

# Calibration and measurement capabilities for carbon dioxide in nitrogen and synthetic air<sup>†</sup>

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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 assumed to be independent of the amount-of-substance fraction, and above the relative expanded uncertainty is assumed to be 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  $0.1 \text{ mol mol}^{-1}$ , and into a relative expanded uncertainty of 10% at  $1.0 \mu\text{mol mol}^{-1}$ .

This report revisits the calibration and measurement capabilities (CMCs) for carbon dioxide 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 [1].

Based on the calculations as presented, the relationship between standard uncertainty and amount-of-substance fraction can be described as  $\log u = -3.587 + 0.905 \log x$ . The relative expanded uncertainty ranges from 0.21% at  $0.5 \mu\text{mol mol}^{-1}$  to 0.06% at 50%. There is no meaningful difference in uncertainty between the measurement of the amount-of-substance fraction carbon dioxide 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) [2]. 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  $0.1 \text{ mol mol}^{-1}$ , and into a relative expanded uncertainty of 10% at  $1.0 \mu\text{mol mol}^{-1}$ . The introduction of this extrapolation scheme

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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 be increased for no other reason than that the extrapolation scheme [2] 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 [3, 4] and analysis [1], 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 report describes a model for calculating CMCs for carbon dioxide in nitrogen and synthetic air, as well as the development of a customised extrapolation scheme. The results of the international comparisons for carbon dioxide in nitrogen or air CCQM-K3 [5], CCQM-P41 [6], CCQM-K52 [7], Euramet.QM-S1 [8], Euramet.QM-S4 [9], Euramet.QM-S5 [10] and CCQM-K120 [11] are included in this work.

## 2 Default extrapolation scheme

The amount-of-substance fraction range described in the GAWG Strategy [2] 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., [2]

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

According to the same strategy document, calibration and measurement capabilities can be supported in two different ways by key comparisons [2]:

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 CMCs 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 Calculation of CMCs

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  $i^{\text{th}}$  data point,  $\mu$  the expected value at time 0,  $A$  the degradation rate,  $t_i$  the time of the  $i^{\text{th}}$  data point,  $B_i$  the bias in data point  $i$ , and the random measurement error  $\varepsilon_i$ . The mixed effects model in equation (2) is an extension of the simple mixed effects

model for stability study in reference material production [12, 13]. The term  $B_i$  enables accounting for an excess variance [14] 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 [15] and meta-analysis [14], 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 carbon dioxide in nitrogen and air.

In the following, the excess variance  $\tau^2 = \text{var}(B_i)$  and the variance computed from the  $i^{\text{th}}$  measurement  $\sigma^2 = \text{var}(\varepsilon_i)$ . The latter variance is computed using the procedure of ISO 6143 [1]. 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  $\tau$  would be larger. For the data for carbon dioxide, the assumption that  $\sigma$  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 data of the stability study is then assessed for a trend [12]. 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 [16]

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

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

The calibration and measurement capability is then calculated as

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

where  $\sigma$  denotes the standard uncertainty computed in accordance with ISO 6143,  $k$  the coverage factor and  $U$  the CMC. This computation is made for several amount-of-substance fractions across the entire range for which measurement standards of CO<sub>2</sub> in nitrogen and synthetic air are maintained.

## 4 Results and discussion

The first subrange is the range of amount-of-substance fractions from 1  $\mu\text{mol mol}^{-1}$  to 10  $\mu\text{mol mol}^{-1}$ . These analysis are performed on a gas chromatograph using a flame ionization detector with a nickel catalyst (GC-FID NiCat). Figure 1 shows the calibration data (top left), the calibration function (bottom left), and the residuals in both directions (right-hand side). The calibration function is a linear function. All residuals are meeting the criteria of ISO 6143, save the  $y$ -residuals at 50 a.u. and 62.5 a.u.. Previous measurements in the same range showed full consistency with the criteria of ISO 6143 for the residuals.

The calibration functions for the amount-of-substance fraction range from 10  $\mu\text{mol mol}^{-1}$  to 100  $\mu\text{mol mol}^{-1}$ , 100  $\mu\text{mol mol}^{-1}$  to 1000  $\mu\text{mol mol}^{-1}$ , and 500  $\mu\text{mol mol}^{-1}$  to 2500  $\mu\text{mol mol}^{-1}$  are also obtained using a GC-FID NiCat (see figures 2, 3, and 5, respectively). The calibration functions for all of

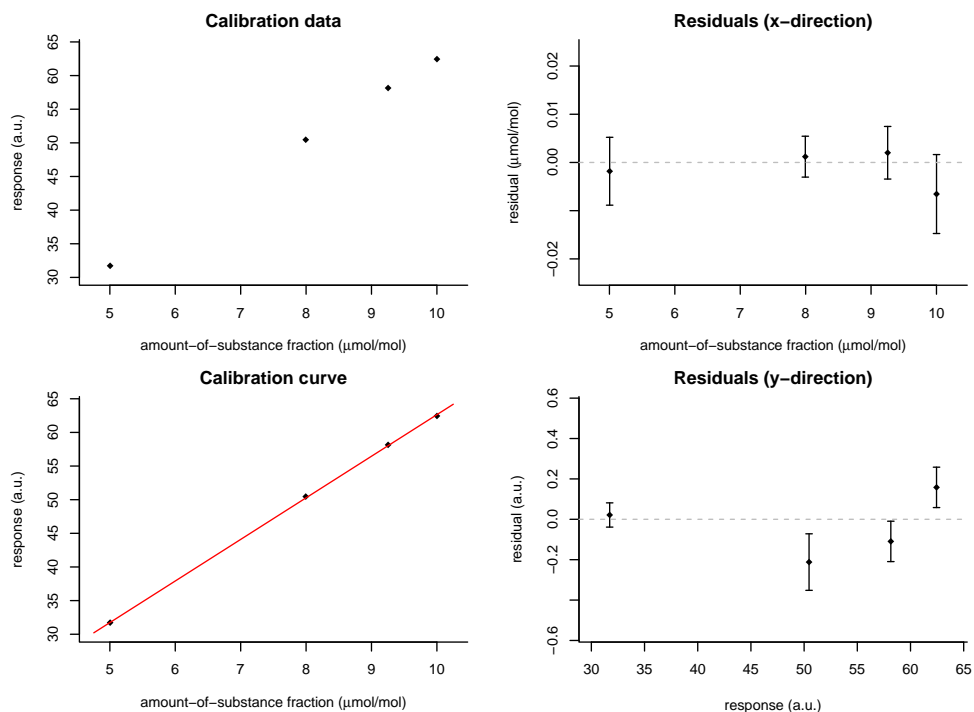


Figure 1: Calibration data, function and residuals for carbon dioxide in nitrogen on a gas chromatograph using a flame ionization detector with a nickel catalyst (GC-FID NiCat) calibrated in accordance with ISO 6143 [1]. The uncertainty bars represent 95 % coverage intervals.

these amount-of-substance fraction ranges are second-order polynomial and show full consistency with the criteria of ISO 6143 for the residuals.

The calibration function for the amount-of-substance fraction range from  $100 \mu\text{mol mol}^{-1}$  to  $1000 \mu\text{mol mol}^{-1}$  in synthetic air is shown in figure 4. The calibration function is a second-order polynomial. All residuals meet the criteria of ISO 6143.

The datasets obtained for the other  $\text{CO}_2$  subranges in nitrogen, i.e., 0.1 % to 1.0 %, 1.0 % to 12.5 %, 12.5 % to 35.0 %, and 12.0 % to 50.0 %, are measured using a gas chromatograph with thermal conductivity detector (GC-TCD). The calibration functions for all of these amount-of-substance fraction ranges are also quadratic. With one exception, all residuals meet the criteria of ISO 6143 (see figures 6, 7, 8, and 9, respectively). The small discrepancy in the y-residual of the PSM at 19.9 % (see figure 9) has negligible influence on the calculation of the CMC.

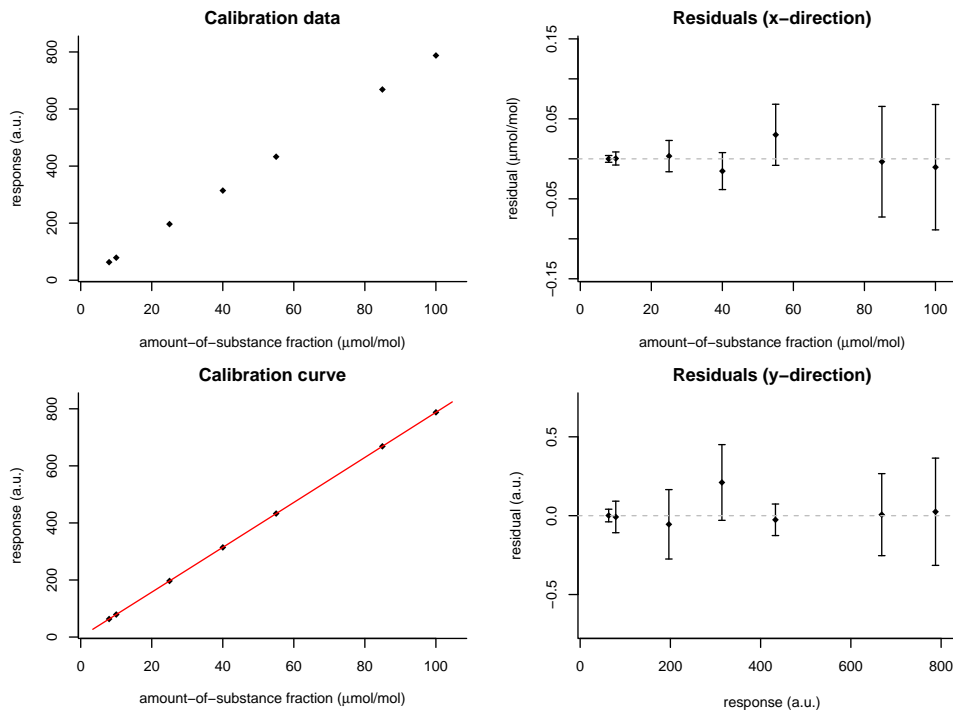


Figure 2: Calibration data, function and residuals for carbon dioxide in nitrogen on a gas chromatograph using a flame ionization detector with a nickel catalyst (GC-FID NiCat) calibrated in accordance with ISO 6143 [1]. The uncertainty bars represent 95 % coverage intervals.

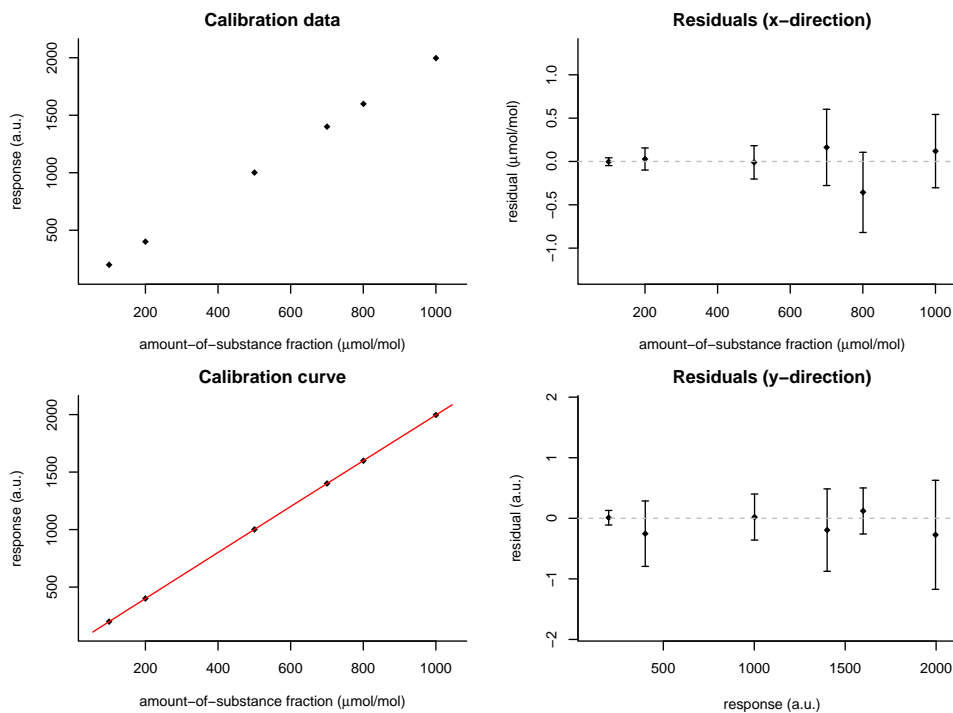


Figure 3: Calibration data, function and residuals for carbon dioxide in nitrogen on a gas chromatograph using a flame ionization detector with a nickel catalyst (GC-FID NiCat) calibrated in accordance with ISO 6143 [1]. The uncertainty bars represent 95 % coverage intervals.

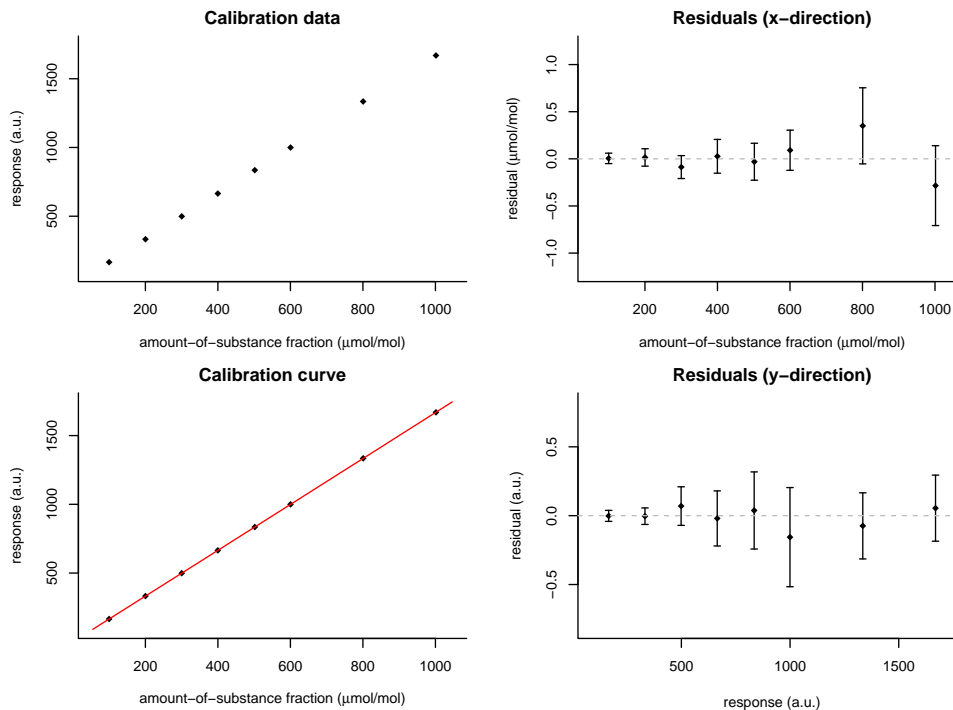


Figure 4: Calibration data, function and residuals for carbon dioxide in synthetic air on a gas chromatograph using a flame ionization detector with a nickel catalyst (GC-FID NiCat) calibrated in accordance with ISO 6143 [1]. The uncertainty bars represent 95 % coverage intervals.

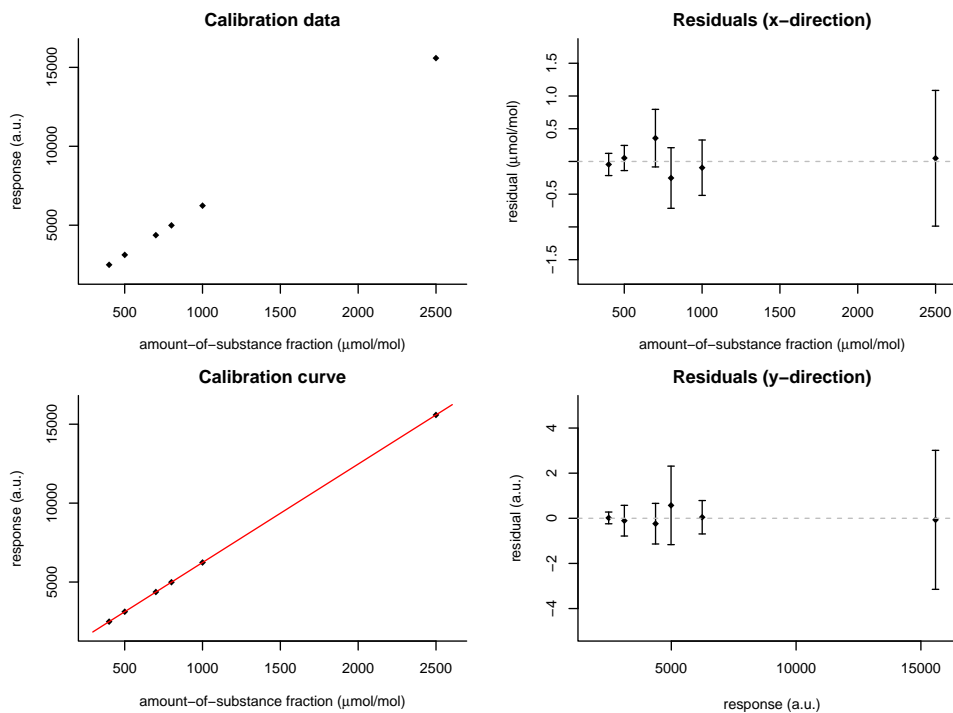


Figure 5: Calibration data, function and residuals for carbon dioxide in nitrogen on a gas chromatograph using a flame ionization detector with a nickel catalyst (GC-FID NiCat) calibrated in accordance with ISO 6143 [1]. The uncertainty bars represent 95 % coverage intervals.

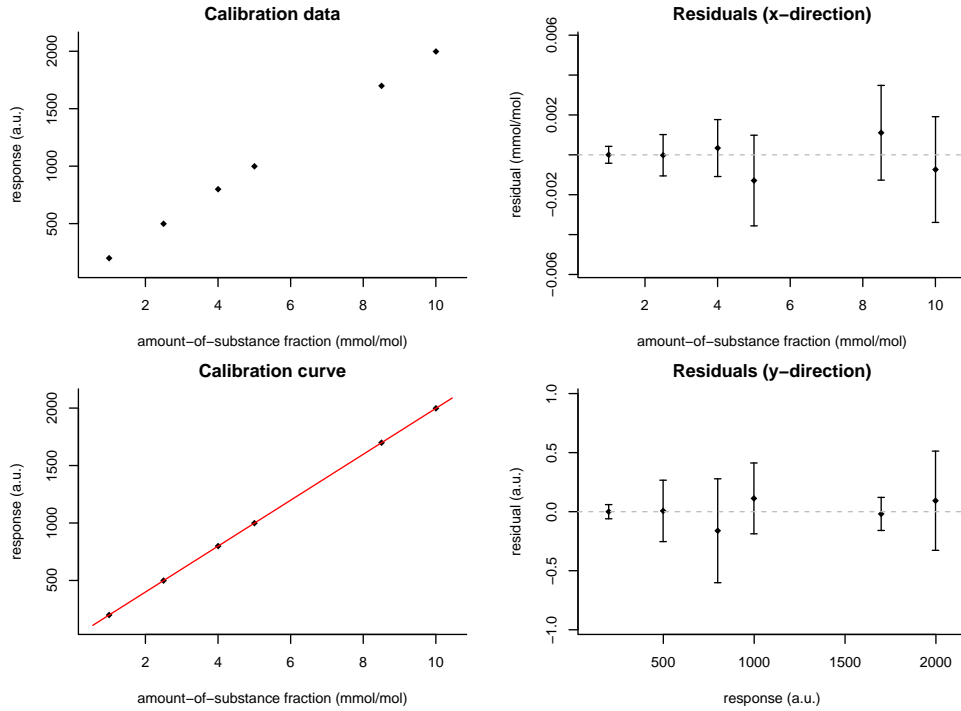


Figure 6: Calibration data, function and residuals for carbon dioxide in nitrogen on a gas chromatograph with thermal conductivity detector (GC-TCD) calibrated in accordance with ISO 6143 [1]. The uncertainty bars represent 95 % coverage intervals.

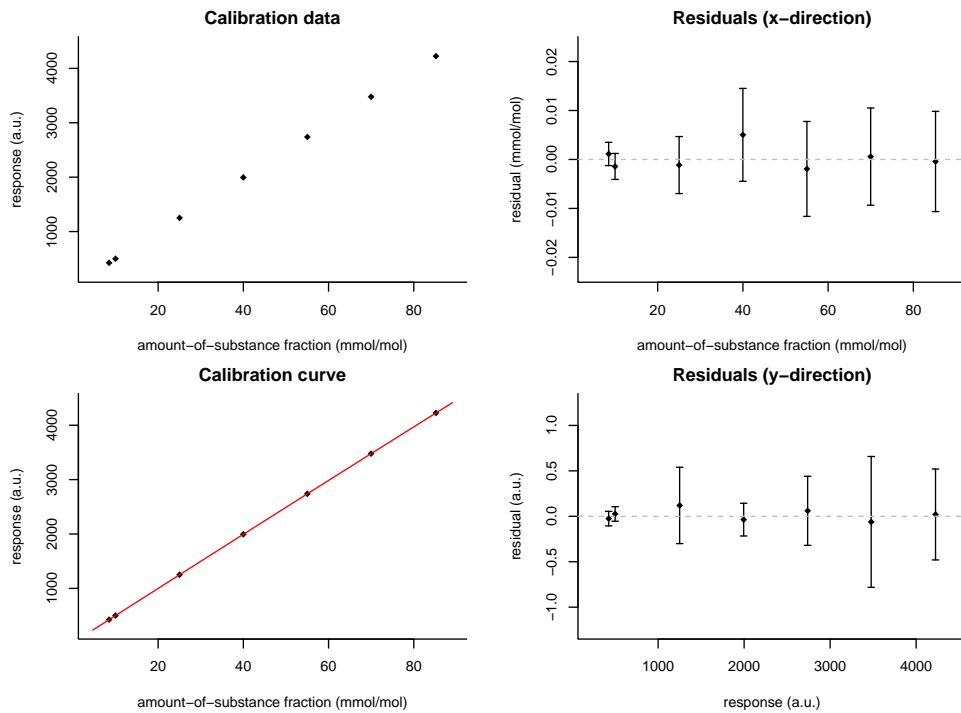


Figure 7: Calibration data, function and residuals for carbon dioxide in nitrogen on a gas chromatograph with thermal conductivity detector (GC-TCD) calibrated in accordance with ISO 6143 [1]. The uncertainty bars represent 95 % coverage intervals.

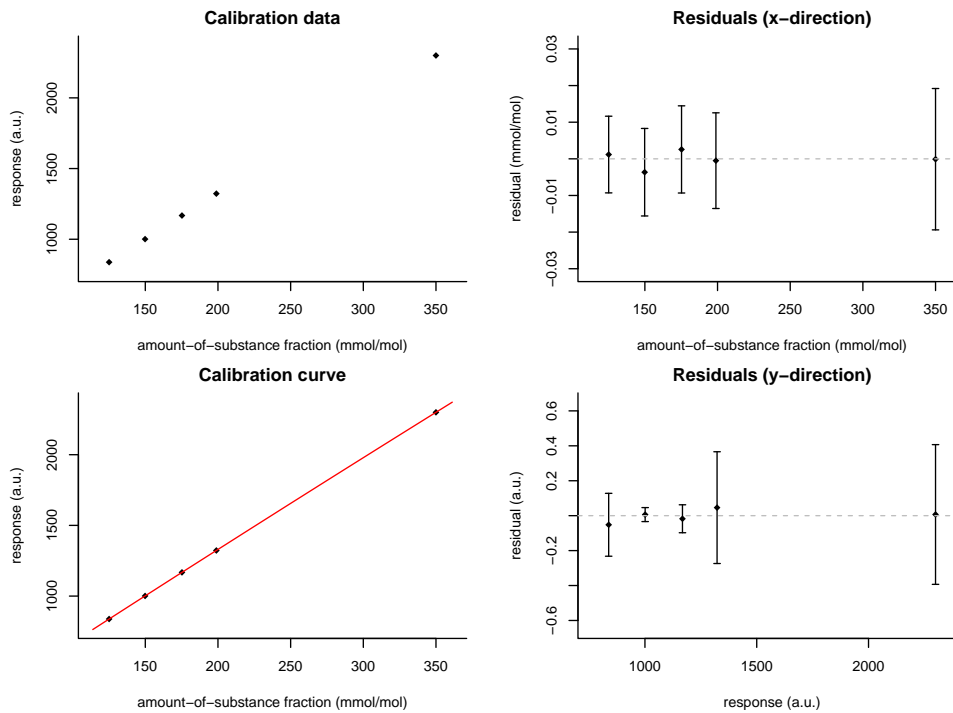


Figure 8: Calibration data, function and residuals for carbon dioxide in nitrogen on a gas chromatograph with thermal conductivity detector (GC-TCD) calibrated in accordance with ISO 6143 [1]. The uncertainty bars represent 95 % coverage intervals.

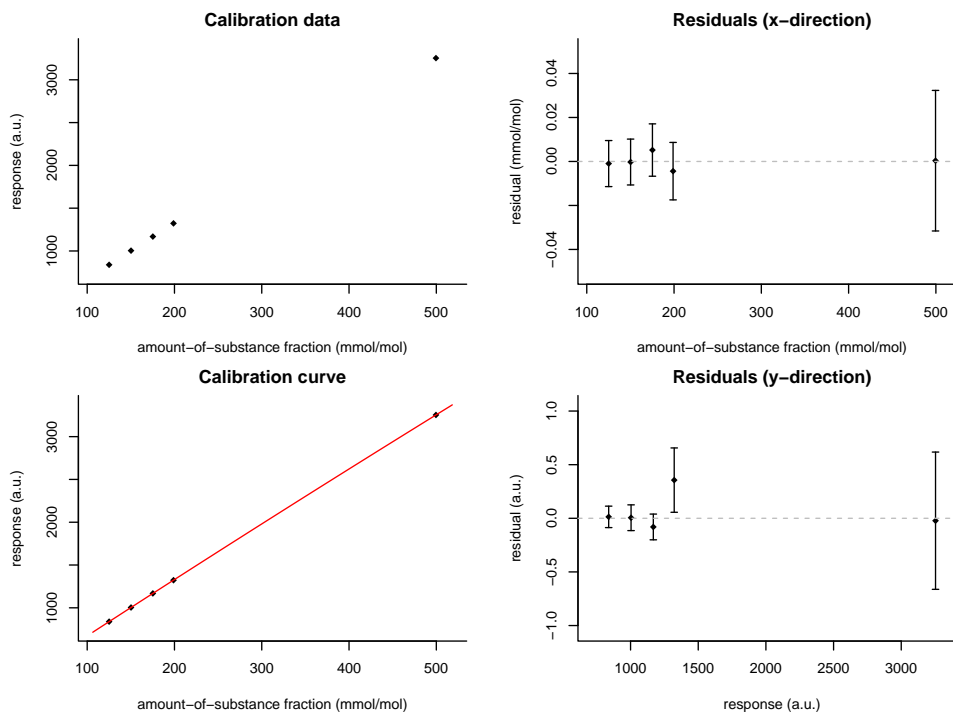


Figure 9: Calibration data, function and residuals for carbon dioxide in nitrogen on a gas chromatograph with thermal conductivity detector (GC-TCD) calibrated in accordance with ISO 6143 [1]. The uncertainty bars represent 95 % coverage intervals.



Table 1: Results from the meta-analysis performed on the calibration gas mixtures used to assess the long-term behaviour of carbon dioxide in nitrogen and synthetic air mixtures.  $\tau$  denotes the coefficient of variation between-groups, and  $\sigma$  that within-groups (expressed in %).  $x_0$  denotes the amount-of-substance fraction carbon dioxide, as computed using ISO 6142-1.

Mixture	$x_0$	$\tau$	$\sigma$	$\sqrt{\tau^2 + \sigma^2}$
VSL149636 <sup>a</sup>	$1.95 \times 10^{-1}$	0.02	0.01	0.02
VSL206347 <sup>b</sup>	$7.00 \times 10^{-2}$	0.02	0.02	0.03
VSL117909 <sup>b</sup>	$7.00 \times 10^{-3}$	0.04	0.02	0.04
VSL206293 <sup>b</sup>	$5.50 \times 10^{-3}$	0.05	0.02	0.05
VSL302696 <sup>b</sup>	$7.00 \times 10^{-4}$	0.04	0.02	0.05
VSL117910 <sup>b</sup>	$7.01 \times 10^{-4}$	0.04	0.02	0.04
VSL229432 <sup>b</sup>	$4.01 \times 10^{-4}$	0.09	0.02	0.10
VSL200386 <sup>b</sup>	$5.51 \times 10^{-5}$	0.07	0.04	0.08

<sup>a</sup> Carbon dioxide in nitrogen mixtures

<sup>b</sup> Carbon dioxide in synthetic air mixtures

The results of the meta-analysis on the long-term stability study data are shown in table 1. The within-group standard deviations are computed using the procedure of ISO 6143 [1]. The results of the international comparisons CCQM-K3 [5], CCQM-P41 [6], CCQM-K52 [7], Euramet.QM-S1 [8], Euramet.QM-S4 [9], Euramet.QM-S5 [10] and CCQM-K120 [11] are summarised in table 2.

The relationship between the amount-of-substance fraction and the standard uncertainty is visualised in figure 10. In the figures, also the results of the international comparisons are included. It is important to note that (1) the results in these comparisons were consistent, and (2) the calculated standard uncertainty matches well with the standard uncertainties summarised in table 1.

From figure 10a, it can be seen that in first approximation the data can be described by a model of the kind

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

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  $a_1 = 0$ . Fitting the data using ordinary least squares (OLS) [17] yields for  $a_1 = 0.905$  (see figure 11). In the figure, the 90% coverage interval is also given. Three points lie slightly outside the interval, but otherwise the equation gives a good prediction of the CMCs across the entire range of amount-of-substance fractions.

## 5 Interpolation scheme for CMCs

The present CMCs for carbon dioxide in nitrogen and synthetic air range from 2.0%  $\rightarrow$  0.1% for amount-of-substance fractions CO<sub>2</sub> from 0.5  $\mu\text{mol mol}^{-1}$  to 10  $\mu\text{mol mol}^{-1}$ . For amount-of-substance fractions CO<sub>2</sub> from 10  $\mu\text{mol mol}^{-1}$  to 50%, the current expanded uncertainty is 0.1%. Based on the calculations as presented, this relationship becomes

$$\log u = -3.587 + 0.905 \log x \quad (7)$$

which means a relative expanded uncertainty of 0.21% at 0.5  $\mu\text{mol mol}^{-1}$ , 0.15% at 10  $\mu\text{mol mol}^{-1}$ , and 0.06% at 50%. There is no difference between the CMCs for carbon dioxide in nitrogen and carbon dioxide in synthetic air.

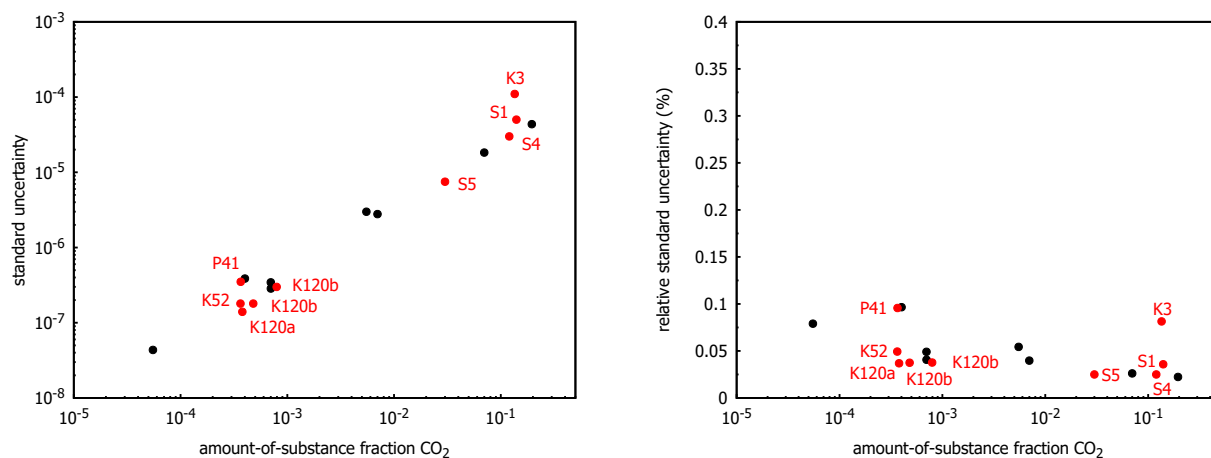
Table 2: Reported expanded uncertainty (including verification) in CCQM and Euramet comparisons; all results were consistent with the key comparison reference value.

Project	$x$ mol mol <sup>-1</sup>	$U(x)$ mol mol <sup>-1</sup>	$U_{rel}(x)$
Euramet.QM-S4 <sup>a</sup>	$1.20 \times 10^{-1}$	$6.00 \times 10^{-5}$	0.05
CCQM-K3 <sup>a</sup>	$1.35 \times 10^{-1}$	$2.20 \times 10^{-4}$	0.16
Euramet.QM-S1 <sup>a</sup>	$1.40 \times 10^{-1}$	$5.00 \times 10^{-5}$	0.04
Euramet.QM-S5 <sup>b</sup>	$3.00 \times 10^{-2}$	$1.50 \times 10^{-5}$	0.05
CCQM-K52 <sup>c</sup>	$3.64 \times 10^{-4}$	$3.60 \times 10^{-7}$	0.10
CCQM-P41 <sup>c</sup>	$3.66 \times 10^{-4}$	$7.00 \times 10^{-7}$	0.19
CCQM-K120a <sup>c</sup>	$3.79 \times 10^{-4}$	$2.80 \times 10^{-7}$	0.07
CCQM-K120b <sup>c</sup>	$4.80 \times 10^{-4}$	$3.60 \times 10^{-7}$	0.07
CCQM-K120b <sup>c</sup>	$7.95 \times 10^{-4}$	$6.00 \times 10^{-7}$	0.08

<sup>a</sup> Automotive

<sup>b</sup> Carbon dioxide in nitrogen

<sup>c</sup> Carbon dioxide in synthetic air



(a) Standard uncertainty as a function of the amount-of-substance fraction CO<sub>2</sub> in nitrogen and synthetic air.

(b) Coefficient of variation as a function of the amount-of-substance fraction CO<sub>2</sub> in nitrogen and synthetic air.

Figure 10: CMCs as a function of the fraction CO<sub>2</sub> in nitrogen and synthetic air.

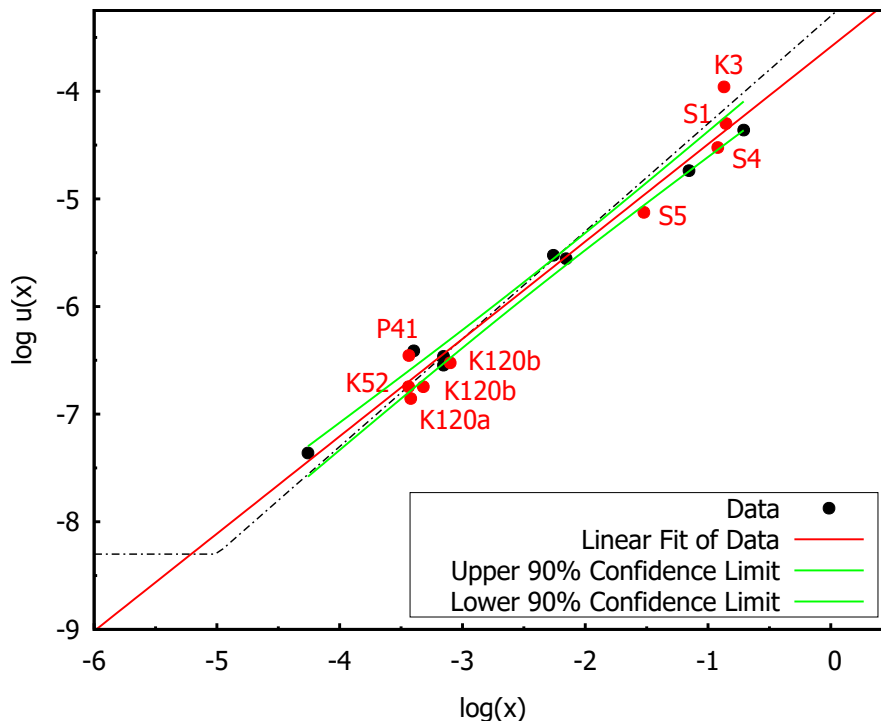


Figure 11: Regression of the standard uncertainty as a function of the amount-of-substance fraction CO<sub>2</sub> in nitrogen. The dotted lines indicate the extrapolation scheme from the GAWG.

## 6 Conclusions

The approach developed for relating the expanded uncertainty of the analysis of carbon dioxide in nitrogen and synthetic air to the amount-of-substance fraction provides satisfactory results. The use of meta-analysis is helpful in characterising the dispersion due to, a combination of, reproducibility of the measurement method, effects of cylinder walls and regulators. The standard deviation  $\tau$  from the DerSimonian-Laird model is combined with the standard uncertainty computed from the multipoint calibration from ISO 6143 to determine the calibration and measurement capability (CMC). The results of the participation in different international comparisons agree well with the CMCs determined from the long-term behaviour of the standards of carbon dioxide in nitrogen and synthetic air.

The dedicated extrapolation scheme gives quite similar results in comparison to the GAWG scheme. It gives similar values for the (relative) expanded uncertainty, which are concordant with empirical evidence. The proposed model for calculating the CMCs works well from 0.5  $\mu\text{mol mol}^{-1}$  carbon dioxide in nitrogen or synthetic air to the highest fractions in the range.

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