calibration from
234 ISO 6143 to determine the calibration and measurement capability (CMC), based on the verification
235 uncertainty under reproducibility conditions. The uncertainty from gravimetric gas mixture prepara-
236 tion is negligible in view of the verification uncertainty. The results of the participation in different
237 international comparisons agree well with the CMCs determined from the long-term behaviour of the
238 standards of propane in nitrogen and propane in synthetic air.

239 The dedicated extrapolation scheme gives quite similar results in comparison to the GAWG scheme.
240 For most amount fractions, the dedicated extrapolation scheme gives slightly higher values for the (rel-
241 ative) expanded uncertainty, which are concordant with empirical evidence. The proposed model for
242 calculating the CMCs works well from 1 μmol mol⁻¹ propane in nitrogen to the highest fractions in the
243 range. The same applies to the model for propane in air.

244 The differences between the two extrapolation schemes are at the edges. The GAWG extrapolation is
245 overly conservative, but that makes sense, as it is based on results from key comparisons of which there
246 are only a few below 10 μmol mol⁻¹. The long-term behaviour of the measurement standards indicate

247 that also below $10 \mu\text{mol mol}^{-1}$, the extrapolation using the relative expanded uncertainty is valid albeit
248 that it is not conservative. Hence, it is appropriate that NMIs seeking better support provide empirical
249 evidence. It is also known that the relative expanded uncertainty (slightly) decreases when the amount
250 fraction increases; this decrease is however small, yet for providing services at the high end of the range
251 still important.

252 References

- 253 [1] ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories.
254 ISO, International Organization for Standardization, Geneva, Switzerland, 2017. Third edition.
- 255 [2] CIPM. Mutual recognition of national measurement standards and of calibration and measurement
256 certificates issued by national metrology institutes, October 1999.
- 257 [3] ISO 13528 Statistical methods for use in proficiency testing by interlaboratory comparison. ISO,
258 International Organization for Standardization, Geneva, Switzerland, 2015. Second edition.
- 259 [4] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, and OIML. *Guide to the Expression of Uncertainty in*
260 *Measurement, JCGM 100:2008, GUM 1995 with minor corrections*. BIPM, 2008.
- 261 [5] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, and OIML. *Supplement 1 to the 'Guide to the Expression*
262 *of Uncertainty in Measurement' – Propagation of distributions using a Monte Carlo method, JCGM*
263 *101:2008*. BIPM, 2008.
- 264 [6] International Conference on Weights and Measures. Guidelines for CIPM key comparisons. Tech-
265 nical report, CIPM, Sèvres, France, 1999.
- 266 [7] ISO/IEC 17043 Conformity assessment – General requirements for proficiency testing. ISO, Inter-
267 national Organization for Standardization, Geneva, Switzerland, 2010. First edition.
- 268 [8] Katsuhiko Shirono and Maurice Cox. Statistical reassessment of calibration and measurement
269 capabilities based on key comparison results. *Metrologia*, 56(4):045001, jun 2019.
- 270 [9] A Alink. The first key comparison of primary standard gas mixtures. *Metrologia*, 37(1):35–49, feb
271 2000.
- 272 [10] A Alink and A M H van der Veen. Uncertainty calculations for the preparation of primary gas
273 mixtures. part 1: Gravimetry. *Metrologia*, 37(6):641–650, dec 2000.
- 274 [11] Adriaan M H van der Veen, Hans-Joachim Heine, Freek N C Brinkmann, Paul R Ziel, Ed W B
275 de Leer, Wang Lin Zhen, Kenji Kato, Leonid A Konopelko, Tatjana A Popova, Yuri I Alexandrov,
276 Elena N Kortchagina, Yuri A Kustikov, Stanislav Musil, Martin J T Milton, Franklin Guenther, and
277 George Rhoderick. International comparison CCQM-K16: Composition of natural gas types IV and
278 V. *Metrologia*, 42(1A):08003, 2005.

- 279 [12] Adriaan M H van der Veen, Paul R Ziel, Ed W B de Leer, Damian Smeulders, Laurie Besley, Val-
280 nei Smarçao da Cunha, Zei Zhou, Han Qiao, Hans-Joachim Heine, Jan Tichy, Teresa Lopez Esteban,
281 Tatiana Mace, Zsófia Nagyné Szilágyi, Jin-Chun Woo, Hyun-Kil Bae, Alejandro Perez Castorena,
282 Melina Perez Urquiza, Francisco Rangel Murillo, Victor M Serrano Caballero, Carlos E Carbajal
283 Alarcón, Carlos Ramírez Nambo, Manuel de Jesús Avila Salas, Agata Rakowska, Florbela Dias,
284 Leonid A Konopelko, Tatjana A Popova, V V Pankratov, M A Kovrizhnih, A V Meshkov, O V Efre-
285 mova, Yury A Kustikov, Stanislav Musil, Frantisek Chromek, Miroslava Valkova, and Martin J T Mil-
286 ton. Final report on international comparison CCQM-K23ac: Natural gas types I and III. *Metrolo-*
287 *gia*, 44(1A):08001–08001, dec 2006.
- 288 [13] P Brewer and A. M. H. van der Veen. GAWG strategy for comparisons and CMC claims. GAWG,
289 Gas Analysis Working Group, Sévres, France, October 2016.
- 290 [14] ISO 6142–1 Gas analysis – Preparation of calibration gas mixtures – Gravimetric method for Class I
291 mixtures. ISO, International Organization for Standardization, Geneva, Switzerland, 2015. First
292 edition.
- 293 [15] ISO 6145 Gas analysis – Preparation of calibration gas mixtures using dynamic methods. ISO
294 6145, International Organization for Standardization, Geneva, Switzerland. 11 parts.
- 295 [16] ISO 6143 Gas analysis – Comparison methods for determining and checking the composition of
296 calibration gas mixtures. ISO, International Organization for Standardization, Geneva, Switzer-
297 land, 2001. Second edition.
- 298 [17] Adriaan M H van der Veen, J Wouter van der Hout, Paul R Ziel, Rutger J Oudwater, Andreia L
299 Fioravante, Cristiane R Augusto, Mariana Coutinho Brum, Shinji Uehara, Dai Akima, Hyun Kil
300 Bae, Namgoo Kang, Jin-Chun Woo, Christina E Liaskos, George C Rhoderick, Mudalo Jozela,
301 James Tshilongo, Napo G Ntsasa, Angelique Botha, Paul J Brewer, Andrew S Brown, Sam Bartlett,
302 Michael L Downey, L A Konopelko, A V Kolobova, A A Pankov, A A Orshanskaya, and O V Efremova.
303 International comparison CCQM-K111 — Propane in nitrogen. *Metrologia*, 54(1A):08009–08009,
304 jan 2017.
- 305 [18] Adriaan M H van der Veen, J Wouter van der Hout, Paul R Ziel, Mudalo Jozela, James Tshilongo,
306 Napo G Ntsasa, and Angelique Botha. International comparison CCQM-K111.1 — Propane in
307 nitrogen. *Metrologia*, 54(1A):08022–08022, jan 2017.
- 308 [19] ISO 14167 Gas analysis – General quality aspects and metrological traceability of calibration gas
309 mixtures. ISO, International Organization for Standardization, Geneva, Switzerland, 2018. First
310 edition.
- 311 [20] ISO 6142 Gas analysis – Preparation of calibration gas mixtures – Gravimetric method. ISO,
312 International Organization for Standardization, Geneva, Switzerland, 2001. Second edition.

- 313 [21] T. P. J. Linsinger, J. Pauwels, A. M. H. van der Veen, H. Schimmel, and A. Lamberty. Homogeneity
314 and stability of reference materials. *Accreditation and Quality Assurance*, 6(1):20–25, jan 2001.
- 315 [22] Adriaan M. H. van der Veen, Thomas P. J. Linsinger, Andree Lamberty, and Jean Pauwels. Uncer-
316 tainty calculations in the certification of reference materials. 3. Stability study. *Accreditation and*
317 *Quality Assurance*, 6(6):257–263, may 2001.
- 318 [23] ISO Guide 35 Reference materials – Guidance for characterization and assessment of homogeneity
319 and stability. ISO, International Organization for Standardization, Geneva, Switzerland, 2017.
320 Fourth edition.
- 321 [24] Guido Schwarzer, James R Carpenter, and Gerta Rücker. *Meta-Analysis with R (Use R!)*. Springer,
322 2015.
- 323 [25] A. M. H. van der Veen, T. P. Linsinger, and J. Pauwels. Uncertainty calculations in the certification
324 of reference materials. 2. Homogeneity study. *Accreditation and Quality Assurance*, 6(1):26–30,
325 jan 2001.
- 326 [26] Rebecca DerSimonian and Nan Laird. Meta-analysis in clinical trials. *Controlled Clinical Trials*,
327 7(3):177–188, 1986.
- 328 [27] A M H van der Veen. CCQM key comparison CCQM-K3 of measurements of CO, CO₂, and C₃H₈
329 in N₂. *Metrologia*, 39(1):121–122, feb 2002.
- 330 [28] Adriaan M H van der Veen, Rutger Oudwater, Paul R Ziel, Janneke I T van Wijk, Cristiane Ro-
331 drrigues Augusto, Andreia de Lima Fioravante, Claudia Cipriano Ribeiro, Denise Cristine Gonçalves
332 Sobrinho, Valnei Cunha, Florbela Dias, Gonçalo Baptista, Angelique Botha, Miroslava Valkova,
333 and Zuzana Durisova. Supplementary comparison EURAMET.QM-S4: automotive gas mixtures.
334 *Metrologia*, 48(1A):08016, 2011.
- 335 [29] Maite López, Belén Martín, Florbela Dias, Michela Segá, Elena Amico di Meane, and Rob Wessel.
336 Final report on comparison EURO.QM-S1: Automotive exhaust gas. *Metrologia*, 45(1A):08003,
337 2008.
- 338 [30] Norman R. Draper and Harry Smith. *Applied Regression Analysis*. Wiley-Blackwell, apr 1998.