

International comparison CCQM-P41 Greenhouse gases. 2. Direct comparison of Primary Standard gas Mixtures

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Field

Amount of substance

Subject

Greenhouse gases (carbon dioxide and methane in air)

Participants

NMIA¹ (AU), BAM (DE), CEM (ES), IMGC (IT), NMIJ (JP), KRISS (KR), CENAM (MX), NMi VSL (NL), GUM (PO), NPL (UK), NIST (US)

Organising body

CCQM

Rationale

The World Meteorological Organization (WMO) coordinates worldwide monitoring of greenhouse gases in the background atmosphere. Emissions of the key greenhouse gases such as carbon dioxide and methane are increasing as a result of human activities and are implicated in global climate change. In 1992, the United Nations Framework Convention on Climate Change was established, resulting in the proposal of legally binding limits (the 1997 Kyoto Protocol) aimed at reducing these emissions. The accuracy and traceability of greenhouse gas monitoring over the global space-scale and the decade-to-century time-

¹ At the time of participation, NMIA was known as CSIRO-National Metrology Laboratory

scale of the enhanced greenhouse effect become critical issues, with an increasing role for National Metrology Institutes (NMIs).

This second part of the project focuses a comparison to evaluate the preparative capability. The objective is to compare under repeatability conditions how well PSMs (primary standard gas mixtures) agree.

Measurement standards

The nominal composition of the mixtures has been based on current figures regarding the average composition of air. Table 1 gives the nominal composition used throughout this comparison.

Table 1: Nominal composition for the comparison

Component	x (mmol/mol)
Methane	0.0018
Carbon dioxide	0.365
Argon	9.3
Oxygen	209
Nitrogen	balance

For this part of the project, an amended version of the protocol of CCQM-P23 [3] has been used. As a consequence, the nominal composition of the gas mixtures to be submitted to the pilot laboratory had to be grouped, so that a stable regression analysis on the data would be possible.

For the gravimetric comparison, the following target compositions have been fixed (table 2).

Table 2: Mixtures for comparing gravimetric capabilities

Laboratory	CO ₂ (μ mol/mol)	CH ₄ (μ mol/mol)
BAM	350	1.8
NMi VSL	365	2.0
KRISS	380	1.6
NMIA	380	2.0
CEM	350	2.0
GUM	365	1.6
NIST	380	1.8
NPL	365	2.0
NMIJ	365	1.6

Schedule

The schedule for this part of the comparison was as follows:

May 15, 2002	Start of preparation mixtures by participants
December 15, 2002	Shipment of cylinders from participants for gravimetric comparison
January 15, 2003	Arrival of cylinders for gravimetric comparison in Delft
March 15, 2003	Measurement of cylinders for gravimetric comparison

Measurement protocol

The measurement protocol was taken from CCQM-P23 [3]. Two quality control cylinders were used for controlling the measurements, and one cylinder for monitoring drift. No relevant drift influence was found. The data were to be fitted using generalised distance regression (GDR) and a straight line as model.

The measurement of carbon dioxide was carried out using a HP5890 Series II gas chromatograph, equipped with a TCD detector. The column used was a Porapak R, 10 ft, OD 1/8", 80-100 mesh. Helium was used as carrier gas, with a flow of 28 ml/min.

Samples were introduced in the sample loop through a Multi Position Valve (MPV) followed by a switching valve (open/close, enabling injection at ambient pressure). Both MPV position and measurement were controlled by BASIC-program running on an HP3396-integrator. Measurement data were acquired through an A/D-converter and processed using HP GC ChemStation software (Rev. A.09.03 [1417] (2002)). Initial experiments had shown that the integration, using the internal software of the HP 3396 integrator, was too inaccurate for the measurements to be conducted in this project. Manual integration showed that a significant improvement in the data treatment was possible; the use of the GC ChemStation software allowed enhancing the performance of the GC (including data processing) significantly.

The preparation for the measurements was started on 21 February 2003. Reducers were connected to the cylinders, and the system was checked over the weekend for possible leakages. On 24 February, some small leaks were fixed by tightening connections. Reducers were subsequently rinsed four times, distributed over two days.

The first measurement took place on 26 February. All reducers were rinsed 8 times prior to measurement. The reducers were adjusted to 2 bar pressure, in order to ensure injection directly after reaching ambient pressure in the sample loop. The tubing was rinsed automatically for 180 seconds before starting the measurement. Before injection, the tubing and sample loop were rinsed for another 180 seconds. A measurement consisted of 7 subsequent injections with a time interval of 2 minutes. The sample loop is continuously rinsed (except when injecting). This measurement procedure was repeated on 27 and 28 February. The reducers and port positions were varied as given in tables 3 and 4. The measurements were taken in the exact order as given in table 4.

Table 3: Configuration of reducers during the measurement of carbon dioxide

Reducer no.	Measurement #1	Measurement #2	Measurement #3
1	BAM	CEM	KRISS
2	CEM	BAM	BAM
3	<i>QC (low)</i>	NMi VSL	NPL
4	Nmi VSL	NPL	<i>QC (high)</i>
5	GUM	<i>QC (low)</i>	NMi VSL
6	NPL	<i>QC (high)</i>	GUM
7	<i>QC (high)</i>	GUM	<i>QC (low)</i>
8	KRISS	NMIJ	NMIA
9	NMIJ	NMIA	NIST
10	NMIA	NIST	CEM
11	NIST	KRISS	NMIJ
12	<i>QC (drift)</i>	<i>QC (drift)</i>	<i>QC (drift)</i>

Table 4: Measurement sequence and port position of cylinders during measurement of carbon dioxide

Port position on MPV	Measurement #1	Measurement #2	Measurement #3
1	<i>QC (low)</i>	<i>QC (low)</i>	<i>QC (low)</i>
2	NPL	BAM	GUM
3	NMIJ	NIST	CEM
4	<i>QC (drift)</i>	<i>QC (drift)</i>	<i>QC (drift)</i>
5	NIST	CEM	KRISS
6	GUM	NMIJ	BAM
7	<i>QC (high)</i>	<i>QC (high)</i>	<i>QC (high)</i>
8	NMIA	NMi VSL	NPL
9	CEM	NPL	NIST
4	<i>QC (drift)</i>	<i>QC (drift)</i>	<i>QC (drift)</i>
10	KRISS	NMIA	NMi VSL
11	NMi VSL	KRISS	NMIA
12	BAM	GUM	NMIJ
1	<i>QC (low)</i>	<i>QC (low)</i>	<i>QC (low)</i>

The measurement of methane was carried out on an HP6890 gas chromatograph, equipped with an FID detector. The column was a Molsieve 5A, 6 ft, OD 1/8", 60-80 mesh. Nitrogen was carrier gas, and the flow rate was 31 ml/min. The sampler was connected to sampling valve through an electronic pressure controller inside GC.

The reducers were connected on 3-4 March 2003. The configuration of the reducers was not changed after last measurement of carbon dioxide, with two exceptions. Only the reducer of the NIST-cylinder was moved from the cylinder containing carbon dioxide in air to that containing methane in air. The reducer of the BAM cylinder was also dismantled and remounted, in order to allow exchanging connections with other than DIN 14. Directly after connecting both reducers were flushed (3 times with reducer open and 8 times where reducer was only opened to let the gas flow out). On 5-6 March the reducers were rinsed three times, twice on the 5th and once on the 6th.

The measurements started 6 March 2003. The reducers were rinsed 8 times and cylinders were connected to the multi-position valve (MPV). The regulators were adjusted so that pressure in sample loop was more than 250 kPa above ambient. Injection took place at 200 kPa above ambient, as controlled by a electronic pressure regulator in the GC. As in the case of carbon dioxide, 7 injections per cylinder were made, 2 minutes between each of them, and the sample loop was continuously rinsed. The reducers and port positions were varied as given in tables 5 and 6. The measurements were taken in the exact order as given in table 6.

All results are appended to this report in annexes A and B.

Table 5: Configuration of reducers during the measurement of methane

Reducer no.	Measurement #1	Measurement #2	Measurement #3
1	KRISS	NMIJ	BAM
2	BAM	KRISS	CSIRO-NML
3	NPL	NMi	NIST
4	QC (high)	QC (low)	GUM
5	NMi	NPL	QC (high)
6	GUM	NIST	NMi
7	QC (low)	QC (high)	NPL
8	CSIRO-NML	CEM	KRISS
9	NIST	GUM	QC (low)
10	CEM	CSIRO-NML	NMIJ
11	NMIJ	BAM	CEM
12	QC (drift)	QC (drift)	QC (drift)

Table 6: Measurement sequence and port position of cylinders during measurement of methane

Port position on MPV	Measurement #1	Measurement #2	Measurement #3
1	QC (low)	QC (low)	QC (low)
2	NPL	BAM	GUM
3	NMIJ	NIST	CEM
4	QC (drift)	QC (drift)	QC (drift)
5	NIST	CEM	KRISS
6	GUM	NMIJ	BAM
7	QC (high)	QC (high)	QC (high)
8	CSIRO-NML	NMi	NPL
9	CEM	NPL	NIST
4	QC (drift)	QC (drift)	QC (drift)
10	KRISS	CSIRO-NML	NMi
11	NMi	KRISS	CSIRO-NML
12	BAM	GUM	NMIJ
1	QC (low)	QC (low)	QC (low)

Regression

In this type of comparison, a regression is carried out to compare the PSMs submitted by the participating NMIs. The comparison is designed in such a way, that a straight line can be used as model. The regression appreciates the uncertainties of the x - and y -coordinates, the amount-of-substance fraction and the response respectively. The sum of squared residuals is defined as [5]

$$\chi^2 = \sum_{i=1}^n \left\{ \left(\frac{x_i - \hat{x}_i}{u(x_i)} \right)^2 + \left(\frac{y_i - \hat{y}_i}{u(y_i)} \right)^2 \right\} \quad (1)$$

subject to

$$\hat{y}_i = a_1 + a_2 \hat{x}_i \quad (2)$$

as in this case the straight line has been chosen as model. Minimising χ^2 leads to the values for the model parameters a_1 and a_2 for which χ^2 has a minimum value.

This type of regression has been described with widely differing nomenclature. For example, ISO 6143 [5] uses the term "Deming's generalised least squares", after the author of one of the first comprehensive publications on this subject, Deming [6]. Unfortunately, the term "generalised least squares" is also used in the context of what is sometimes called "ordinary least squares", i.e., the least squares regression where the uncertainty of the x -coordinate is assumed to be zero (see, e.g., [7]). In two systematic treatises [8,9] on the subject, the regression problem given in (1) is called "Generalised Distance Regression". Furthermore, it is also known as "Errors-in-variables regression" (EIV) and "total least squares" (TLS) [7,10]. Given the treatise in [8] and the consistent discussion of algorithms for solving the resulting least squares problem in [9], *Generalised Distance Regression* will be used in this report to denote this type of regression analysis.

The minimisation problem given in (1) can be reformulated [11]² to become

$$\chi^2 = \sum_{i=1}^n \left\{ \frac{(y_i - \hat{y}_i)^2}{u^2(y_i) + a_2^2 u^2(x_i)} \right\} \quad (3)$$

The regression analysis in this project has been carried out using the algorithm given in section 15.3 of [7]. The code has been implemented in a small Windows-based application compiled with Borland C++ Builder Version 3. The regression results and residuals have been crosschecked with the output of XGenLine V7 [12].

For the *Generalised Distance Regression*, the residuals can be calculated as follows. The method is based on introducing a Lagrange multiplier λ . The predicted values of the GDR can be expressed as [13]

$$\hat{x}_i = x_i - \frac{\lambda a_2}{w(x_i)} \quad (4)$$

and

$$\hat{y}_i = y_i + \frac{\lambda}{w(y_i)} \quad (5)$$

where

$$\lambda = \frac{w(x_i)w(y_i)}{a_2^2 w(y_i) + w(x_i)} \{a_1 + a_2 x_i - y_i\} \quad (6)$$

and finally

$$w(x_i) = \frac{1}{u^2(x_i)}; w(y_i) = \frac{1}{u^2(y_i)} \quad (7)$$

Results

The responses for CO₂ have been corrected for atmospheric pressure influence, using the equation

$$y' = y - 13864 \left(1 - \frac{P_0}{P} \right) \quad (8)$$

² Originally published in: Ripley B. D., Thompson M., "Regression techniques for the detection of analytical bias", *Analyst* 112 (1987), pp. 177-183

where p_0 equals 1013.25 hPa. p is the recorded atmospheric pressure. The correction has been derived from the data from both quality control cylinders. After the correction, the remaining scatter in the data has been used to calculate the standard deviation of the responses.

Table 7 shows the results for carbon dioxide. The amount of substance fraction (x), as supplied by the NMI is given, together with its associated standard uncertainty, and the average response corrected response (y'), together with its associated uncertainty. The average response has not been corrected for any pressure influence.

The regression line reads as follows

$$y' = -607.78 + 47.87x. \tag{9}$$

The standard uncertainty of the intercept is 81.94, that of the slope 0.22, and the covariance is -18.26.

Table 7: Results for carbon dioxide

NMI	x $\mu\text{mol/mol}$	$u(x)$ $\mu\text{mol/mol}$	y' a.u.	$u(y')$ a.u.	\hat{x} $\mu\text{mol/mol}$	\hat{y} a.u.
NPL	363.15	0.29	16797.1	8.2	363.47	16791.8
NMIJ	372.63	0.08	17209.9	1.8	372.28	17213.6
NIST	366.59	0.04	16948.5	2.1	366.65	16944.1
GUM	363.83	0.73	16823.3	7.2	364.11	16822.7
NMIA	377.31	0.26	17441.3	5.3	377.08	17443.3
CEM	348.10	0.14	15993.8	3.4	347.06	16006.6
KRISS	379.09	0.02	17534.4	4.4	379.08	17539.4
NMi VSL	360.78	0.10	16695.3	1.6	361.38	16692.1
BAM	348.48	0.23	16105.0	2.9	349.08	16102.9

The standard deviation of the x -residuals is 0.52 $\mu\text{mol/mol}$ (0.14% relative). Figure 1 shows the results of the GDR and the data points. All uncertainty bars in all figures are expanded uncertainties with $k = 2$.

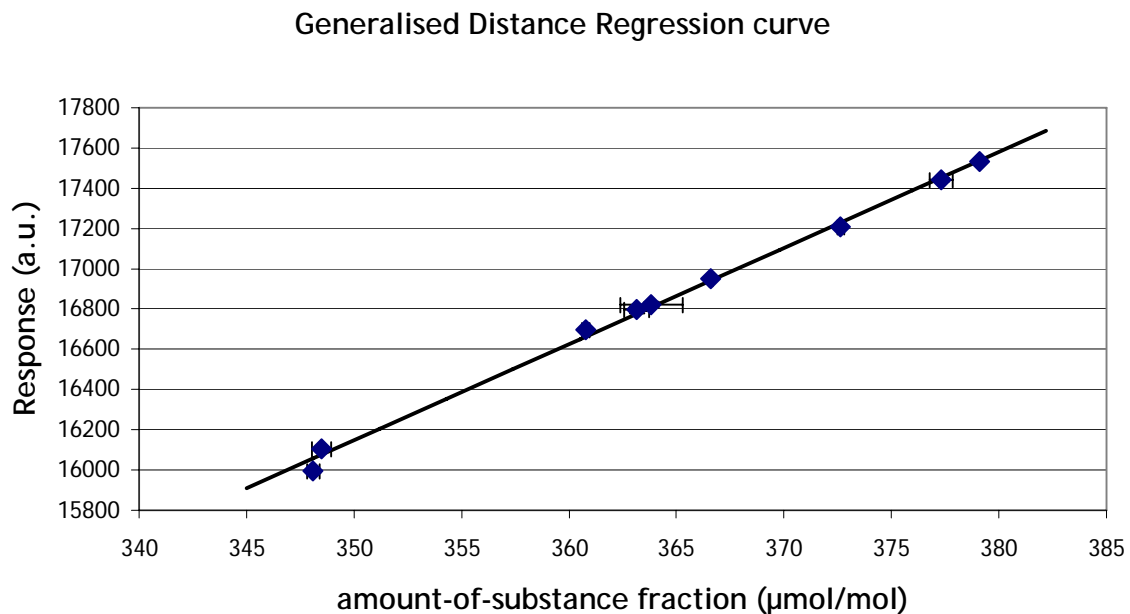


Figure 1: GDR of carbon dioxide data

The residuals in x -direction are shown in figure 2 and those in y -direction in figure 3.

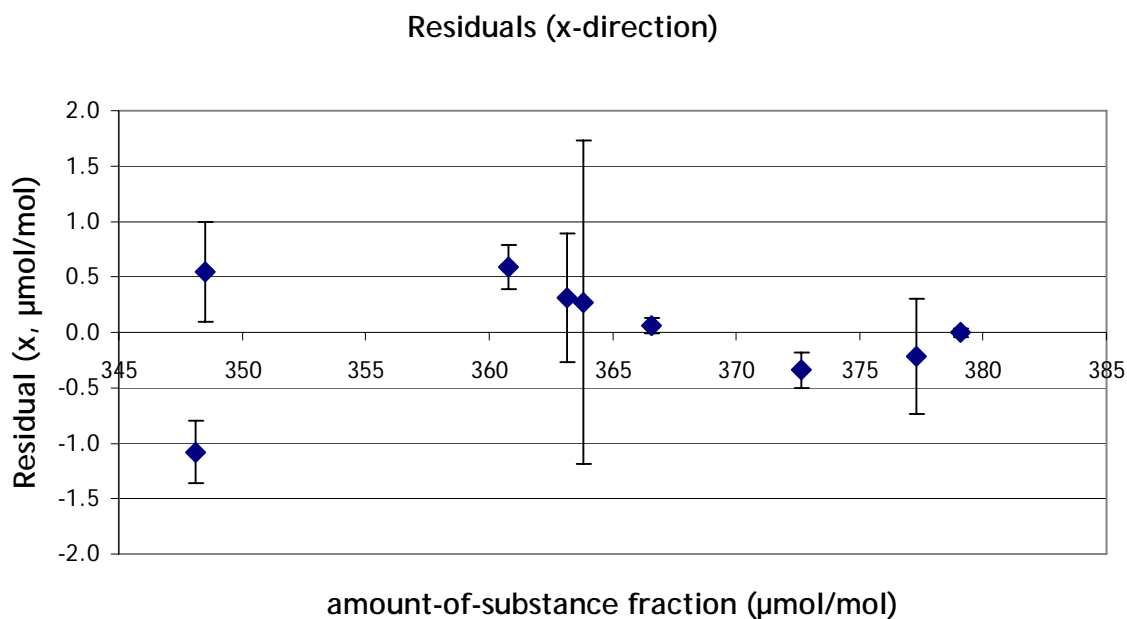


Figure 2: Residuals in x -direction for carbon dioxide

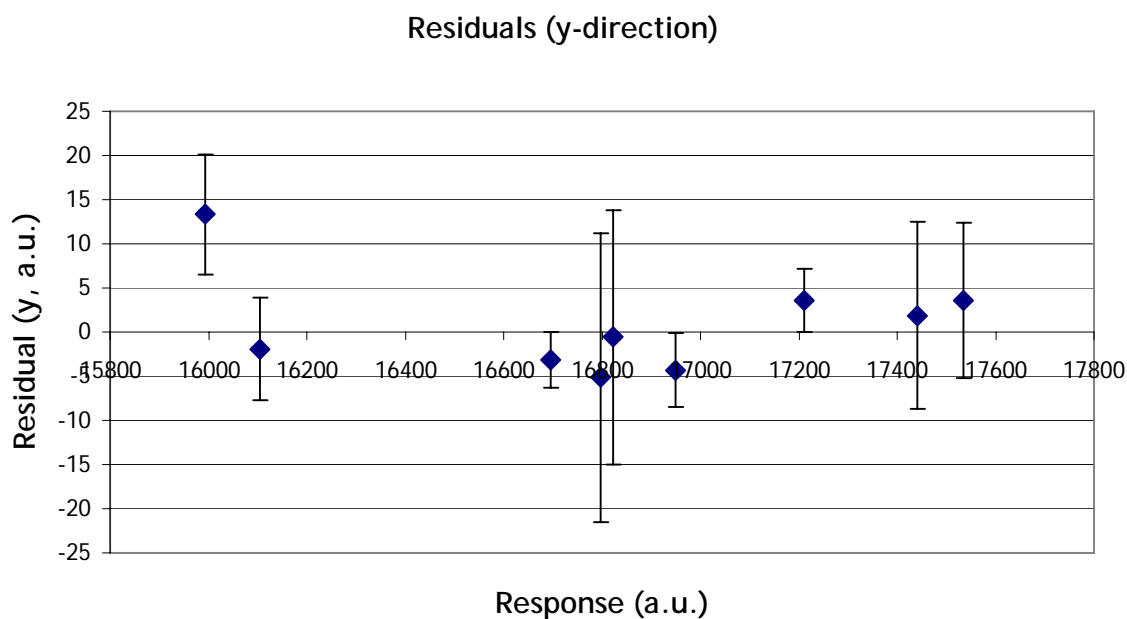


Figure 3: Residuals in y -direction for carbon dioxide

The regression of the carbon dioxide data clearly shows that with respect to the regression line most of the data points are not consistent within their uncertainty, that is the criterion [5]

$$|x_i - \hat{x}_i| \leq k \cdot u(x_i) \tag{10}$$

is not satisfied for most data points. This criterion can both be found in ISO 6142 [4] and ISO 6143 [5]. Satisfying this criterion implies consistency with the other calibration

standards. The regression line should be regarded as a weighted consensus. The standard deviation of the residuals in x -direction ($0.52 \mu\text{mol/mol}$) is appreciably larger than most of the uncertainties stated. In the protocol for this comparison, it was requested to base the uncertainty associated with the amount-of-substance fraction from preparation to comprise effects from gravimetric preparation and purity analysis only. The measurement model therefore reads as

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} \quad (11)$$

Under the presumption that the uncertainties associated with the gravimetric preparation ($x_{i,grav}$) and the purity verification ($\Delta x_{i,purity}$) have been properly estimated, the graph of the residuals in x -direction (figure 2) suggests that there are other factors to be appreciated. In a paper discussing the statistical aspects of key comparisons in the gas analysis area, the measurement model has been augmented to account for (in)stability effects and a fraction "non-recoverable" (due to, e.g., adsorption) [14]

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} + \Delta x_{i,stab} + \Delta x_{i,nr} \quad (12)$$

Perhaps between-cylinder effects due to e.g., adsorption account for the discrepancy between the regression line and the submitted data.

There is another aspect to the regression analysis and the resulting consensus line. If the standard deviation of the x -residuals is adopted as estimate for the uncertainty associated with the amount-of-substance fraction values as obtained from preparation, that is, the data should satisfy the criterion

$$|x_i - \hat{x}_i| \leq k \cdot s(\Delta x_i) \quad (13)$$

where

$$\Delta x_i = x_i - \hat{x}_i \quad (14)$$

there is one cylinder that lies outside the 95%-interval³ (CEM). Furthermore, the cylinder does not satisfy the criterion [5]

$$|y_i - \hat{y}_i| \leq k \cdot u(y_i) \quad (15)$$

which is required for a consistent fit of the data.

Leaving out this cylinder, the regression line improves (figure 4) and so do the x -residuals (figure 5).

³ Assuming $k = 2$.

Generalised Distance Regression curve

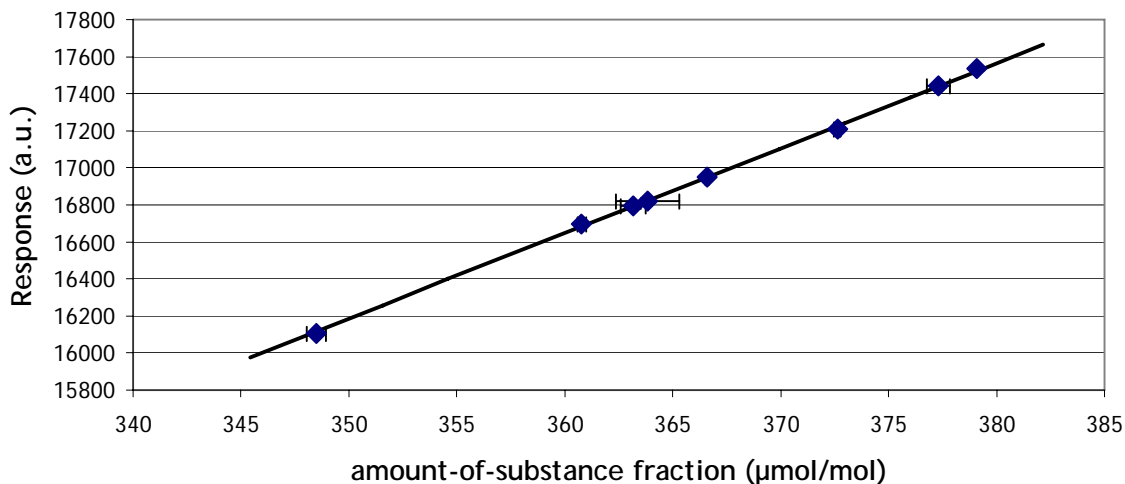


Figure 4: GDR of carbon dioxide data without cylinder from CEM

The equation for the regression line reads as

$$y' = 107.22 + 45.94x \tag{16}$$

The standard uncertainty associated with the intercept is 100.54, and that of the slope is 0.27. The intercept for the amended regression line is insignificantly different from zero (t -test, 95% level of confidence), which is to be expected for GC data. (The response tends to zero when the amount-of-substance fraction tends to zero.)

Residuals (x-direction)

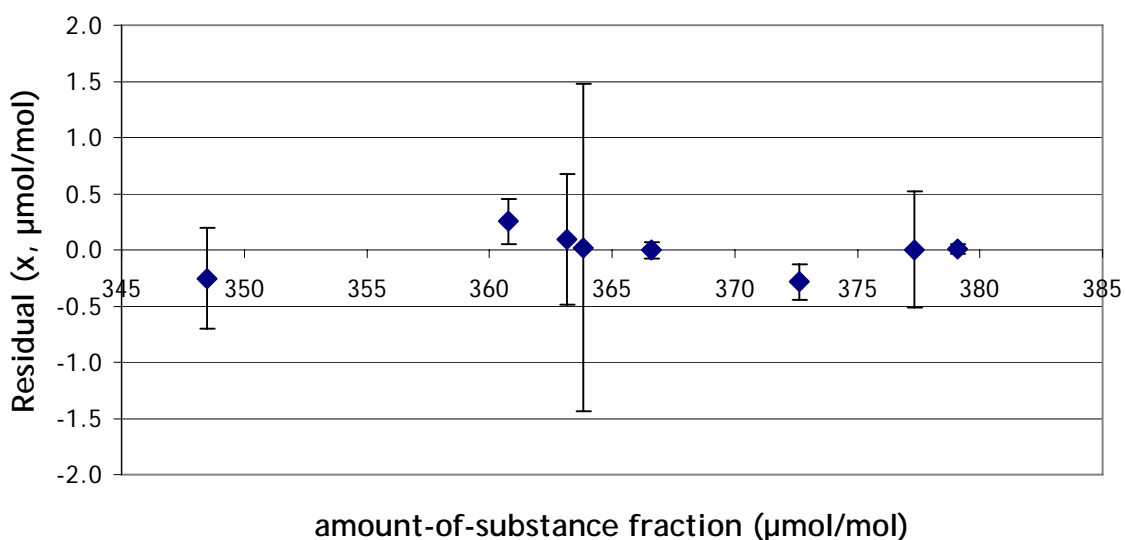


Figure 5: Residuals in x -direction for carbon dioxide, after removal of the CEM cylinder

The standard deviation of the residuals is 0.18 $\mu\text{mol/mol}$ (0.05% relative), which is substantially closer to the uncertainties estimated. Two cylinders are still not consistent with the regression line, namely those from NMI VSL and NMIJ.

The standard deviation of the x -residuals cannot and must not be interpreted as a standard uncertainty that would apply to all cylinders in the comparison. The cylinders are weighted according to their uncertainties (by the reciprocal of their respective variances) and ideally it would be expected that all cylinders satisfy criterion given by equation (10). The heavier the weight assigned to a cylinder in the regression, the stricter this criterion becomes. As the regression line represents a consensus, there can be some influence from the results of the other cylinders in the comparison whether for a particular cylinder the criterion is met. This phenomenon is clearly illustrated by removing the CEM cylinder from the data and investigating the influence of this action.

The protocol of the comparison did not foresee removal of "outliers" or "stragglers" however, so that this analysis of the data should be seen from the perspective of giving an idea of how well the mixtures agree, and to see whether there are cylinders that have a profound influence on the regression line. The fact that the intercept of the regression line after removal of the CEM cylinder does not deviate significantly from zero can be seen as an argument in favour of the statistics derived from the reduced dataset.

To conclude the discussion on the carbon dioxide data, the data have also been processed after pooling the uncertainties associated with the responses. The uncertainties stated in tables 7 and 8 have been calculated directly from the data, but there is little reason to believe that the uncertainty associated with the response for one cylinder would be much different from another, so that pooling of the uncertainties to get a better estimate is justified. The influence of pooling of these uncertainties on the regression line is negligible.

Figure 5 shows that in y -direction the data points are (within the respective uncertainties) consistent with the regression line.

The results for methane are shown in table 8. The symbols have the same meaning as those used for carbon dioxide.

Table 8: Results for methane

NMI	x $\mu\text{mol/mol}$	$u(x)$ $\mu\text{mol/mol}$	y' a.u.	$u(y')$ a.u.	\hat{x} $\mu\text{mol/mol}$	\hat{y} a.u.
NPL	2.0440	0.0155	5355.7	5.0	2.0507	5355.4
NMIJ	1.5685	0.0021	4138.3	1.5	1.5784	4136.3
NIST	1.8470	0.0060	4833.1	2.2	1.8483	4833.0
GUM	1.6200	0.0100	4208.2	2.1	1.6063	4208.4
NMIA	2.0080	0.0140	5197.1	7.2	1.9901	5198.9
CEM	2.0000	0.0040	5207.3	2.5	1.9937	5208.3
KRISS	1.6035	0.0006	4195.4	1.5	1.6024	4198.2
NMI VSL	1.9988	0.0037	5203.1	2.2	1.9921	5204.0
BAM	1.8060	0.0020	4756.7	4.1	1.8138	4744.0

The regression line reads as follows

$$y = 62.27 + 2581x . \tag{17}$$

The standard uncertainty of the intercept is 26.51, that of the slope 16, and the covariance -425.

The standard deviation of the x -residuals is 0.010 $\mu\text{mol/mol}$ (0.53% relative). The regression line is shown in figure 6.

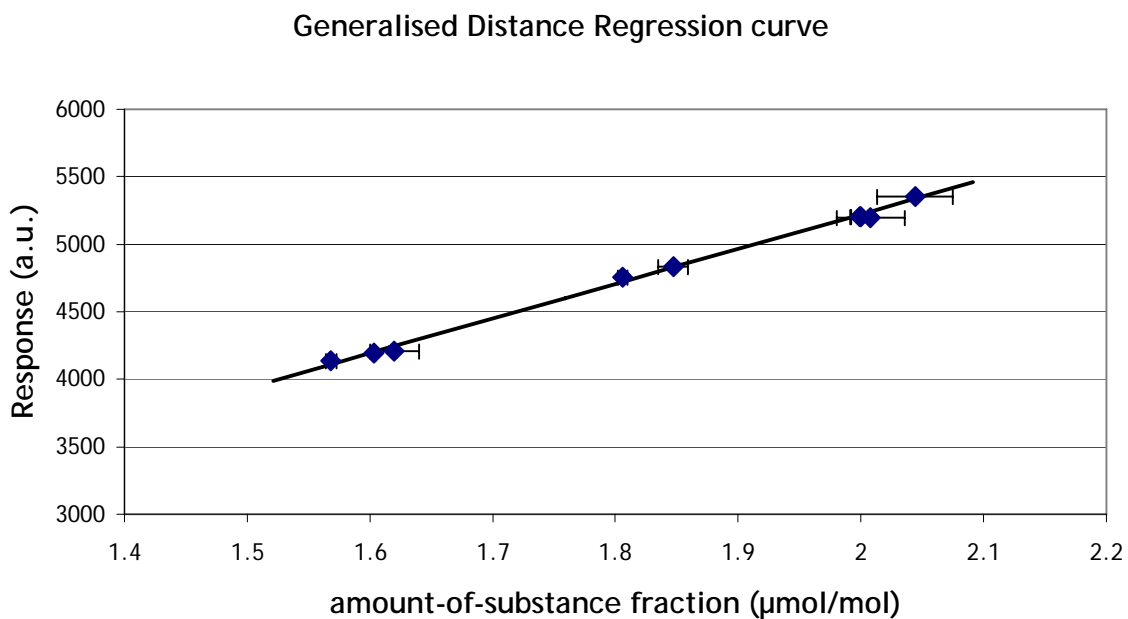


Figure 6: GDR of methane data

The residuals in x - and y -direction are shown in figures 7 and 8 respectively.

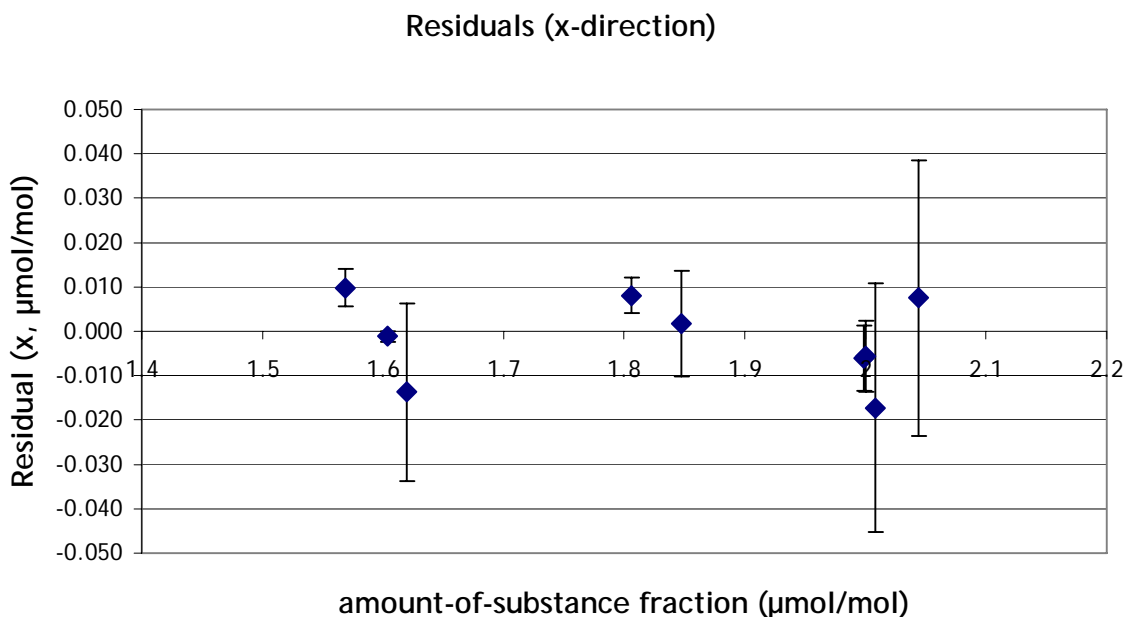


Figure 7: Residuals in x -direction for methane

The agreement between the cylinders seems to be better for methane than for carbon dioxide, taking into consideration the respective uncertainties. There are three cylinders not satisfying the criterion given in equation (10): BAM, KRISS, and NMIJ. As the uncertainties associated with the amount-of-substance fractions assigned to these mixtures are quite small in comparison with the other cylinders in the dataset, there can be some impact on the regression results. The use of a cut-off value for the weights based on the uncertainties associated with the amount-of-substance fractions may assist this

problem. A regression with $u(x) = 0.011 \mu\text{mol/mol}$ for BAM, KRISS, and NMIJ gives almost the same results. The standard deviation of the x -residuals is $0.011 \mu\text{mol/mol}$ (the same as in the original regression). The intercept (value 142; standard uncertainty 80) becomes insignificantly different from zero (t -test, 95% level of confidence).

Another option is to remove the results from BAM, KRISS, and NMIJ from the data set. The standard deviation of the x -residuals becomes then $0.009 \mu\text{mol/mol}$ (0.49% relative). The intercept (value 45; standard uncertainty 123) becomes insignificantly different from zero (t -test, 95% level of confidence).

Both alternatives give a slightly better goodness-of-fit, judging the intercept. The standard deviation of the x -residuals is somewhat better when removing the three cylinders from the dataset. The improvements are however minor in comparison to the removal of CEM from the dataset of carbon dioxide.

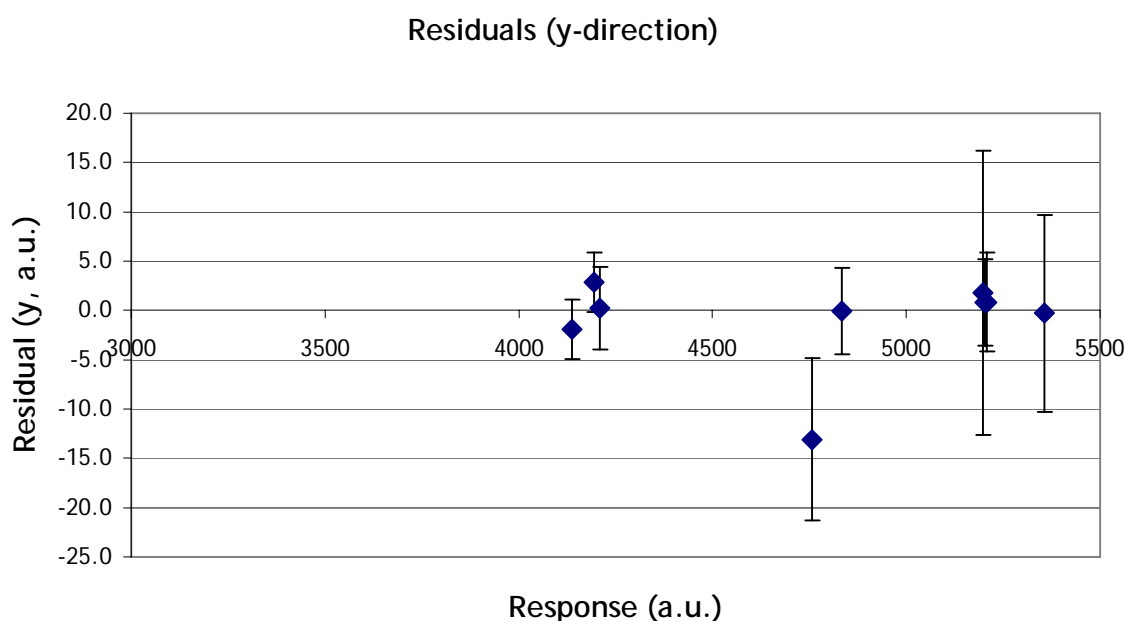


Figure 8: Residuals in y -direction for methane

The residuals in the y -direction show a discrepancy for the cylinder from BAM.

Discussion and conclusions

The direct comparison of the gravimetrically prepared gas mixtures shows agreement for carbon dioxide at $365 \mu\text{mol/mol}$ nominal within $0.52 \mu\text{mol/mol}$ (0.14% relative) standard uncertainty. At the same time, it is observed that many stated uncertainties are substantially smaller than this standard deviation of the x -residues, which leads to the situation that there is a significant difference between the (consensus) regression line and 5 (out of 9) amount-of-substance fractions. One cylinder lies between the 95% and 99% boundaries of the regression line, and after removing this cylinder from the dataset the standard deviation of the x -residuals reduces to $0.18 \mu\text{mol/mol}$ (0.05% relative). This value for the standard deviation is for several cylinders substantially greater than the stated standard uncertainties.

The analysis of the carbon dioxide data suggests that some of the stated uncertainties are too small. The protocol requested the NMIs to state the uncertainty from preparation only, which in most cases comprise factors influencing the gravimetric process and the purity analysis only. Under the presumption, that the evaluation of the uncertainty associated

with these steps is well understood, the data suggest that there are factors missing in the uncertainty budget, which may be associated with e.g., adsorption effects. These effects can be small and reversible, but nevertheless may differ in size and value from one cylinder to another.

The standard deviation of the x -residuals for methane at 1.8 $\mu\text{mol/mol}$ nominal is 0.011 $\mu\text{mol/mol}$. The discrepancy between the stated uncertainties associated with the amount-of-substance fractions is smaller than for carbon dioxide, which is reflected in 3 (out of 9) cylinders that satisfy the consistency agreement of ISO 6143. The influence of these cylinders on the regression results is small.

It is important to keep in mind that the regression line in this type of comparison represents a consensus, and that individual laboratories can demonstrate that the uncertainty associated with their result is (substantially) smaller than the standard deviation of the results. The standard deviations stated reflect in this sense some kind "consensus" or "over-all" performance.

Finally, it can be concluded that more work is needed in explaining where the observed discrepancies come from. Both datasets do not meet the requirements laid down in ISO 6142 and ISO 6143 for accepting the preparation data (ISO 6142) and the regression results (ISO 6143), which are obviously closely connected. The method of comparing gas mixtures under repeatability conditions can be a helpful tool to assess improvements in the uncertainty budgets for the amount-of-substance fractions derived from preparation.

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Annex A: Analytical data carbon dioxide

Table 9: Measurement data for carbon dioxide

Cylinder	P (mbar)	y (a.u.)	u(y) (a.u.)	Series	Seq. #
BAM 5020	1015.7	16142	11	Measurement #1	13
BAM 5020	1018.3	16168	9	Measurement #2	16
BAM 5020	1022.5	16232	9	Measurement #3	34
CEM DZ2442	1015.5	16029	11	Measurement #1	9
CEM DZ2442	1017.5	16054	14	Measurement #2	19
CEM DZ2442	1022.0	16106	15	Measurement #3	31
CSIR MD5712	1015.6	17470	7	Measurement #1	8
CSIR MD5712	1018.9	17511	8	Measurement #2	25
CSIR MD5712	1023.0	17584	8	Measurement #3	40
GUM ML6726	1015.4	16847	4	Measurement #1	6
GUM ML6726	1017.4	16894	13	Measurement #2	27
GUM ML6726	1022.1	16935	6	Measurement #3	30
KRISS MEO430	1018.1	17609	14	Measurement #2	26
KRISS MEO430	1015.4	17558	5	Measurement #1	11
KRISS MEO430	1022.4	17656	6	Measurement #3	33
NIST X138333	1015.4	16974	11	Measurement #1	5
NIST X138333	1017.8	17013	11	Measurement #2	17
NIST X138333	1022.9	17081	10	Measurement #3	37
NMIJ CPB28681	1015.1	17237	5	Measurement #1	3
NMIJ CPB28681	1019.1	17286	10	Measurement #2	20
NMIJ CPB28681	1023.3	17348	5	Measurement #3	41
NPL 163135	1015.0	16816	8	Measurement #1	2
NPL 163135	1017.7	16874	37	Measurement #2	23
NPL 163135	1022.9	16917	7	Measurement #3	36
VSL203667	1015.2	16864	6	Measurement #1	4
VSL203667	1015.5	16873	10	Measurement #1	10
VSL203667	1017.7	16902	15	Measurement #2	18
VSL203667	1018.6	16920	10	Measurement #2	24
VSL203667	1022.1	16963	14	Measurement #3	32
VSL203667	1022.9	16972	8	Measurement #3	38
VSL203673	1015.5	17991	50	Measurement #1	7
VSL203673	1017.9	18072	20	Measurement #2	21
VSL203673	1022.6	18116	34	Measurement #3	35
VSL205144	1015.6	16725	8	Measurement #1	12
VSL205144	1018.8	16774	12	Measurement #2	22
VSL205144	1022.9	16826	5	Measurement #3	39
VSL501113	1015.0	15885	11	Measurement #1	1
VSL501113	1015.8	15894	11	Measurement #1	14
VSL501113	1017.2	15918	10	Measurement #2	15
VSL501113	1019.2	15941	9	Measurement #2	28
VSL501113	1022.2	15981	12	Measurement #3	29
VSL501113	1023.4	15995	6	Measurement #3	42

Annex B: Analytical data methane

Table 10: Measurement data for methane

Cylinder	P (mbar)	y (a.u.)	u(y) (a.u.)	Series	Seq. #
BAM5020	1017.2	4765	12	Measurement #1	13
BAM5020	1021.9	4755	7	Measurement #3	34
BAM5020	1017.0	4751	8	Measurement #2	16
CEMDZ2442	1017.7	5211	6	Measurement #1	9
CEMDZ2442	1022.7	5202	8	Measurement #3	31
CEMDZ2442	1017.4	5209	5	Measurement #2	19
CSIR MD5712	1018.3	5190	5	Measurement #2	25
CSIR MD5712	1019.0	5190	6	Measurement #3	40
CSIR MD5712	1017.8	5211	7	Measurement #1	8
GUMML6726	1018.0	4212	7	Measurement #1	6
GUMML6726	1022.9	4206	6	Measurement #3	30
GUMML6726	1018.7	4207	7	Measurement #2	27
KRISS ME0430	1017.4	4198	3	Measurement #1	11
KRISS ME0430	1018.5	4195	7	Measurement #2	26
KRISS ME0430	1022.2	4193	10	Measurement #3	33
NIST X110522	1017.1	4829	4	Measurement #2	17
NIST X110522	1020.6	4834	10	Measurement #3	37
NIST X110522	1018.3	4837	11	Measurement #1	5
NMIJ CPB28681	1017.5	4140	5	Measurement #2	20
NMIJ CPB28681	1018.8	4135	5	Measurement #3	41
NMIJ CPB28681	1018.7	4139	11	Measurement #1	3
NPL163135	1021.1	5349	8	Measurement #3	36
NPL163135	1018.8	5365	7	Measurement #1	2
NPL163135	1017.8	5353	7	Measurement #2	23
VSL203667	1018.6	4700	9	Measurement #1	4
VSL203667	1017.6	4692	6	Measurement #1	10
VSL203667	1017.2	4686	6	Measurement #2	18
VSL203667	1017.9	4686	7	Measurement #2	24
VSL203667	1022.6	4694	7	Measurement #3	32
VSL203667	1020.2	4686	6	Measurement #3	38
VSL203673	1017.8	5483	7	Measurement #1	7
VSL203673	1017.7	5469	15	Measurement #2	21
VSL203673	1021.5	5477	8	Measurement #3	35
VSL205144	1017.3	5208	5	Measurement #1	12
VSL205144	1017.8	5202	7	Measurement #2	22
VSL205144	1019.8	5200	6	Measurement #3	39
VSL501113	1018.9	3890	10	Measurement #1	1
VSL501113	1017.1	3894	6	Measurement #1	14
VSL501113	1016.6	3882	9	Measurement #2	15
VSL501113	1018.9	3889	5	Measurement #2	28
VSL501113	1023.1	3890	7	Measurement #3	29
VSL501113	1018.6	3887	7	Measurement #3	42