

Calibration and measurement capabilities for methane in nitrogen and air[†]

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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-of-substance 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 an absolute expanded uncertainty of $0.1 \mu\text{mol mol}^{-1}$ at $1.0 \mu\text{mol mol}^{-1}$ (= 10 % relative).

This report revisits the calibration and measurement capabilities for the measurement of the fraction methane in nitrogen and 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.

Based on the analysis, the relationship between standard uncertainty and amount-of-substance fraction can be described as $\log u = -3.291 + 0.909 \log x$. The relative expanded uncertainty ranges from 0.4 % at $0.5 \mu\text{mol mol}^{-1}$ to 0.12 % at 2 cmol mol^{-1} in air or nitrogen. There is no meaningful difference in uncertainty between the measurement of the amount-of-substance fraction methane in nitrogen and that in (synthetic) air.

1 Introduction and rationale

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 calibration and measurement capability (CMC) [1]. This extrapolation scheme has a tipping point at $10 \mu\text{mol mol}^{-1}$. Below this amount-of-substance 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 an absolute expanded uncertainty of $0.1 \mu\text{mol mol}^{-1}$ 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 ppm-levels of nitrogen monoxide and propane. The claimed calibration and measurement capabilities for these services had to

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be increased for no other reason than that the extrapolation scheme [1] predicted something different from that what could be justified on the basis of, e.g., the multipoint calibration of the analyser and propagating the uncertainty from gas mixture preparation [2, 3] and analysis [4], among other uncertainty sources.

The decision was taken to revisit the data collected over the years concerning the status of the national measurement standards (in most cases suites of Primary Standard gas Mixtures, PSMs) and related measurement and preparative facilities and to develop for all groups of measurement standards a customised extrapolation scheme that relates the expanded uncertainty for calibrations and reference materials to the amount-of-substance fractions for the entire range for which services are provided.

This paper describes the calculation of CMCs for methane, and the development of a customised extrapolation scheme. VSL participated in the following international comparisons for methane in air: CCQM-P41 [5, 6] and in key comparison CCQM-K82 [7] and comparison organized within the project EMRP ENV52 “Metrology for high-impact greenhouse gases”. As the results of CCQM-P41 have been superseded by the results obtained in CCQM-K82 and the comparison in the project EMRP ENV52, these have not been included in this work.

2 Default extrapolation scheme

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

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

According to the same strategy document, calibration and measurement capabilities can be supported in two different ways by key comparisons [1]:

1. a dedicated key comparison (track A, track B, or track C)
2. for selected components and ranges, the combination of the last three track A key comparisons

Where possible, VSL seeks to support its calibration and measurement capabilities through the default scheme, i.e., using dedicated key comparisons. The flexible scheme, involving the last three track A key comparisons, is used in exceptional cases. In 2017, VSL was requested to resubmit their CMCs based on the performance in the last three track A key comparisons. The pooling of the past three participations in track A key comparisons gave an relative expanded uncertainty of 0.09% at $x_0 = 10 \mu\text{mol mol}^{-1}$.

3 Uncertainty calculations

The calculation of CMCs is based on the following mixed effects model

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

where y_i denotes the amount-of-substance fraction of the i^{th} data point, μ the expected value at time $t = 0$, A the degradation rate, t_i the time of the i^{th} data point, B_i the bias in data point i , and the random

measurement error ε_i . The mixed effects model in equation (2) is an extension of the simple mixed effects model for stability study in reference material production [8, 9]. The term B_i enables accounting for an excess variance [10] due to a reproducibility effect in the stability study measurements. For stable gas mixtures, $A = 0$ and the model in equation (2) reduces to a random effects model as known from between-bottle homogeneity studies [11] and meta-analysis [10], i.e.,

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

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

In the following, the excess variance $\tau^2 = \text{var}(B_i)$ and the variance computed from the i^{th} measurement $\sigma^2 = \text{var}(\varepsilon_i)$. The latter variance is computed using the procedure of ISO 6143 [4]. For evaluating the long-term stability study data, the variance computed for the last measurement is used in the subsequent meta-analysis. If there would be an improvement in the performance of the measurement method, then this would result in an understatement of the standard uncertainty of older measurements. Consequently, the value obtained for τ would be larger. For the data for propane, the assumption that σ did not change during the stability study is justified, for there have not been any meaningful improvements in the instrumentation and methods used.

The data from the gas mixtures used for long-term stability monitoring have been used. At regular time intervals, these gas mixtures are analysed using a suite of Primary Standard gas Mixtures (PSMs). The amount-of-substance fraction is calculated in accordance with ISO 6143 [4]. For this purpose, the calibration function is used [12]. The data of the stability study is then assessed for a trend [8]. If no trend is observed, the data is then fitted to the DerSimonian-Laird model to assess whether there is an excess variance. This excess variance is a reproducibility component, and calculated as [13]

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

where \bar{Y}_i denotes a group mean, $w_i = 1/s_i^2$, s_i the within-group standard deviation, a the number of groups, and $\bar{\bar{Y}} = \sum_i w_i \bar{Y}_i / \sum_i w_i$. Similar to traditional ANOVA, in meta-analysis $\tau^2 = 0$ when the result of equation (4) is negative. The meta-analysis using the DL-method does not use pooling of the within-group variances.

The calibration and measurement capability is determined as

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

where σ denotes the standard uncertainty computed in accordance with ISO 6143, k the coverage factor and $U(x)$ the CMC. This computation was made for several amount-of-substance fractions across the entire range for which measurement standards of CH₄ in nitrogen and in synthetic air are maintained.

In the frame of the EMRP project ENV52 ‘‘Metrology for high-impact greenhouse gases’’, an experimental programme was carried out to optimise the analytical method for determining the amount-of-substance fraction methane in synthetic air at ambient levels (approximately 1.8 $\mu\text{mol mol}^{-1}$). The data of this study have been used to determine the reproducibility component of these measurements after optimisation. For this purpose, the data have been fitted using the random effects model

4 Results and discussion

Methane standards in nitrogen are maintained in the range from 1 $\mu\text{mol mol}^{-1}$ to 30 cmol mol^{-1} , whereas methane measurement standards in synthetic range are maintained in the range from 1 $\mu\text{mol mol}^{-1}$

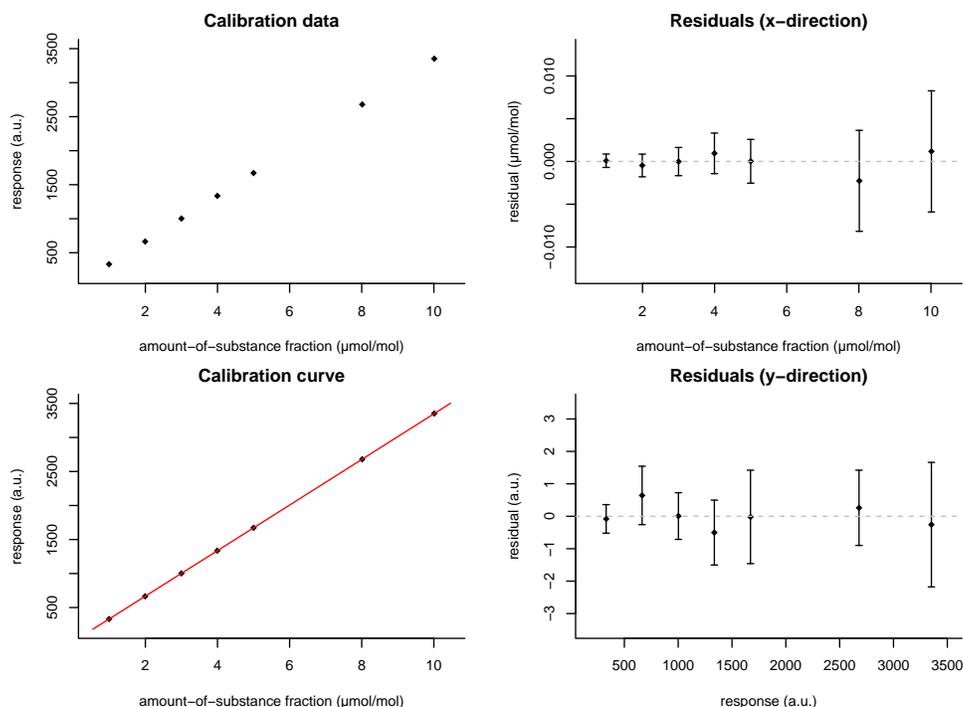


Figure 1: Calibration data, function and residuals for methane in nitrogen on GC-FID calibrated in accordance with ISO 6143 [4]. The uncertainty bars represent 95 % coverage intervals.

to $2.2 \text{ cmol mol}^{-1}$. The analyses up to $2.2 \text{ cmol mol}^{-1}$ are performed using a gas chromatograph with flame ionisation detector (GC-FID). The analyses above that fraction are performed using gas chromatograph with thermal desorption detector (GC-TCD).

The calibration function for all sub ranges is a second-order polynomial. Figures from 1 to figure 9 shows the calibration data (top left), the calibration function (bottom left), and the residuals in both directions (right-hand side). The first sub-range is the amount-of-substance fractions from $1 \mu\text{mol mol}^{-1}$ to from $10 \mu\text{mol mol}^{-1}$ in synthetic air.

The calibration function for the amount -of-substance fraction range from $1 \mu\text{mol mol}^{-1}$ to $10 \mu\text{mol mol}^{-1}$ in nitrogen is shown at the figure 1. All residuals meet the criteria of ISO 6143.

The calibration function for the amount-of-substance fraction for the range $10 \mu\text{mol mol}^{-1}$ to $100 \mu\text{mol mol}^{-1}$ in nitrogen is shown at the figure 2. All residuals meet the criteria of ISO 6143.

The calibration function for the amount-of-substance fraction range from $10 \mu\text{mol mol}^{-1}$ to $100 \mu\text{mol mol}^{-1}$ in synthetic air shown at the figure 3 show full consistency with the criteria of ISO 6143 for the residuals.

Figure 5 present the calibration function for amount-of-substance fractions from $100 \mu\text{mol mol}^{-1}$ to $1000 \mu\text{mol mol}^{-1}$ in synthetic air. All residuals meet the criteria of ISO 6143.

The calibration function for the amount-of-substance fraction for the $100 \mu\text{mol mol}^{-1}$ to $1000 \mu\text{mol mol}^{-1}$ in nitrogen is shown at the figure 4. All residuals meet the criteria of ISO 6143.

Figure 6 shows the calibration function for the amount-of-substance fraction for subrange from $0.1 \text{ cmol mol}^{-1}$ to 1 cmol mol^{-1} in nitrogen. All residuals but one meet criteria of ISO 6143.

The calibration function for the amount-of-substance fraction range from $0.1 \text{ cmol mol}^{-1}$ to 1 cmol mol^{-1} in synthetic air (see figure 7) shows consistency with the criteria of ISO 6143 for the residuals.

The calibration function and residuals for amount-of-substance fraction range from 1 cmol mol^{-1} to 10 cmol mol^{-1} are shown at the figure 8 in nitrogen. All residuals meet criteria of ISO 6143.

Figure 9 shows the calibration function for the amount-of-substance fraction for the range 5 cmol mol^{-1}

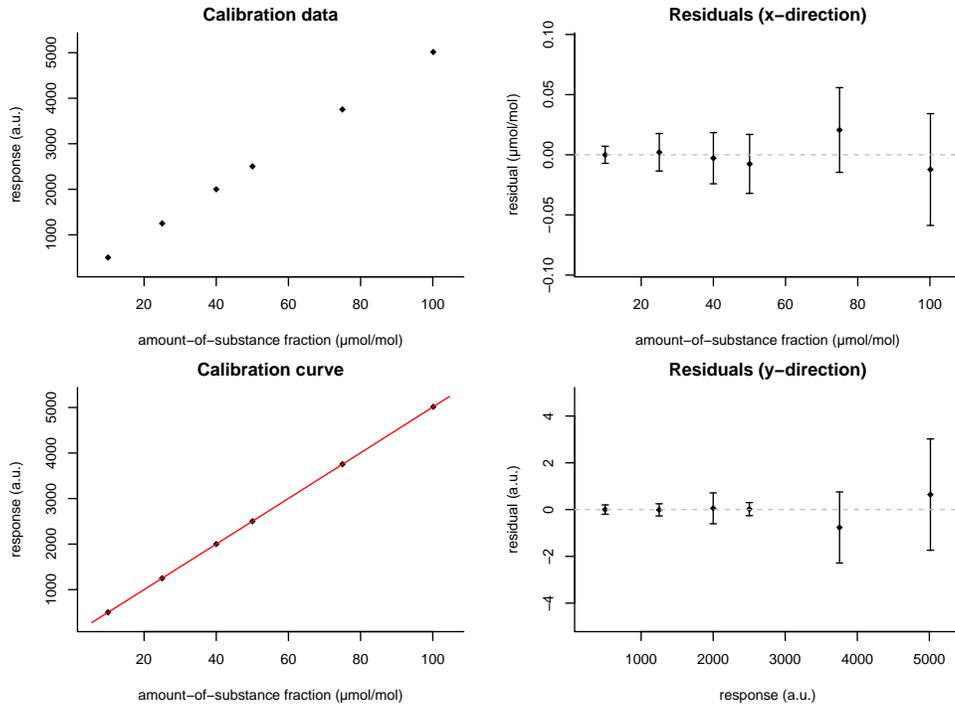


Figure 2: Calibration data, function and residuals for methane in nitrogen on GC-FID calibrated in accordance with ISO 6143 [4]. The uncertainty bars represent 95 % coverage intervals.

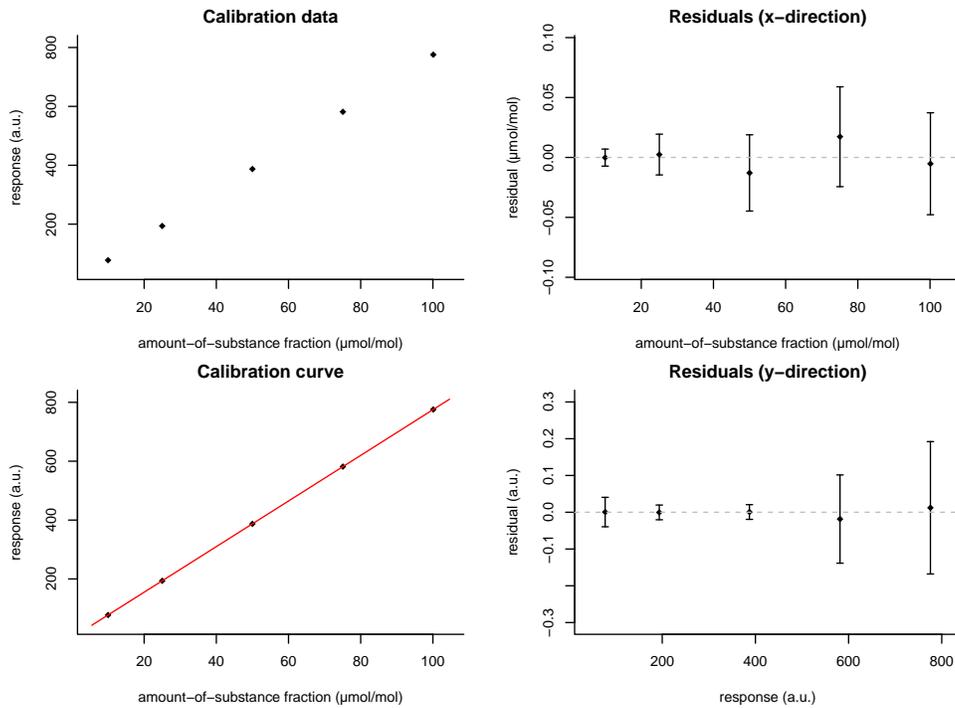


Figure 3: Calibration data, function and residuals for methane in synthetic air on GC-FID calibrated in accordance with ISO 6143 [4]. The uncertainty bars represent 95 % coverage intervals.

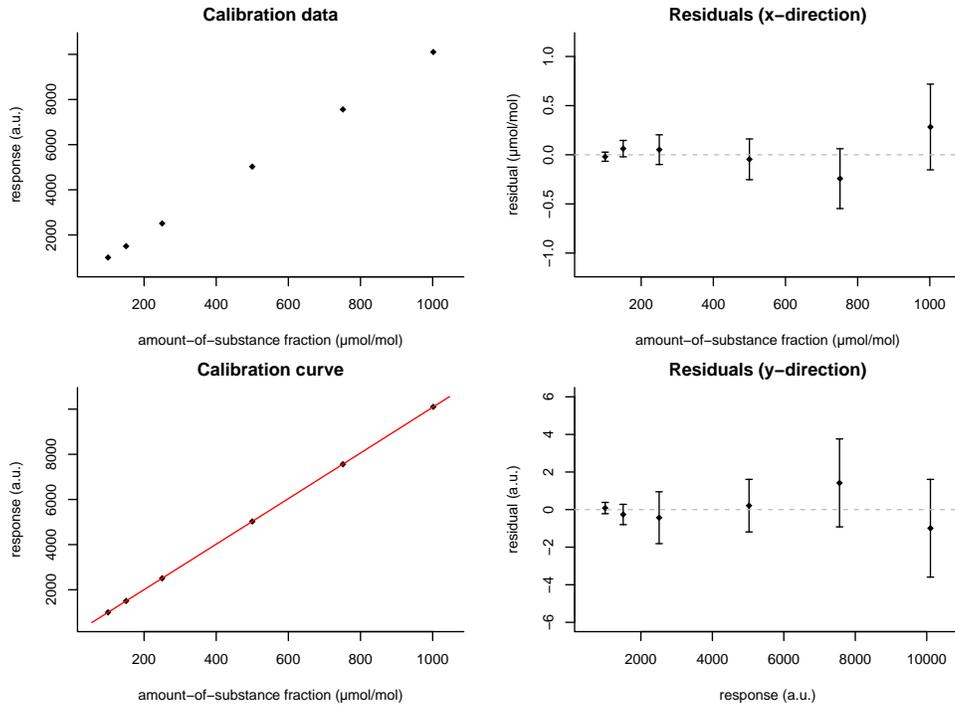


Figure 4: Calibration data, function and residuals for methane in nitrogen on GC-FID calibrated in accordance with ISO 6143 [4]. The uncertainty bars represent 95 % coverage intervals.

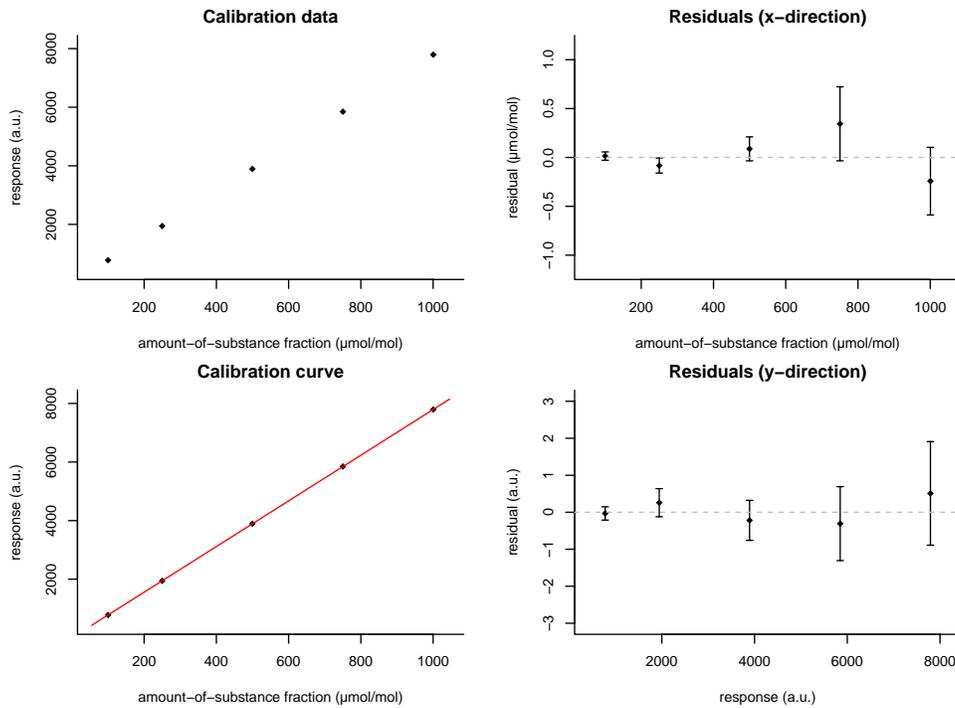


Figure 5: Calibration data, function and residuals for methane in synthetic air on GC-FID calibrated in accordance with ISO 6143 [4]. The uncertainty bars represent 95 % coverage intervals.

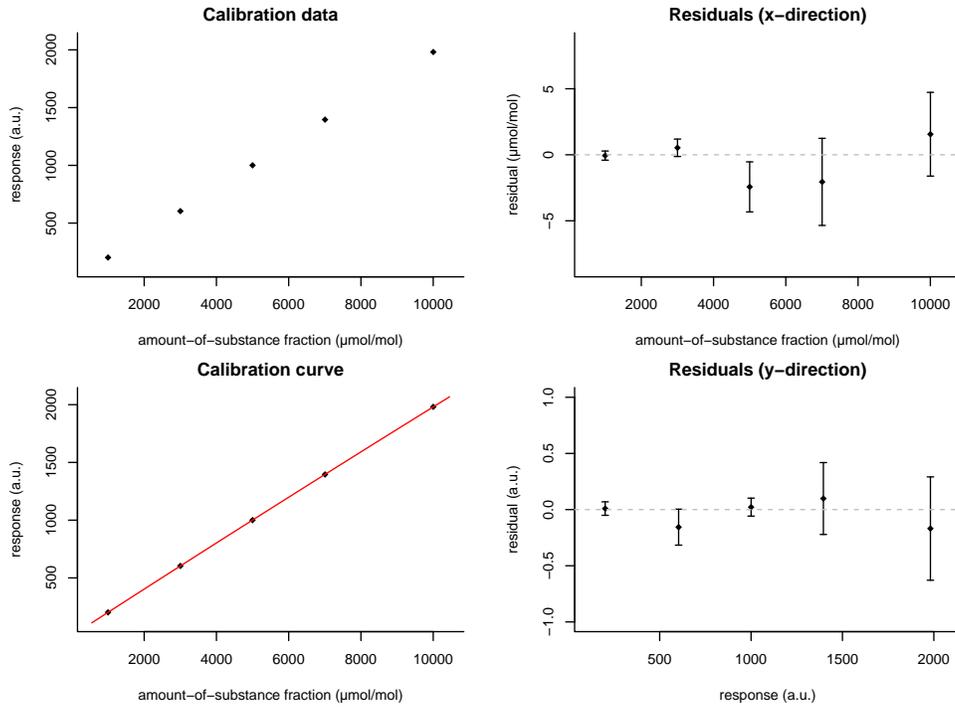


Figure 6: Calibration data, function and residuals for methane in nitrogen on GC-FID calibrated in accordance with ISO 6143 [4]. The uncertainty bars represent 95 % coverage intervals.

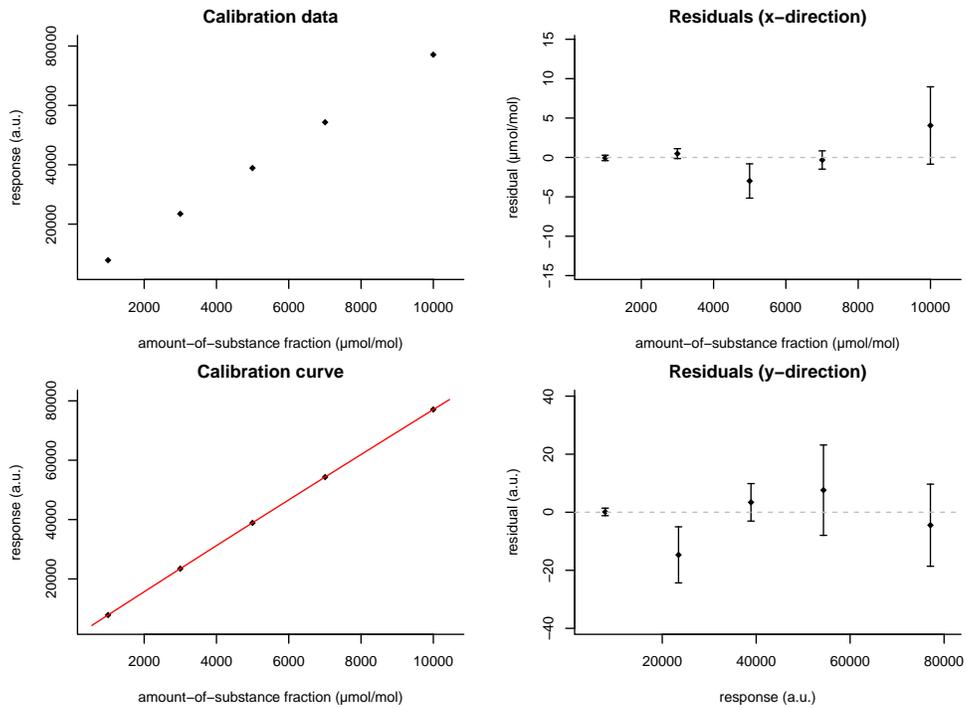


Figure 7: Calibration data, function and residuals for methane in synthetic air on GC-FID calibrated in accordance with ISO 6143 [4]. The uncertainty bars represent 95 % coverage intervals.

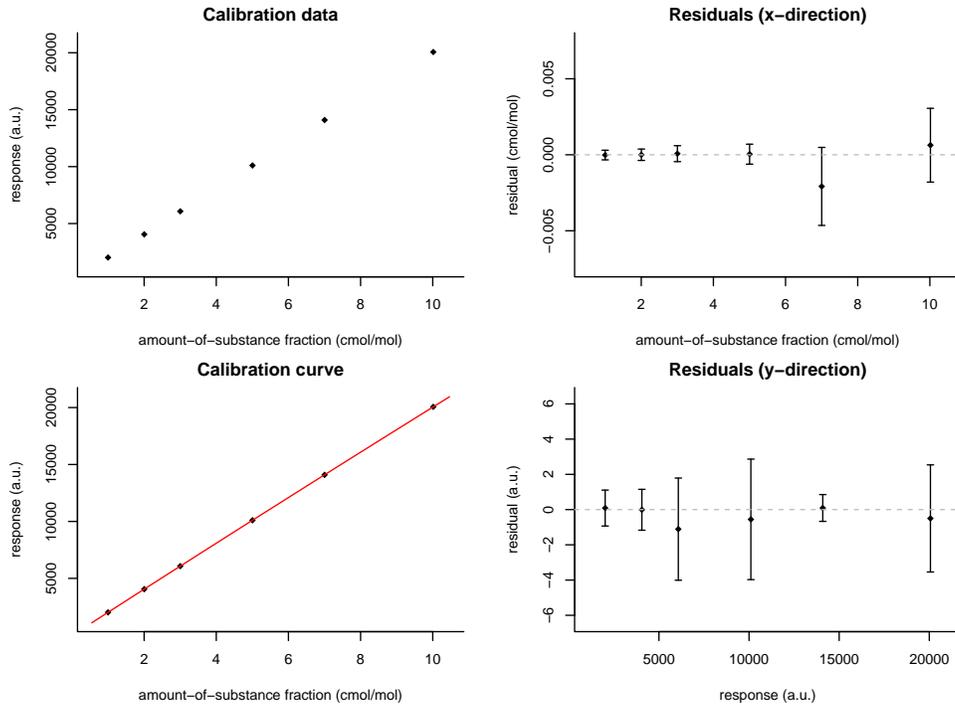


Figure 8: Calibration data, function and residuals for methane in nitrogen on GC-TCD calibrated in accordance with ISO 6143 [4]. The uncertainty bars represent 95 % coverage intervals.

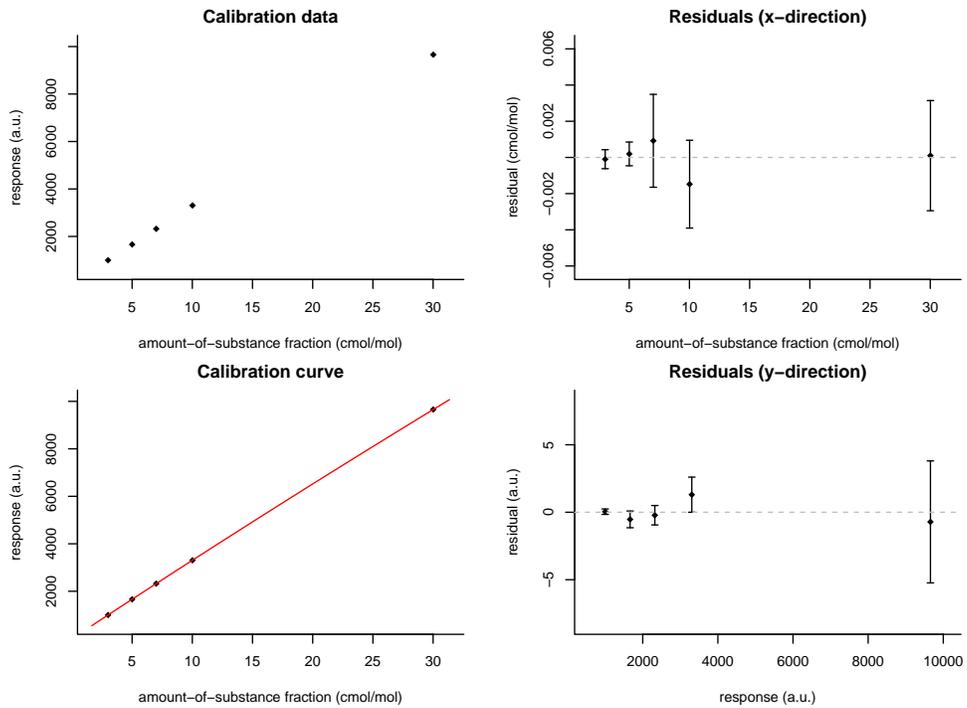
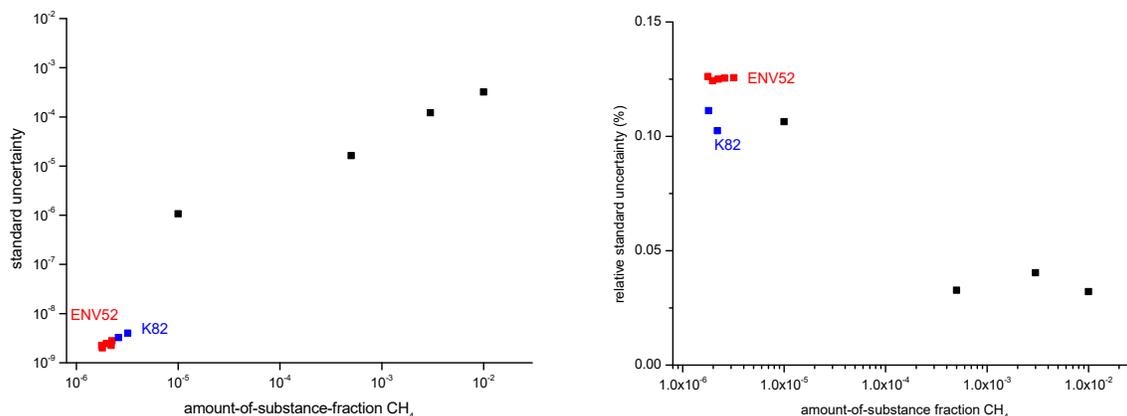


Figure 9: Calibration data, function and residuals for methane in nitrogen on GC-TCD calibrated in accordance with ISO 6143 [4]. The uncertainty bars represent 95 % coverage intervals.

to 30 cmol mol^{-1} in nitrogen. All residuals meet the criteria of ISO 6143 for the residuals.

The results of the meta-analysis on the long-term stability for the amount-of-substance fraction above $10 \mu\text{mol mol}^{-1}$ are shown in the table 2. The between-group standard deviations (expressed as coefficient of variation) is typically below 0.1 %.



(a) Standard uncertainty as a function of the amount-of-substance fraction CH₄ (b) Coefficient of variation as a function of the amount-of-substance fraction CH₄

Figure 10: CMCs as a function of the fraction CH₄

In the framework of the project EMRP ENV52, an extensive study has been performed on the reproducibility of methane-in-air measurements at ambient level. The stability study data have been processed using the random effects model as underlying the DL model. Instead of using the DL model, a Bayesian model has been used, using weakly informative prior probability distributions on the parameters. Details of this model are given elsewhere [15]. The results are summarised in table 1.

Table 1: Deviation with respect to gravimetry (μ), excess standard deviation (τ), repeatability standard deviation σ , expressed relative to the gravimetric amount-of-substance fraction methane

Mixture	μ %	$s(\mu)$ %	τ %	$s(\tau)$ %	σ %	$s(\sigma)$ %
VSL220184	-0.002	0.059	0.168	0.052	0.083	0.010
VSL249187	0.172	0.042	0.114	0.039	0.079	0.009
VSL144110	0.077	0.052	0.146	0.047	0.083	0.010
VSL144498	0.111	0.051	0.143	0.046	0.083	0.010
VSL208589	0.114	0.047	0.128	0.043	0.091	0.011
VSL144455	-0.058	0.041	0.109	0.039	0.091	0.011
VSL299649	-0.035	0.047	0.132	0.044	0.080	0.009
VSL276555	0.049	0.039	0.106	0.037	0.082	0.010
NP3844	-0.100	0.041	0.112	0.037	0.074	0.009
NP6303	-0.165	0.061	0.175	0.054	0.075	0.009

The results of the participation in international comparisons are summarised in the table 3. In all cases, the difference of the degree-of-equivalence was smaller than the associated expanded uncertainty.

Table 2: Results from the meta-analysis performed on the calibration gas mixtures used to assess the long-term behaviour of methane in nitrogen mixtures. τ denotes the coefficient of variation between-groups, and σ that within-groups. x denotes the amount-of-substance fraction nitrogen monoxide, as computed using ISO 6142-1.

Mixture	x mol mol ⁻¹	τ %	σ %	$\sqrt{\tau^2 + \sigma^2}$ %
PRM148904	1.00×10^{-5}	0.08	0.07	0.11
VSL328501	5.00×10^{-4}	0.02	0.02	0.03
PRM151987	3.00×10^{-3}	0.04	0.01	0.04
VSL505204	1.00×10^{-2}	0.02	0.03	0.03

The relationship between the amount-substance-fraction and the standard uncertainty is presented at the figure 10a. The results of the latest comparison CCQM-K82 and comparison to global scales done within EMRP ENV52 are also presented.

To get an acceptable distribution of the data points at the graph the logarithmic scale on both axes was used (see figure 10a). The model can be described as:

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

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

Table 3: Reported expanded uncertainty (including verification) in CCQM-K82 [7] and comparison to global scales within EMRP ENV52 “Metrology for high-impact greenhouse gases” [16]; all results were consistent with the assigned value

Project	x mol mol ⁻¹	$U(x)$ mol mol ⁻¹	$U_{\text{rel}}(x)$
CCQM-K82	1.80×10^{-6}	4.00×10^{-9}	0.22%
CCQM-K82	2.20×10^{-6}	4.50×10^{-9}	0.20%
EMRP ENV52	1.78×10^{-6}	4.50×10^{-9}	0.25%
EMRP ENV52	1.97×10^{-6}	4.90×10^{-9}	0.25%
EMRP ENV52	2.24×10^{-6}	5.60×10^{-9}	0.25%
EMRP ENV52	2.59×10^{-6}	6.50×10^{-9}	0.25%
EMRP ENV52	3.19×10^{-6}	8.00×10^{-9}	0.25%

5 Interpolation scheme for CMCs

The present CMCs for methane are from 2% \rightarrow 0.09% for amount-of-substance fractions CH₄ and from 0.5 μ mol mol⁻¹ \rightarrow 2%. Based on the calculations as presented, this relationship becomes

$$\log u = -3.291 + 0.909 \log x \quad (7)$$

The regression line and the 90% coverage interval are shown in figure 11. With the exception of the data point at 10 μ mol mol⁻¹, all data points lie in the coverage interval. The long-term behaviour of this gas mixture is unrepresentative for methane in nitrogen or methane in air standards.

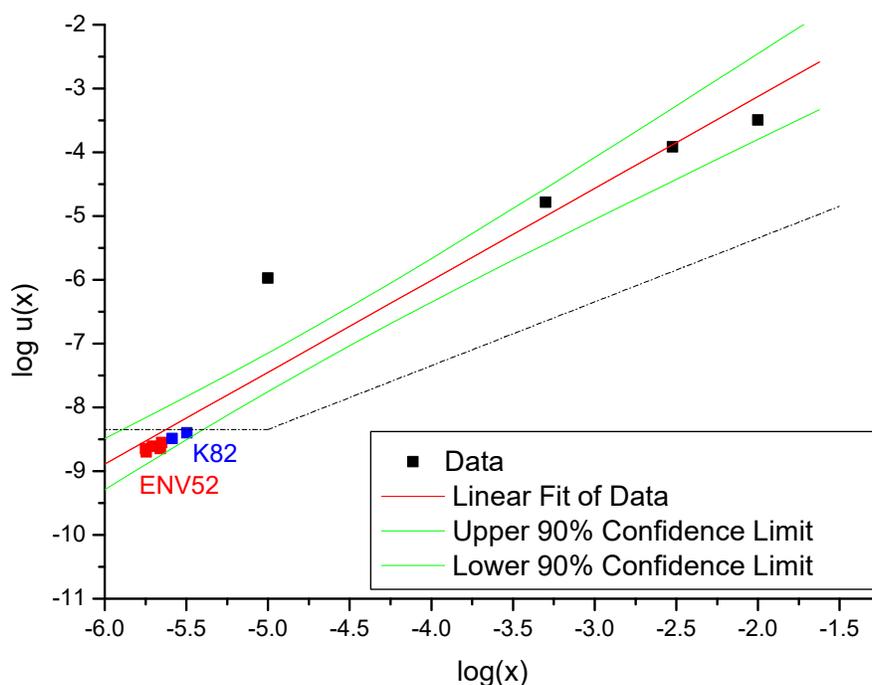


Figure 11: Regression of the standard uncertainty as a function of the amount-of-substance fraction CH_4 . The dotted lines indicate the extrapolation scheme from the GAWG

Based on equation (7), the relative expanded uncertainty ranges from 0.36 % \rightarrow 0.12 % for amount-of-substance fractions from $1 \times 10^{-6} \text{ mol mol}^{-1}$ to 10 %. There is no difference between the CMCs for methane in nitrogen and methane in air.

6 Conclusions

The developed method for calculating CMCs for methane in nitrogen and in synthetic air gives satisfactory results. The performed meta-analysis for the long-term stability data takes into account reproducibility of the measurement data such as measurement method, effects of cylinders walls or regulators. Combining the standard uncertainty computed from ISO 6143 with standard deviation τ from characterisation of dispersion of the data performed using the DerSimonian-Laird model helps to determine more reliable CMC's. The results of the latest international comparisons agree with the calculated model for CMCs.

The dedicated extrapolation scheme gives quite similar results between $2 \mu\text{mol mol}^{-1}$ and $10 \mu\text{mol mol}^{-1}$, but vastly different results otherwise. For most amount-of-substance fractions, the dedicated extrapolation scheme gives higher values for the (relative) expanded uncertainty, which are concordant with empirical evidence. The proposed model for calculating the CMCs works well from the ambient level of methane in air to the highest fractions in the range.

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