21GRD06 MetCCUS

Results of analyser comparison in measuring CO_2 impurities: H_2O (Endress + Hauser J22 TDLAS gas analyser and MEECO AquaVolt 2™ moisture analyser) and O_2 (Endress + Hauser OXY5500 Optical Oxygen Analyzer)

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Summary

This report presents the results of a round-robin comparison performed as part of activity A3.3.4 from the Partnership on Metrology project “Metrology for the support for Carbon Capture Utilisation and Storage” (MetCCUS). This work is focusing on the performance evaluation of three commercial analysers, the Endress Hauser J22 TDLAS and the MEECO AquaVolt 2 for measuring water (H_2O) impurities in carbon dioxide (CO_2) and the Endress + Hauser Oxy5500 analyser for oxygen (O_2). All analysers were tested with calibration gas mixtures in the range of 5 µmol mol^{-1} to 60 µmol mol^{-1} H_2O or O_2, relevant to carbon capture, usage, and storage (CCUS). The report details performance parameters including response time, precision, bias, linearity, detection limits, and measurement uncertainty. These findings support instrument manufacturers in demonstrating the fitness of their equipment for CO_2 composition monitoring, while also supplying valuable data that can be used to refine and advance technologies for more accurate CO_2 analysis in the future.

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1. Results for H_2O analysers: Endress + Hauser J22 TDLAS gas analyser and MEECO AquaVolt 2™ moisture analyser

1.1 Introduction

The aim of this comparison is to evaluate commercial instruments that are used for measurements of impurities in carbon dioxide (CO_2). The analysers' performance were assessed according to the protocol (see Appendix A) for the comparison of analysers measuring impurities in carbon dioxide within the MetCCUS project. The Endress+Hauser J22, included in this study, employs tunable diode laser absorption spectroscopy (TDLAS), where a laser beam passes through a flowing gas sample and is partially absorbed by H_2O molecules at characteristic wavelengths. The transmitted intensity is measured and directly related to the water concentration, providing fast and reliable detection. The MEECO AquaVolt 2™ moisture analyser included in this study is based on Faraday's Law of Electrolysis, where water vapor in the sample gas is quantitatively absorbed by a phosphorus pentoxide (P_2O_5) film and electrolyzed between two electrodes, generating a current directly proportional to the moisture content.

The measurement were performed using calibration gas mixtures with H_2O in CO_2 in the range of 5 µmol mol^{-1} to 60 µmol mol^{-1}. For the measurement conducted with the Endress+ Hauser analyser, the range was 10 µmol mol^{-1} to 60 µmol mol^{-1} These calibration gas mixtures were prepared using a dynamic system equipped with thermal mass flow controllers (MFCs) and operated in accordance with ISO 6145-7 (1). This setup includes two MFCs connected to pure CO_2 and one MFC connected to a premixture (587 µmol mol^{-1} H_2O in CO_2). A pressure controller, adjustable within the range of 1–5 bar(a), feeds into the analyser's inlet. Dynamic dilutions are achieved by automatically adjusting the flow rates from the MFCs using a software program. The flow from the MFCs is calibrated against VSL primary flow meters. An overview of the gas mixtures used, including their amount fractions and total flow rates, is provided in Table 1.

Table 1 Overview of gas mix amount fractions and total flows

	Amount fraction	**Total flow**
Mix	(µmol/mol)	mL/min
1	0 ppm	1000
2	5 ppm	1000
3	10 ppm	1000
4	20 ppm	1000
5	30 ppm	1000
6	40 ppm	1000
7	50 ppm	900
8	60 ppm	750

Additionally, Table 2 summarizes the measurement dates and the specific performance characteristics evaluated for Endress + Hauser analyser, including response time, linearity (across both increasing and decreasing concentration ranges), repeatability, reproducibility, hysteresis, detection limits, and measurement deviation. Similarly, Table 3 presents the corresponding data for the MEECO analyser.

Table 2. Overview of measurement dates and corresponding performance characteristics for the Endress+ Hauser analyser

Date	Performance characteristics
02/04/2025 (set 1)	All these measurements were performed to assess: • Linearity : calibration from low to high and high to low, including hysteresis, • Repeatability and reproducibility • Detection limit • Precision
03/04/2025 (set 2)	
09/04/2025 (set 3)	
10/04/2025 (set 4)	
02/06/2025	Response time measurements (additional measurements)

Table 3. Overview of measurement dates and corresponding performance characteristics for the MEECO analyser

Date	Performance characteristics
24/03/2025	Response time measurements
03/04/2025 (set 1)	All these measurements were performed to assess: • Linearity : calibration from low to high and high to low, including hysteresis, • Repeatability and reproducibility • Detection limit • Precision
04/04/2025 (set 2)	
09/04/2025 (set 3)	
10/04/2025 (set 4)	

1.2 Response time

1.2.1 Endress + Hauser J22 TDLAS gas analyser

In the graph below, the response time can be seen for the measurement of 40 µmol mol^{-1} H_2O in CO_2 at total flow of 1L/min. The first graph only contains the first 10 minutes. The second graph shows the remaining minutes (two hours). The blue line represents the response of the analyser. The black dotted line represents the T95 level, reached in approximately 8 minutes.

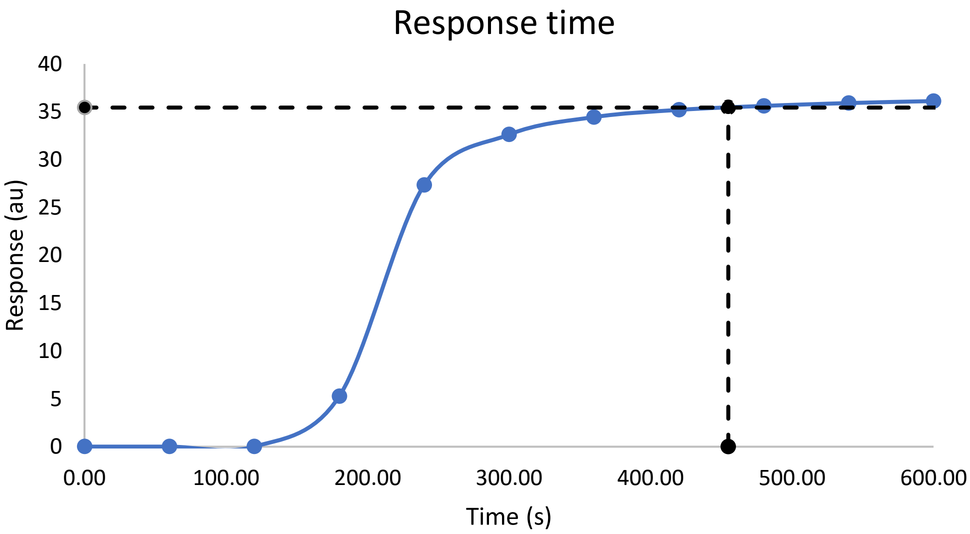


Figure 1 shows the response signal (au) as a function of time (s), with the dashed horizontal line indicating the target response level

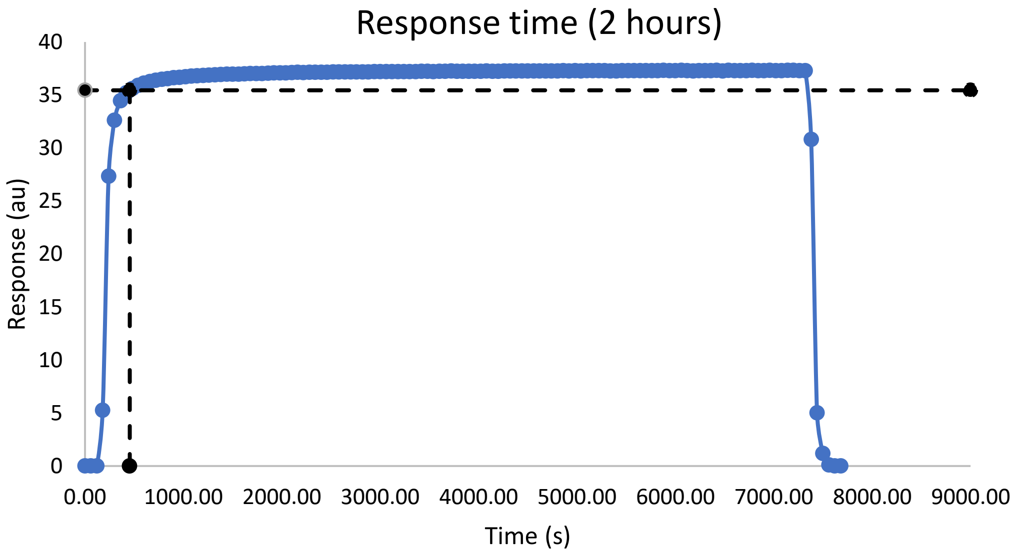


Figure 2 Response time profile over two hours

Additionally we had to lower the flowrate for the highest point in the calibration, 60 µmol mol^{-1} , to a total flow of 750 mL/min from the dynamic dilution system (Table 1). Also, here we tested the response time for 1 hour. The black dotted line represents the T95 level, reached in 4 minutes, See Figure 3.

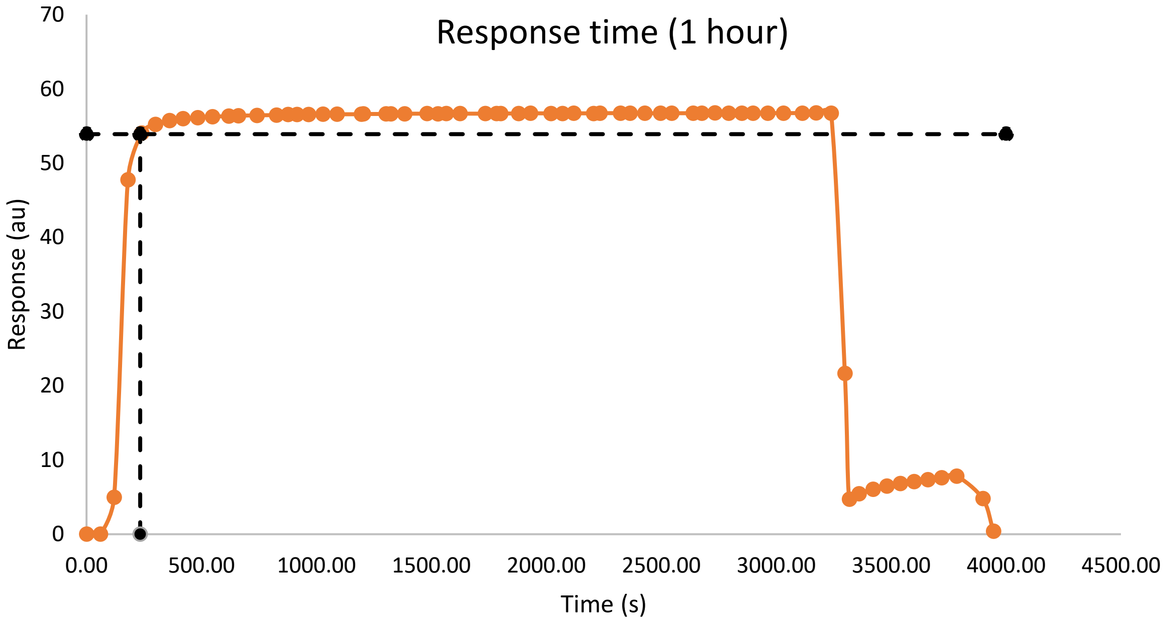


Figure 3 Response time profile over 1 hour of 60 µmol mol^{-1} H_2O. The plot shows the analyser signal (au) as a function of time (s). The black dotted line indicates the T_{95} response level

1.2.2 MEECO AquaVolt 2™ moisture analyser

In the graph below, the response time can be seen for the measurement of 45 µmol mol^{-1} H_2O in CO_2. The first graph only contains the first 10 minutes. The second graph shows the remaining minutes (1hour). The orange line represents the response of the analyser. The black dotted line represents the T95 level, reached in 7.08 minutes

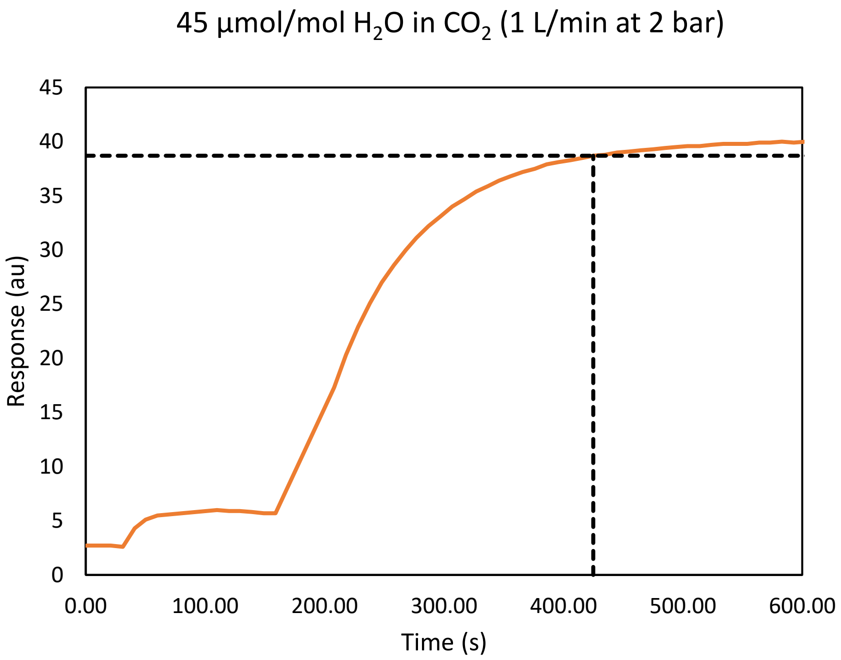


Figure 4 shows the response signal (au) as a function of time (s), with the dashed horizontal line indicating the target response level

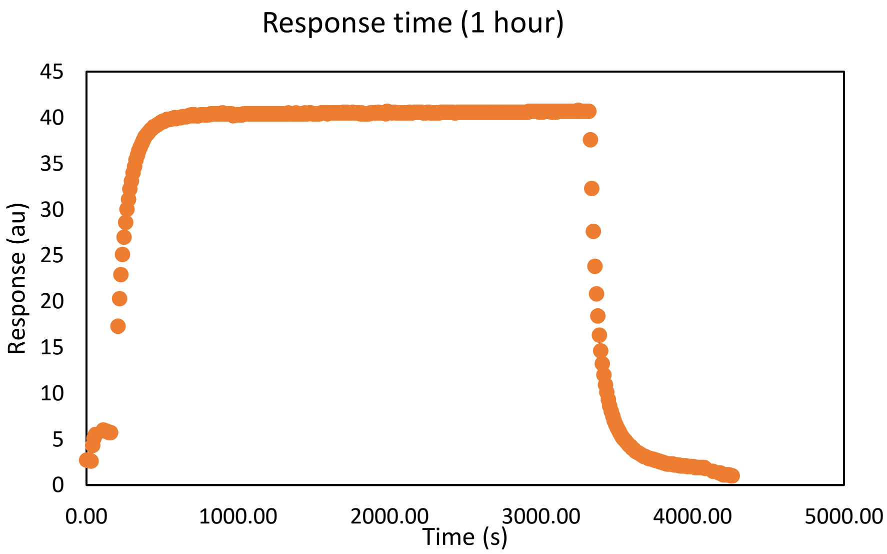


Figure 5 Response time profile over one hour

Additionally we had to lower the flowrate for the highest point in the calibration to a total flow of 750 mL/min (Table 1). Also, here we tested the response time for 2 hours. The black dotted line represents the T95 level, reached in 11.5 minutes, See Figure 5.

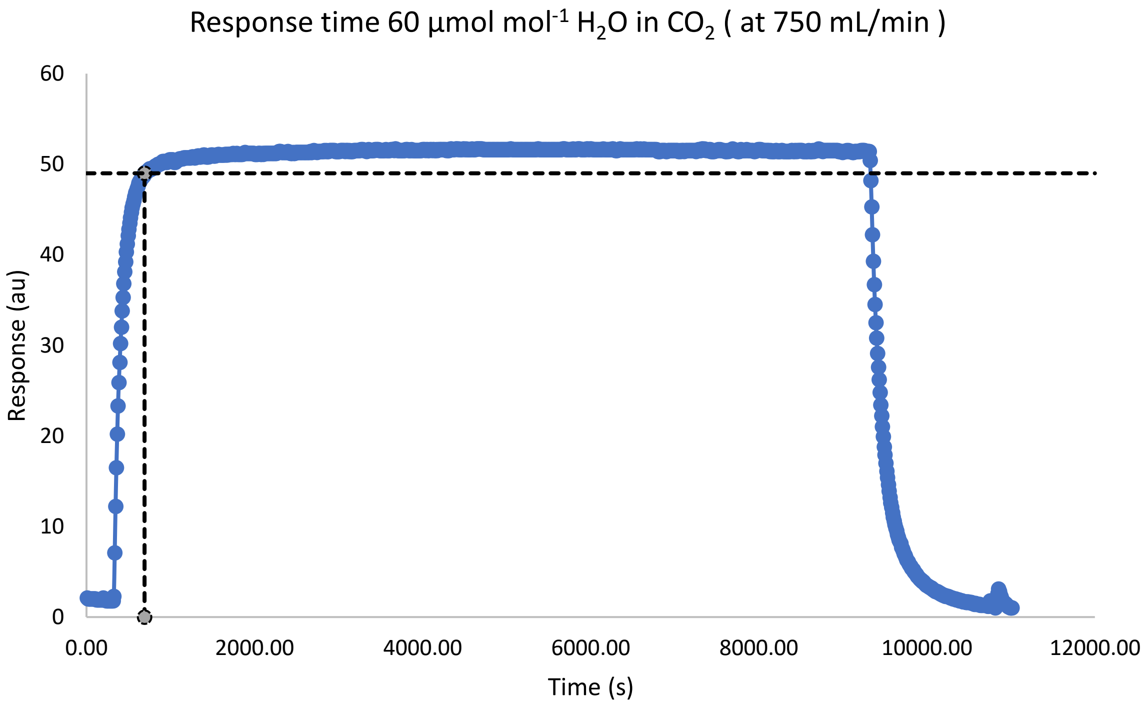


Figure 6 Response time profile over 2 hours of 60 µmol mol^{-1} H_2O. The plot shows the analyser signal (au) as a function of time (s). The black dotted line indicates the T_{95} response level

1.3 Precision

At various fractions the repeatability standard deviation (s(*r*)) and reproducibility standard deviation (s(*R*)) were calculated based on measurements performed across different days (see Table 2 and Table 3). These values were determined according to ISO 5725-2:2019 (2) using analysis of variance (ANOVA).

1.3.1 Endress + Hauser J22 TDLAS gas analyser

Table 4 Repeatability (s(r)) and reproducibility (s(R)) at various concentrations, calculated per ISO 5725-2:2019 using ANOVA

x (mol/mol)	ux (mol/mol)	x (µmol/mol)	s *(r)* (%)	s *(R)* (%)
1.07E-05	3.724E-07	10.69	0.19%	4.37%
2.07E-05	5.066E-07	20.68	0.08%	1.47%
3.07E-05	6.752E-07	30.67	0.04%	0.77%
4.07E-05	8.58E-07	40.67	0.04%	0.42%
5.02E-05	1.038E-06	50.25	0.06%	0.27%
6.02E-05	1.228E-06	60.17	0.04%	0.19%

The data show that both s(*r*) and s(*R*) decrease as the fraction increases. At the lowest fractions (10.7 µmol mol^{-1}), both deviations are relatively high, with s(*r*)=0.19% and s(*R*)=4.37%. When looking at the results obtained for fraction higher than 11 µmol mol^{-1} the average is 0.05% for s(*r*) and 0.63% for s(*R*).

1.3.2 MEECO AquaVolt 2™ moisture analyser

Table 5 Repeatability (s(r)) and reproducibility (s(R)) at various concentrations, calculated per ISO 5725-2:2019 using ANOVA

x (mol/mol)	Ux (mol/mol)	x (µmol/mol)	s *(r)* (%)	s *(R)* (%)
5.70E-06	3.32E-07	5.7	0.75%	3.28%
1.07E-05	3.724E-07	10.69	0.19%	1.93%
2.07E-05	5.066E-07	20.68	0.09%	1.41%
3.07E-05	6.752E-07	30.67	0.14%	1.24%
4.07E-05	8.58E-07	40.67	0.13%	1.31%
5.02E-05	1.038E-06	50.25	0.10%	1.38%
6.02E-05	1.228E-06	60.17	0.10%	1.56%

The data show that both s(*r*) and s(*R*) decrease as the fraction increases. At the lowest fraction(5.7 µmol mol^{-1}), both deviations are relatively high, with s(*r*)=0.75% and s(*R*)=3.28%. When looking at the results obtained for fraction higher than 11 µmol mol^{-1} the average is 0.1% for s(*r*) and 1.3% for s(*R*).

1.4 Bias

The accuracy is derived based on the bias. The deviation (D_{x_i}) and relative deviation (D_{rel}) are the closeness of the response of the analyser (r_i) to the true amount fraction of the gas mixture (x_i) (Equations (1) and (2)).

$$D_{x_i} = r_i - x_i \qquad \text{eq. (1)}$$

$$D_{rel} = \frac{D_{x_i}}{x_i} \qquad \text{eq. (2)}$$

This assessment evaluates the accuracy and stability of an analyser across four calibration sessions by comparing its measured responses to known gravimetric fraction (see table 1). The data is shown in Table 6 for Endress + Hauser and Table 8 for MEECO analyser.

1.4.1 Endress + Hauser J22 TDLAS gas analyser

The analysis focused on the deviation from gravimetric value (Dx) and the relative deviation (Drel). The results as shown in Table 6, consistently show a systematic underestimation of the gravimetric fraction across all calibration sets and in the full range. The bias decreases (in relative terms) with increasing fractions (see Figure 7). The deviation stabilizes above the 20 µmol mol^{-1} (see Figure 14 in the Appendix B)

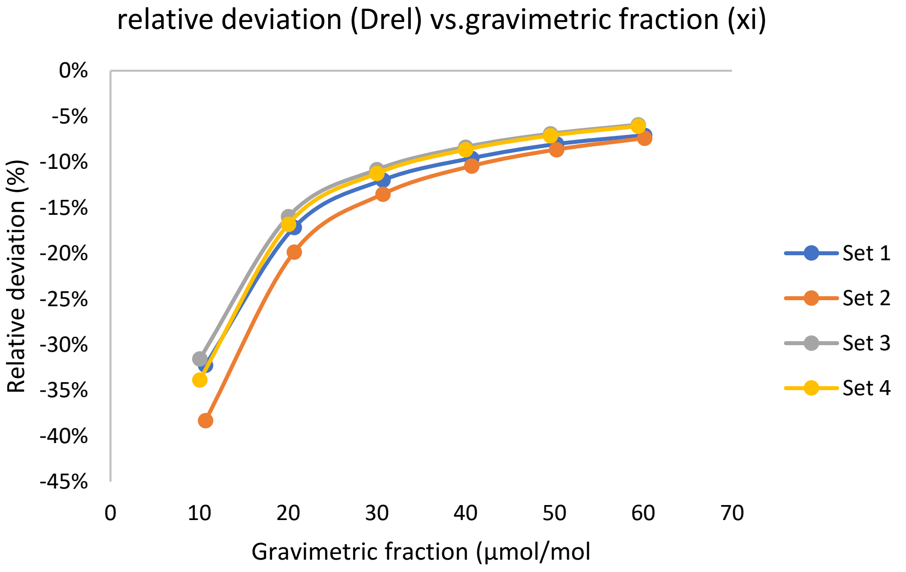


Figure 7 A visual plot showing the relative deviation (Drel%) vs gravimetric fraction (µmol/mol) for all four calibration sets

Table 6 Accuracy assessment based on bias: deviation (Dx) and relative deviation (Drel) between analyser response (ri) and gravimetric fraction (xi)

	x (mol/mol)	x (ppm)	average response (ppm)	Dx	Drel
Set 1	1.0692E-05	10.692	7.246	-3.447	-32%
	2.0683E-05	20.683	17.135	-3.548	-17%
	3.0674E-05	30.674	27.004	-3.671	-12%
	4.0666E-05	40.666	36.771	-3.895	-10%
	5.0247E-05	50.247	46.213	-4.034	-8%
	6.0166E-05	60.166	55.917	-4.249	-7%
Set 2	1.0692E-05	10.692	6.595	-4.097	-38%
	2.0684E-05	20.684	16.576	-4.108	-20%
	3.0675E-05	30.675	26.533	-4.141	-14%
	4.0666E-05	40.666	36.425	-4.241	-10%
	5.0248E-05	50.248	45.913	-4.335	-9%
	6.0165E-05	60.165	55.724	-4.441	-7%
Set 3	1.005E-05	10.05	6.879	-3.171	-32%
	2.0029E-05	20.029	16.830	-3.199	-16%
	3.0007E-05	30.007	26.758	-3.249	-11%
	3.9984E-05	39.984	36.646	-3.338	-8%
	4.9551E-05	49.551	46.132	-3.419	-7%
	5.9452E-05	59.452	55.939	-3.513	-6%
Set 4	1.0051E-05	10.051	6.647	-3.404	-34%
	2.003E-05	20.03	16.664	-3.366	-17%
	3.0009E-05	30.009	26.636	-3.373	-11%
	3.9985E-05	39.985	36.531	-3.454	-9%
	4.9551E-05	49.551	46.034	-3.517	-7%
	5.9452E-05	59.452	55.846	-3.606	-6%

Manufacture note: The default analyser used for testing was a non-differential TDLAS optical analyser. This technology is commonly used for high concentration moisture measurements typically from 20 to 500 ppm. While the test data is repeatable, it does show some consistent offset. This offset can be removed in the firmware through use of a RATA adjustment. Additional measurement data at various concentrations was collected by VSL with the RATA adjustment applied (Table 7).

Table 7 Overview of additional measurement data after offset adjustment

with offset adjustment				
x (mol/mol)	**x (ppm)**	**average response (ppm)**	**Dx**	**Drel**
1.06207E-05	10.62	8.369	-2.252	-21.2%
3.05571E-05	30.56	28.114	-2.444	-8.0%
5.99724E-05	59.97	57.425	-2.547	-4.2%

For trace moisture applications (typically < 10 ppm) we recommend a differential TDLAS optical analyser that automatically corrects the measurement for any background noise or offset.

1.4.2 MEECO AquaVolt 2™ moisture analyser

The analysis focused on the deviation from true values (Dx) and the relative deviation (Drel). The lowest concentration point (0.70 ppm) was excluded from analysis due to its high deviation and unreliable performance at this level.

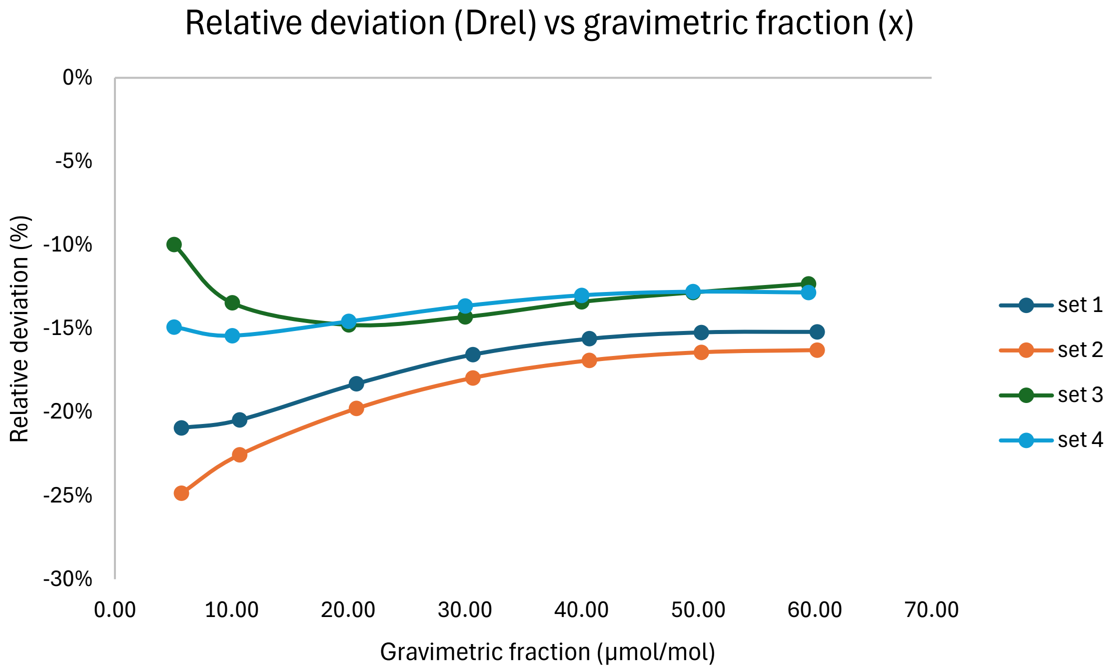


Figure 8 A visual plot showing the relative deviation (Drel%) vs gravimetric fraction (μmol mol^{-1}) for all four calibration sets, excluding the 0.70 ppm point.

The results consistently show a systematic underestimation of the gravimetric fraction across all calibration sets, with negative relative deviations ranging from -10% to -25%.

Table 8 Accuracy assessment based on bias: deviation (Dx) and relative deviation (Drel) between analyser response (ri) and gravimetric fraction (xi)

	x (mol mol^{-1})	x (µmol mol^{-1})	Average response (µmol mol^{-1})	Dx	Drel
Set 1	5.70E-06	5.70	4.50	-1.19	-21%
	1.07E-05	10.69	8.50	-2.19	-20%
	2.07E-05	20.68	16.90	-3.79	-18%
	3.07E-05	30.67	25.59	-5.08	-17%
	4.07E-05	40.67	34.32	-6.35	-16%
	5.03E-05	50.25	42.59	-7.65	-15%
	6.02E-05	60.17	51.02	-9.15	-15%
Set 2	5.70E-06	5.70	4.28	-1.42	-25%
	1.07E-05	10.69	8.28	-2.41	-23%
	2.07E-05	20.68	16.59	-4.09	-20%
	3.07E-05	30.67	25.17	-5.51	-18%
	4.07E-05	40.67	33.79	-6.88	-17%
	5.03E-05	50.25	42.00	-8.25	-16%
	6.02E-05	60.17	50.36	-9.80	-16%
Set 3	5.06E-06	5.06	4.56	-0.51	-10%
	1.01E-05	10.05	8.70	-1.35	-13%
	2.00E-05	20.03	17.07	-2.96	-15%
	3.00E-05	30.01	25.71	-4.29	-14%
	4.00E-05	39.98	34.63	-5.36	-13%
	4.96E-05	49.55	43.19	-6.36	-13%
	5.95E-05	59.45	52.12	-7.33	-12%
Set 4	5.06E-06	5.06	4.31	-0.75	-15%
	1.01E-05	10.05	8.50	-1.55	-15%
	2.00E-05	20.03	17.11	-2.92	-15%
	3.00E-05	30.01	25.91	-4.10	-14%
	4.00E-05	39.98	34.78	-5.20	-13%
	4.96E-05	49.55	43.21	-6.34	-13%
	5.95E-05	59.45	51.82	-7.64	-13%

Manufacturer note: We posit that the relative deviation between the gravimetric/dilution and the measured value may derive from either a flow effect or an incorrect flow correction factor for CO_2. Alternately, upon review, we find that departing from the Standard Operating Procedure in our manual by restricting the bypass flow may have let to unintended consequences. We are investigating that at our factory as well.

However, when measuring a 100.45 ppm water standard in nitrogen at VSL, the relative deviation was only 0.12%, indicating that the instrument operates well within the specified uncertainty range as shown in Table 9.

Table 9 Measurement result of a 100 ppm H_2O/N_2 standard

	Average response ($mol\ mol^{-1}$)	**Gravimetric value x ($mol\ mol^{-1}$)**	**Drel**
100 ppm standard (H_2O/N_2)	100.57	100.45	0.12%

1.5 Linearity

1.5.1 Endress + Hauser J22 TDLAS gas analyser

The linearity of the analyser have been determined in the range of 10-60 µmol mol^{-1} H_2O in CO_2 for all calibration sets. The results have been fitted using VSL's curvefit software which model is based on weighted GDR following ISO 6143 and the residuals in both x (H_2O µmol mol^{-1}) and y (response) directions.

Table 10 The table contains 8 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties (calibration set 1)

	x (µmol mol^{-1})	**ux (µmol mol^{-1})**	**Y**	**uy**
1	10.692	0.372	7.246	0.023
2	20.683	0.507	17.135	0.013
3	30.674	0.675	27.004	0.016
4	40.666	0.858	36.771	0.032
5	50.247	1.038	46.213	0.120
6	60.166	1.228	55.917	0.027

The results from the table above have been linear fitted with the uncertainties in Curvefit, which yielded in the results below.

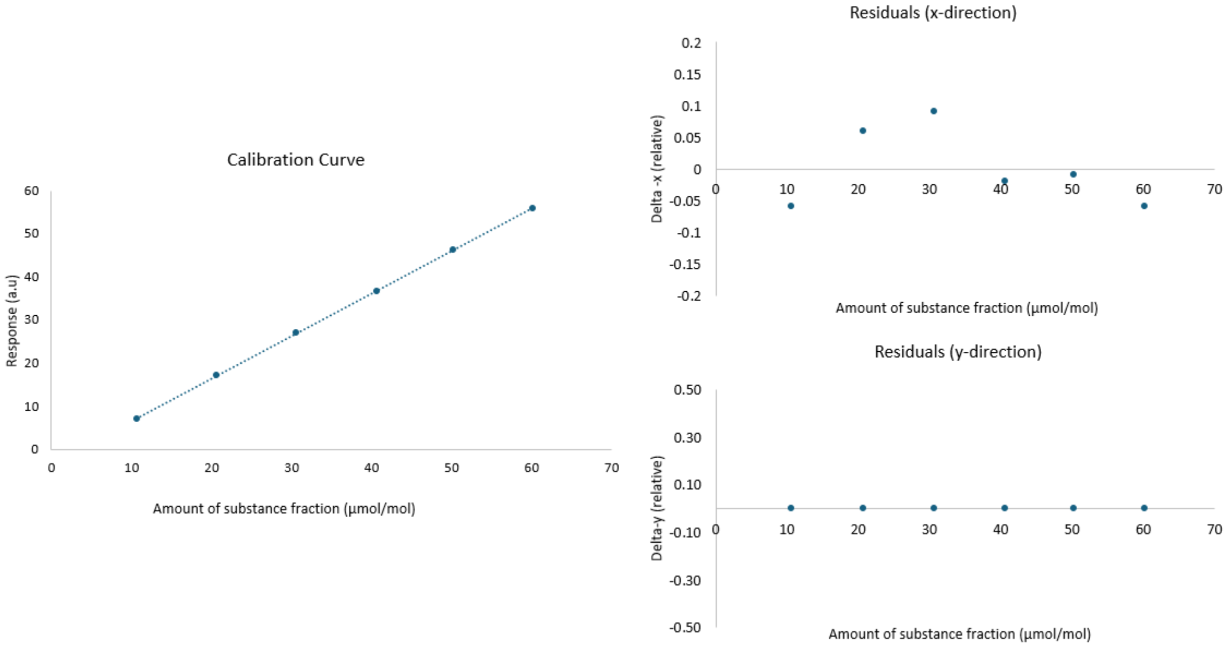


Figure 9 Calibration fit and residual analysis in x- and y-direction (set 1)

The results shows a goodness-of-fit (ISO 6143 (2)) at 0.07, which is a good-fitting model; the value is well below 2, indicating that the linear approach is appropriate. Table 11 shows the goodness of fit and the coefficient of the regression model of other calibration sets. See appendix B for other calibration sets.

Table 11 . Regression model coefficients and goodness-of-fit (ISO 6143) for four calibration sets.

Calibration Set	Intercept (a_0)	Uncertainty a_0	Slope (a_1)	Uncertainty a_1	Goodness-of-fit (ISO 6143)	LoD
Set 1	-3.2641	0.4601	0.9849	0.0173	0.0851	1.44E-02
Set 2	-4.0140	0.4645	0.9942	0.0174	0.0756	1.43E-02
Set 3	-3.1001	0.5886	0.9940	0.0248	0.0319	1.43E-02
Set 4	-3.3588	0.5909	0.9975	0.0248	0.0591	1.42E-02

Across all calibration sets (see Table 1), the analyser demonstrates reliable and statistically linear behaviour in the tested range of 10–60 µmol mol^{-1} H_2O in CO_2. The regression models show minimal deviation, consistent sensitivity and goodness-of-fit indicators well below 2.

1.5.2 MEECO AquaVolt 2™ moisture analyser

The linearity of the analyser have been determined in the range of 5-60 µmol mol^{-1} H_2O in CO_2 for all calibration sets . The results have been fitted using VSL's curvefit software which model is based on weighted GDR following ISO-6143 (3) and the residuals in both x (H_2O µmol mol^{-1}) and y (response) directions.

Table 12 The table contains 8 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties

	x (µmol mol^{-1})	ux (µmol mol^{-1})	Y	uy
1	0.700	0.320	0.600	2.26E-16
2	5.697	0.332	4.503	0.036
3	10.692	0.372	8.503	0.036
4	20.684	0.507	16.897	0.037
5	30.675	0.675	25.594	0.049
6	40.666	0.858	34.316	0.090
7	50.248	1.038	42.594	0.115
8	60.165	1.228	51.019	0.098

The results from the Table 12 have been fitted with the uncertainties in Curvefit, which yielded in the results below.

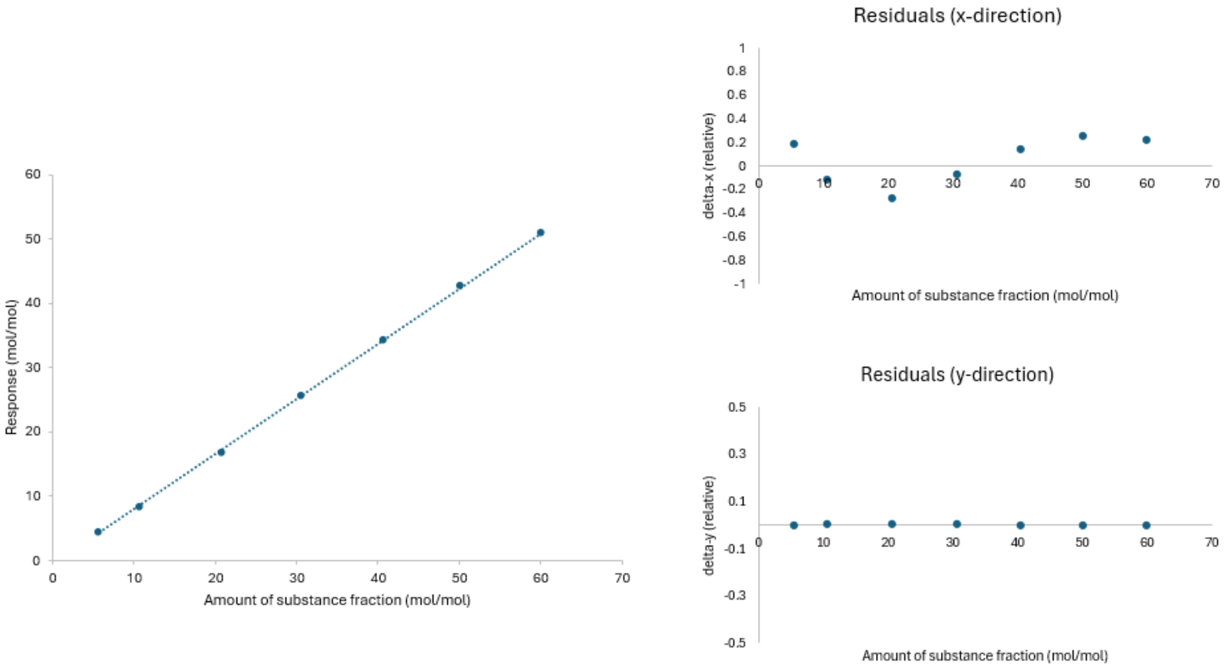


Figure 10 Calibration fit and residual analysis in x- and y-direction (set 1)

The results shows a goodness-of-fit (ISO 6143) at 0.5575, which is a good-fitting model; the value is well below 2, indicating that the linear approach is appropriate. Table 13 shows the goodness of fit and the coefficient of the regression model of other calibration sets. See Appendix C for other calibration sets.

Table 13 . Regression model coefficients and goodness-of-fit (ISO 6143) for four calibration sets.

Calibration Set	Intercept (a_0)	Uncertainty a_0	Slope (a_1)	Uncertainty a_1	Goodness-of-fit (ISO 6143)	I_{det}
Set 1	-0.5141	0.2648	0.8535	0.0122	0.5575	0.1019
Set 2	-0.6713	0.2685	0.8451	0.0122	0.5011	0.1029
Set 3	0.0693	0.3160	0.8641	0.0175	0.4827	0.1006
Set 4	-0.1410	0.3559	0.8712	0.0177	0.3136	0.0998

Across all calibration sets (see Table 1), the analyser demonstrates reliable and statistically linear behaviour in the tested range of 5–60 µmol mol^{-1} H_2O in CO_2. The regression models show minimal deviation, consistent sensitivity and goodness-of-fit indicators well below 2.

1.6 Detection limit

The limit of detection will be expressed as the lowest fraction that can be measured with statistical significance by the analysers.

The detection limit (l_{det}) is calculated using equation below.

$$l_{det} = 3.3 \times \frac{S_{r,z}}{b} \qquad \text{eq. (3)}$$

Here, $S_{r,z}$ represents the repeatability standard deviation at the lowest concentration detectable by the analyser. For the **Endress + Hauser analyser**, this value was determined at 0.0043. The slope (b) of the calibration function was determined by the linearity test (see table 11). The average detection limit is 1.43E-02 µmol mol^{-1}.

For the **MEECO analyser**, $S_{r,z}$ was calculated based on pure CO_2 measurements using ANOVA method, resulting in a value of 0.03. The slope (b) of the calibration function was determined by the linearity test (see table 13). The average detection limit is 0.11 µmol mol^{-1}.

1.7 Measurement uncertainty

The measurement uncertainty of the analyser has been determined based on the main contributing components: the reproducibility standard deviation s(R), the uncertainty of the reference material (including the applied dilution), and the detection limit.

For the **Endress + Hauser analyser**, the individual standard uncertainties for each component are summarized in the Table 14. The expanded measurement uncertainty U, representing a 95% confidence level, was calculated by multiplying the combined standard uncertainty by a coverage factor k = 2:

U = k × uc ≈ 2 × 0.65 ≈ 1.3 µmol mol^{-1}

Accordingly, the reported measurement result at a concentration of 30 µmol/mol is associated with an expanded uncertainty of: 30 µmol mol-1 ± 1.3 µmol mol-1 (at k = 2).

Table 14 Summary of the standard uncertainty components contributing to the combined measurement uncertainty of the analyser at a response level of 30 µmol/mol

Component	**Standard uncertainty (µmol mol^{-1})**
Reproducibility	0.20
Reference (with dilution)	0.62
Detection limit	0.00143

For the **MEECO analyser**, the corresponding uncertainty components are listed in Table 15. Similarly, the expanded measurement uncertainty U, representing a 95% confidence level, was calculated by multiplying the combined standard uncertainty by a coverage factor $k = 2$:

$U = k \times uc \approx 2 \times 0.70 \approx 1.4\ \mu\text{mol mol}^{-1}$

Therefore, the reported measurement result at a concentration of 30 µmol mol^{-1} is associated with an expanded uncertainty of: 30 µmol mol^{-1} ± 1.4 µmol mol^{-1} (at $k = 2$).

Table 15 Summary of the standard uncertainty components contributing to the combined measurement uncertainty of the analyser at a response level of 30 µmol/mol

Component	**Standard uncertainty (µmol mol^{-1})**
Reproducibility	0.32
Reference (with dilution)	0.62
Detection limit	0.10

1.8 Conclusion

Both analysers, Endress + Hauser J22 TDLAS gas analyser and MEECO AquaVolt 2™ moisture analyser were evaluated their performance in measuring CO_2 impurities (H_2O), focusing on key parameters including linearity, precision, bias, detection limit, and measurement uncertainty.

For **Endress + Hauser J22 TDLAS gas analyser**, the linearity assessment across 10–60 µmol mol^{-1} H_2O in CO_2 showed good fit, with a average goodness-of-fit value of 0.07 across the four calibration sets. The analyser showed a T95 response time of approximately 8 minutes at 40 µmol/mol with a flow of 1 L/min. The repeatability standard deviation s(r) averaged 0.05% for fractions above 11 µmol mol^{-1}, while the reproducibility standard deviation s(R) averaged 0.63% in the same range. The analyser consistently showed a systematic underestimation. The bias decreases above 11 µmol mol^{-1}, with average relative deviations ranging from –20% to –6% across all four sets. According to the manufacturer, this offset is typical for non-differential TDLAS systems designed for higher moisture levels (20–500 µmol mol^{-1}) but can be corrected in the firmware using a RATA adjustment, as confirmed by additional measurement data (Table 7). For trace-level applications below 10 µmol mol^{-1}, a differential TDLAS configuration is recommended. The average detection limit was determined to be 1.43E-02 µmol mol^{-1}, calculated based on the repeatability standard deviation and the calibration slope. The combined standard measurement uncertainty at a response of 30 µmol mol^{-1} was calculated as 0.65 µmol mol^{-1}, resulting in an expanded uncertainty of ±1.3 µmol mol^{-1} (at $k = 2$). This corresponds to a relative expanded uncertainty of approximately 4%.

Similarly, **the MEECO AquaVolt 2™ moisture** analyser was evaluated for its performance in measuring CO_2 impurities. The linearity assessment across 5–60 µmol mol^{-1}H_2O in CO_2 showed good fit, with goodness-of-fit values ranging between 0.31 and 0.56, and slopes between 0.84 and 0.87 across the four calibration sets. The repeatability standard deviation s(r) averaged 0.1% for fractions above 11 µmol mol^{-1}, while the reproducibility standard deviation s(R) averaged 1.3% in the same range. The analyser consistently showed a systematic underestimation, with relative deviations between –10% and –25% across sets. The manufacturer notes this may result from flow effects or an incorrect CO_2 flow correction factor. A deviation from the SOP, restricting bypass flow, may also have contributed. This is under investigation. Despite this, a 100 µmol mol^{-1} H_2O/N_2 standard showed only 0.12% deviation, indicating good performance under standard conditions. The average detection limit was determined to be 0.11 µmol mol^{-1}, calculated based on the repeatability standard deviation and the calibration slope. The combined standard measurement uncertainty at a response of 30 µmol/mol was calculated as 0.70 µmol mol^{-1}, resulting in an expanded uncertainty of ±1.4 µmol mol^{-1} (at $k = 2$). This corresponds to a relative expanded uncertainty of approximately 4.7%.

Both analysers demonstrated reliable performance for the intended application, showing stable operation, acceptable linear response across the tested concentration ranges relevant to CO_2 impurity monitoring. Despite a systematic underestimation observed for both instruments, the deviations were consistent and can be corrected by manufacturer. Given their response time, detection limits, and reproducibility, both the Endress + Hauser J22 TDLAS and the MEECO AquaVolt 2™ can be considered fit for purpose as suitable commercial analysers capable of performing quick and reliable measurements of water impurities in CO_2.

21GRD06 MetCCUS

2 Results for OXY5500 Optical Oxygen Analyzer in the comparison of analysers measuring CO_2 impurities (Oxygen)

2.1 Introduction

The aim of this comparison is to evaluate commercial instruments that are used for measurements of impurities in carbon dioxide (CO_2). The analysers' performance were assessed according to the protocol for the comparison of analysers measuring impurities in carbon dioxide within the MetCCUS project. The Endress+Hauser OXY5500 analyser included in this study uses optical fluorescence quenching, where blue LED light excites the sensor, and the presence of oxygen reduces (quenches) the emitted fluorescence. The degree of quenching is proportional to the oxygen concentration.

The measurement were performed using calibration gas mixtures with O_2 in CO_2 in the range of 10 µmol mol^{-1} to 60 µmol mol^{-1}. These calibration gas mixtures were prepared using a dynamic system equipped with thermal mass flow controllers (MFCs) and operated in accordance with ISO 6145-7. This setup includes two MFCs connected to pure CO_2 and one MFC connected to a premixture (400 µmol mol^{-1} O_2 in CO_2). A pressure controller, adjustable within the range of 1–5 bar(a), feeds into the analyser's inlet. Dynamic dilutions are achieved by automatically adjusting the flow rates from the MFCs using a software program. The flow from the MFCs is calibrated against VSL primary flow meters. An overview of the gas mixtures used, including their amount fractions and total flow rates, is provided in Table 16.

Table 16 Overview of gas mix amount fractions and total flows

	Amount fraction	**Total flow**
Mix	(µmol/mol)	mL/min
1	0 ppm	1000
2	10 ppm	1000
3	20 ppm	1000
4	30 ppm	1000
5	40 ppm	750
6	50 ppm	600
7	60 ppm	500

Additionally, Table 17 summarizes the measurement dates and the specific performance characteristics that were evaluated, such as response time, linearity (across both increasing and decreasing concentration ranges), repeatability, reproducibility, hysteresis, detection limits, and measurement deviation.

Table 17 overview of measurement dates and corresponding performance characteristics

Date	Performance characteristics
03/06/2025 (set 1)	All these measurements were performed to assess: • Linearity : calibration from low to high and high to low, including hysteresis, • Repeatability and reproducibility • Detection limit • Precision
04/06/2025 (set 2)	
10/06/2025 (set 3)	
01/06/2025	Response time measurements

2.2 Response time

In the graph below, the response time can be seen for the measurement of 30 µmol mol^{-1} O_2 in CO_2 at total flow of 1L/min. The first graph only contains the first 10 minutes. The second graph shows the remaining minutes (one and half hours). The orange line represents the response of the analyser. The black dotted line represents the T95 level, reached in approximately 3.5 minutes. The signal increases and stabilizes after approximately 5 minutes. An overshoot occurs just after T95, reaching a peak before gradually settling at the final response level

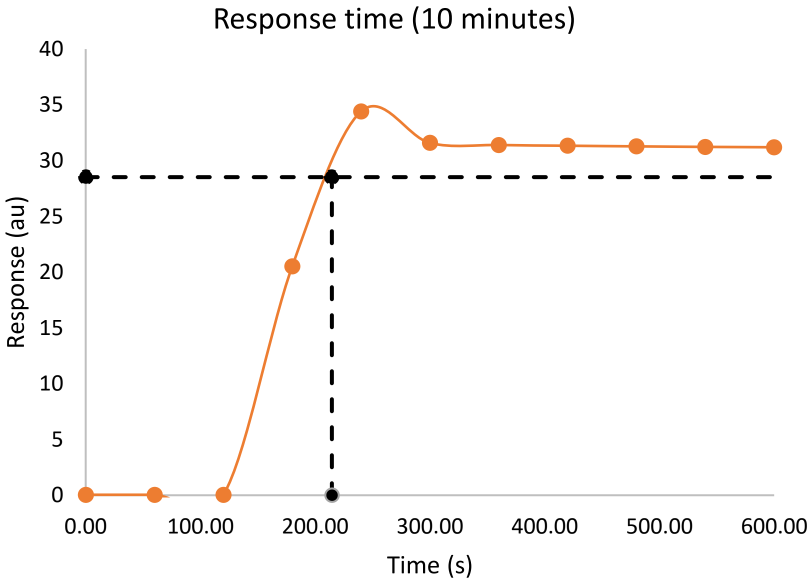


Figure 11 shows the response signal (au) as a function of time (s), with the dashed horizontal line indicating the target response level

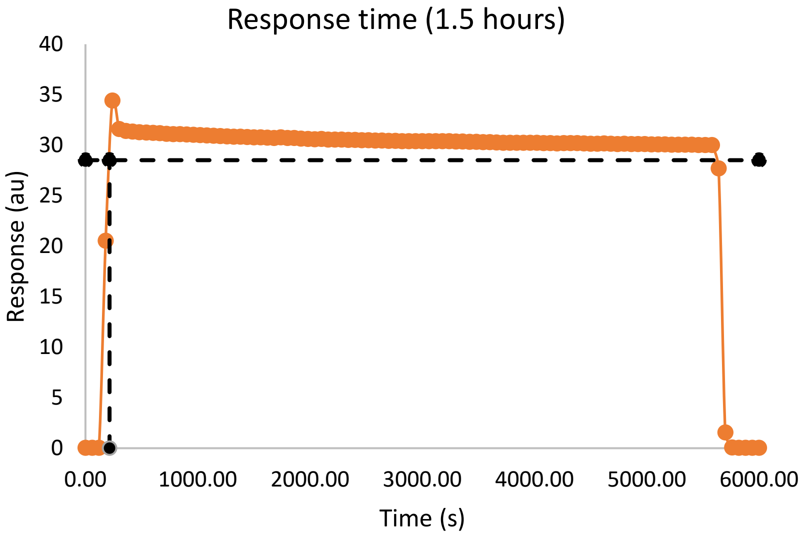


Figure 12 Response time profile over 1.5 hours

Additionally the flowrate had to be lowered for the highest point in the calibration, 60 µmol mol^{-1}, to a total flow of 500 mL/min from the dynamic dilution system (Table 16). Also, here we tested the response time for 1 hour. The black dotted line represents the T95 level, reached in 4 minutes, see Figure 13. Moreover, an overshoot is observed just after T95, after which the signal gradually stabilizes around the 1-hour mark.

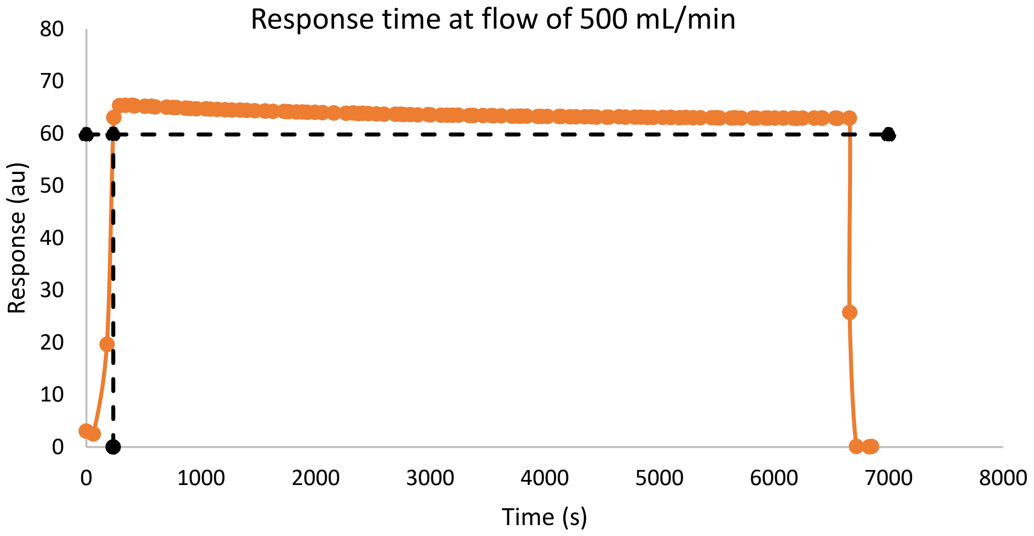


Figure 13 Response time profile over 1 hour of 60 µmol mol^{-1} *O*$_2$*. The plot shows the analyser signal (au) as a function of time (s). The black dotted line indicates the* T_{95} *response level*

<u>Manufacturer's Note</u>: The default analyser setting is one measurement every 30 seconds. The sample rate can be adjusted for measurements as frequently as every 3 seconds. Decreasing the sample rate would greatly improve the T95 response time.

2.3 Precision

The repeatability standard deviation (s(*r*)) and reproducibility standard deviation (s(*R*)) were calculated based on measurements performed across different days (see Table 16). These values were determined according to ISO 5725-2:2019 (2) using analysis of variance (ANOVA).

Table 18 Repeatability (s(r)) and reproducibility (s(R)) at various concentrations, calculated per ISO 5725-2:2019 using ANOVA

x (mol/mol)	x (ppm)	s *(r)* (%)	s *(R)* (%)
1.03E-05	10.26	0.17%	6.10%
2.03E-05	20.29	0.11%	2.18%
3.02E-05	30.23	0.05%	1.36%
4.07E-05	40.74	0.04%	0.96%
5.09E-05	50.87	0.04%	0.82%
6.10E-05	61.00	0.05%	0.68%

The data show that both s(*r*) and s(*R*) decrease as the fraction increases. At the lowest fractions (10.26 µmol/mol), both deviations are high, with s(*r*)=0.17% and s(*R*)=6.10%. When looking at the results obtained for fraction higher than 11 µmol/mol the average is 0.06% for s(*r*) and 1.20 % for s(*R*).

2.4 Bias

The accuracy is derived based on the bias. The deviation (D_{x_i}) and relative deviation (D_{rel}) are the closeness of the response of the analyzer (r_i) to the true amount fraction of the gas mixture (x_i) (Equations (1) and (2)).

$$D_{x_i} = r_i - x_i \qquad \text{eq. (1)}$$

$$D_{rel} = \frac{D_{x_i}}{x_i} \qquad \text{eq. (2)}$$

This assessment evaluates the accuracy and stability of an analyzer across four calibration sessions by comparing its measured responses to known gravimetric fraction (see table 1). The data is shown in Table 19.

Table 19 Accuracy assessment based on bias: deviation (Dx) and relative deviation (Drel) between analyser response (ri) and gravimetric fraction (xi)

	x (mol mol^{-1})	x (µmol mol^{-1})	average response (µmol mol^{-1})	Dx	Drel
Set 1	1.03E-05	10.280	8.386	-1.895	-18%
	2.05E-05	20.458	19.295	-1.163	-6%
	3.02E-05	30.206	29.674	-0.532	-2%
	4.07E-05	40.725	40.926	0.201	0%
	5.09E-05	50.871	51.720	0.849	2%
	6.10E-05	61.009	62.751	1.742	3%
Set 2	1.02E-05	10.243	8.309	-1.933	-19%
	2.02E-05	20.237	18.994	-1.243	-6%
	3.02E-05	30.236	29.650	-0.585	-2%
	4.07E-05	40.750	40.880	0.130	0%
	5.09E-05	50.879	51.680	0.801	2%
	6.10E-05	61.003	62.685	1.682	3%
Set 3	1.02E-05	10.243	9.247	-0.996	-10%
	2.02E-05	20.190	19.826	-0.364	-2%
	3.02E-05	30.235	30.359	0.125	0%
	4.08E-05	40.751	41.584	0.833	2%
	5.09E-05	50.857	52.430	1.572	3%
	6.10E-05	61.003	63.443	2.440	4%

The analysis focused on the deviation from gravimetric value (Dx) and the relative deviation (Drel). The bias increases (in relative terms) with increasing fractions (see Figure 14). At higher concentrations (≥30 µmol/mol) the deviation becomes positive (within ±4%).

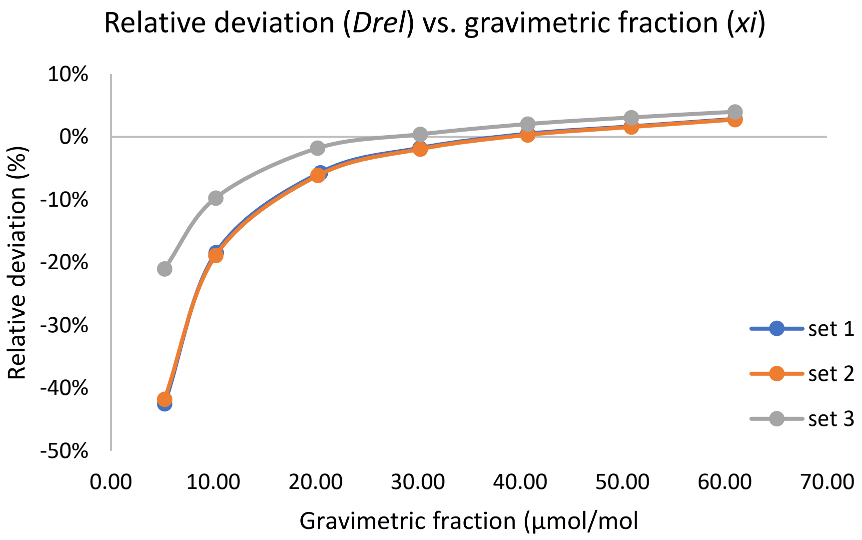


Figure 14 A visual plot showing the relative deviation (Drel%) vs gravimetric fraction (µmol mol^{-1}) for all four calibration sets, excluding the 0.70 ppm point.

2.5 Linearity

The linearity of the analyser have been determined in the range of 10-60 µmol mol^{-1} O_2 in CO_2 for all calibration sets. The results have been linear fitted using VSL's curvefit software which model is based on weighted GDR following ISO-6143 (3) and the residuals in both x (O_2 µmol mol^{-1}) and y (response) directions.

Table 20 The table contains 7 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties (calibration set 1)

	x (µmol mol^{-1})	**ux (µmol mol^{-1})**	**Y**	**uy**
1	10.28	0.0465	8.39	0.018
2	20.46	0.0635	19.30	0.054
3	30.21	0.0824	29.67	0.031
4	40.73	0.1006	40.93	0.027
5	50.87	0.1183	51.72	0.043
6	61.01	0.1371	62.75	0.038

The results from the table above have been linear fitted with the uncertainties in Curvefit, which yielded in the results below.

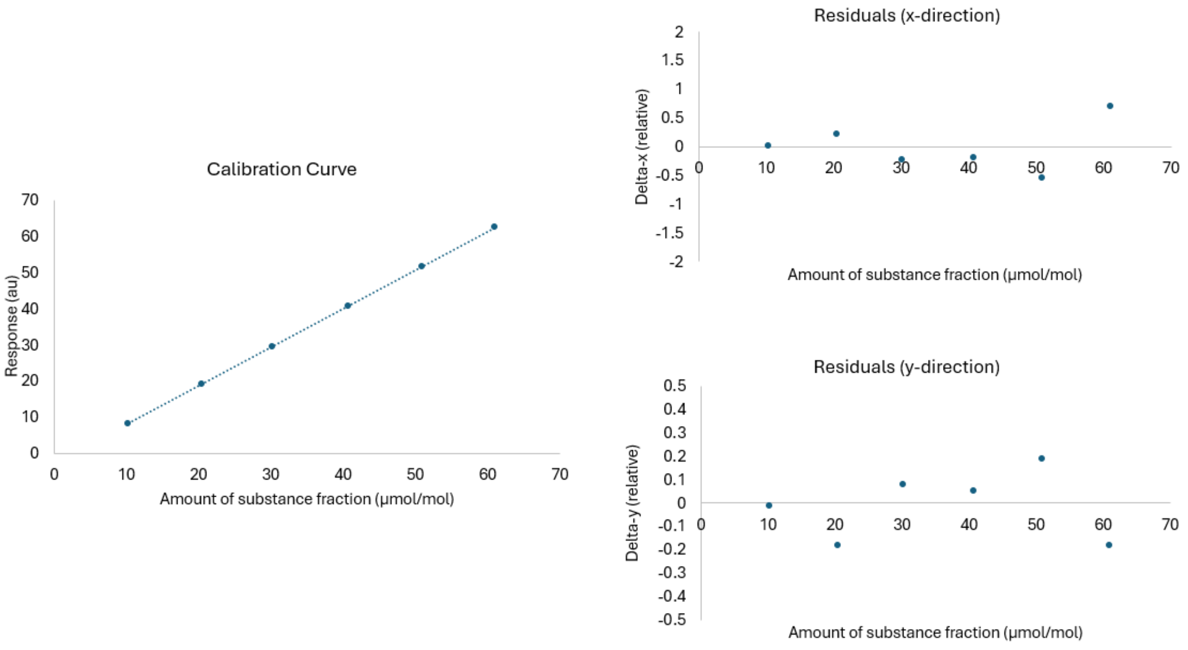


Figure 15 Calibration fit and residual analysis in x- and y-direction (set 1)

The results shows an average goodness-of-fit (ISO 6143) at 0.95, which is a good-fitting model; the value is well below 2, indicating that the linear approach is appropriate. Table 21 shows the goodness of fit and the coefficient of the regression model of other calibration sets. See appendix D for the results of the other calibration sets.

Table 21 . Regression model coefficients and goodness-of-fit (ISO 6143) for four calibration sets.

Calibration Set	**Intercept (a_0)**	**Uncertainty a_0**	**Slope (a_1)**	**Uncertainty a_1**	**Goodness-of-fit (ISO 6143)**	**Lod**
Set 1	-2.6107	0.0645	1.0695	0.00226	0.7011	1.27E-03
Set 2	-2.6469	0.0640	1.0690	0.00224	0.8027	1.27E-03
Set 3	-1.6670	0.0614	1.0635	0.00229	1.3419	1.28E-03

Across all calibration sets (see Table 16), the analyser demonstrates reliable and statistically linear behaviour in the tested range of 10–60 µmol mol^{-1} O_2 in CO_2. The regression models show minimal deviation, consistent sensitivity and goodness-of-fit indicators well below 2.

2.6 Detection limit

The limit of detection will be expressed as the lowest fraction that can be measured with statistical significance by the analysers.

The detection limit (l_{det}) is calculated using equation below.

$$l_{det} = 3.3 \times \frac{S_{r,z}}{b} \qquad \text{eq. (3)}$$

Here, $S_{r,z}$ represents the repeatability standard deviation at the lowest concentration detectable by the analyser, yielding a value of 0.00041. The slope (*b*) of the calibration function was determined by the linearity test (see table 21). The average detection limit is 1.28 E-03 µmol mol^{-1}.

2.7 Measurement uncertainty

The measurement uncertainty of the analyser has been determined based on the main contributing components: the reproducibility standard deviation s(*R*), the uncertainty of the reference material (including the applied dilution), and the detection limit. The individual standard uncertainties for each component are summarized in the Table 22.

Table 22 Summary of the standard uncertainty components contributing to the combined measurement uncertainty of the analyser at a response level of 30 µmol/mol

Component	**Standard uncertainty (µmol mol^{-1})**
Reproducibility	0.41
Reference (with dilution)	0.15
Detection limit	0.00128

The expanded measurement uncertainty U, representing a 95% confidence level, was calculated by multiplying the combined standard uncertainty by a coverage factor $k = 2$:

$U = k \times uc \approx 2 \times 0.44 \approx 0.87$ µmol mol^{-1}

Therefore, the reported measurement result at a concentration of 30 µmol mol^{-1} is associated with an expanded uncertainty of: 30 µmol mol^{-1} ± 0.87 µmol mol^{-1} (at $k = 2$).

2.8 Conclusion

The analyser was evaluated for its performance in measuring CO_2 impurities, focusing on key parameters including linearity, precision, bias, detection limit, and measurement uncertainty. The linearity assessment across 10–60 µmol mol^{-1} O_2 in CO_2 showed good fit, with a average goodness-of-fit value of 0.95 across the three calibration sets. The analyser showed a T95 response time of approximately 3.5 minutes at 30 µmol mol^{-1} with a flow of 1 L/min. The repeatability standard deviation s(r) averaged 0.06% for fractions above 11 µmol mol^{-1}, while the reproducibility standard deviation s(R) averaged 1.20% in the same range. The bias decreases above 11 µmol mol^{-1}, with average relative deviations ranging from –6% to 3% across all three sets.

The average detection limit was determined to be 1.28E-03 µmol mol^{-1}, calculated based on the repeatability standard deviation and the calibration slope. The combined standard measurement uncertainty at a response of 30 µmol mol^{-1} was calculated as 0.65 µmol mol^{-1}, resulting in an expanded uncertainty of ± 0.9 µmol mol^{-1} (at $k = 2$). This corresponds to a relative expanded uncertainty of approximately 3%.

The OXY550 analyser performed consistently within the tested range, showing stable readings and good linearity for oxygen in CO_2. The small deviations observed were within acceptable limits and can be addressed by the manufacturer if required. Overall, its response characteristics and measurement precision confirm that the instrument is fit for purpose for rapid determination of oxygen impurities in CO_2.

Appendix A: Protocol

21GRD06 MetCCUS

Protocol for the comparison of analysers for the analysis to measure impurities in carbon dioxide

Authors: Noor Abdulhussain, Iris de Krom

1. Introduction

The aim of this comparison is to evaluate commercial instruments that are used for quick measurements of impurities in carbon dioxide (CO_2). The analysers' performance will be assessed using calibration gas mixtures with H_2O will range between 10-70 ppm, and O_2 between 10-50 ppm in a CO_2 matrix. The assessment will include important parameters, such as response time, amount fraction range, linearity, bias, and uncertainty. The measurements for the performance evaluation will be conducted at the Van Swinden Laboratory (VSL) in the Netherlands.

This work is part of the European Partnership on Metrology project 21GRD06 MetCCUS (Metrology Support for Carbon Capture Utilisation and Storage), Task 3.3 – Online CO_2 monitoring methods. Metrological traceability plays a crucial role in ensuring the accuracy and reliability of these measurements. The goal of this round robin is to provide support for commercial laboratories and instrument manufacturers when developing, selecting, and operating analysers for CO_2 purity analysis.

Based on the results of the comparison, suitable commercial analysers will be identified that are capable of performing the quick measurement of H_2O an O_2 in CO_2. VSL will analyse the results and produce a report. This report will be made publicly available.

2. Points of contact

Please contact us if you have any technical questions or remarks regarding the comparison. The comparison is organized by VSL. The contact details of the coordinator are given below:

Comparison coordinator	Noor Abdulhussain nabdulhussain@vsl.nl +31615330662
VSL B.V.	
Mailing address; P.O. Box 654, 2600 AR Delft the Netherlands	Visiting address; Thijsseweg 11, 2629 JA Delft the Netherlands

The MetCCUS project is coordinated by VSL. The contact details of the project coordinator are given below:

Project coordinator VSL B.V.	Iris de Krom idekrom@vsl.nl D: +31631119895

3. Measurement procedure

3.1 Gas mixture preparation method

The calibration gas mixtures are provided by means of a dynamic system equipped with thermal mass flow controllers, and operated in accordance with ISO 6145-7. This setup includes two mass flow controllers (MFCs) or more MFCs connected to the premixtures and a pressure controller. The pressure, adjustable within the range of 1-5 bar a, feeds into the analyzer's inlet. Dynamic dilutions are achieved by manually adjusting the flow rates from the MFCs using a software program. The flow from the MFC is calibrated against the VSL primary flow meters.

The composition of the mixtures are determined in accordance with ISO 6143:2001 (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures) using equipment which is calibrated with Primary Standard Gas Mixtures, VSL's own primary standards, to ensure that the values assigned to the mixtures foreseen to be used in the scheme are metrological traceable to international standards, and thereby, ultimately to the SI (International System of Units). The results of the calibration are used as reference values in this comparison.

3.2 Range

The amount fraction range selected are O_2 (10-50 ppm) and H_2O (10-70 ppm, but can be altered based on the input of the suppliers.

3.3 Linearity

VSL will evaluate the measurement data to determine whether the analyser is linear over the range using the regression method. Using the gas mixture described in 3.1, 3 different fractions for each component will be produced. The deviation from a linear model for O_2 and H_2O will be determined. For each of the 3 fractions, at least 5 consecutive measurements will be performed taking into account the instrument sampling and time response specification.

The deviation from a straight line through the origin will be determined by assessing the regression coefficients of an acceptable fit, and the deviations will be calculated as function of the offered amount fraction of the components.

3.4 Response time

The response time of the analyser will be determined. The response time will be determined by first applying pure CO_2 to the analyser. The output will be continuously analysed for at least 2 hours to determine the zero response. After obtaining the zero response, a gas mixture containing H_2O and O_2 in CO_2 will be fed to the analysers. Again, the output will be continuously analysed for at least 2 hours to determine the response time. The response is stable when the standard deviation between the measurements is < 1 % or alternative until the signal has reached 95% of the expected value

3.5 Bias

The deviation (D_{x_i}) and relative deviation (D_{rel}) are the closeness of the response of the analyzer (r_i) to the true amount fraction of the gas mixture (x_i) (Equations (1) and (2)).

$$D_{x_i} = r_i - x_i \qquad \text{eq. (1)}$$

$$D_{rel} = \frac{D_{x_i}}{x_i} \qquad \text{eq. (2)}$$

3.6 Limit of detection

The detection limit ($\boldsymbol{l_{det}}$) is calculated using equation below.

$$\boldsymbol{l_{det}} = \mathbf{3.3} \times \frac{\boldsymbol{S_{r,z}}}{\boldsymbol{b}} \qquad \text{eq. (3)}$$

The repeatability standard deviation is based on ($\boldsymbol{S_{r,z}}$)) the pure CO_2 measurements and the slope (*b*) of the calibration function is determined by the linearity test (3.3). The limit of detection will be expressed as the lowest fraction that can be measured with statistical significance by the analysers.

3.7 Uncertainty

Based on the measurement results VSL will determined the expanded measurement uncertainty (*k* = 2) of the analyser for H_2O and O_2 in CO_2.

3.8 Conditions

VSLs standard lab conditions are:

- Laboratory temperature 20 °C ± 1 °C
- Relative humidity 45 % ± 10 %

Before the measurements, the equipment will be allowed to stabilize in the laboratory conditions for at least 24 hours.

3.9 Comparison period

A maximum period of ten working days (2 weeks) will be reserved for each participating instrument manufacturer.

4. Analyser specifications

VSL expects to receive at least 3 analysers from different suppliers to be able to perform the measurements. To make sure the procedure is as clear as possible some guidelines have been proposed below.

4.1 Instruction manual

The supplier should send an instruction manual or setup guide with the equipment. If desired, it is also possible to send an engineer or other supportive personal to make sure the equipment is properly installed and used. A digital (TEAMS) meeting is also a possibility to ensure proper installation.

4.2 Inlet

The supplier should send any connection pieces needed to get the analyser operational. The dilution system that VSL will be using has an output of 1/8 inch NPT Swagelok connection. The connection should fit to the input of the analyser. We should also be able to use tubing to vent the exhaust, so please also provide the analyser with the ability to connect it to the vent.

4.3 Data output

The supplier should provide a data logger or software that can be used to obtain the data. Preferably VSL can connect a laptop and obtain the raw data to easily process this further with VSL's calibration software or with Excel.

4.4 Other specifications

Please note that it is always best to discuss any operation procedures beforehand. There are some questions beforehand to ensure proper installation and usage of the analyser:

1. Does the analyser have a pomp? Or does it need a pomp?
2. Does the analyser need a continuous flow running through?
3. What kind of flows or pressure is necessary for the analyser to be able to function? With the Dilution system only a pressure slightly above ambient can be obtained.
4. Does the analyser need an additional flow, like nitrogen or air?
5. What kind of power supply is needed? At VSL the power plugs and sockets are of type F. If these are not compatible to your instrument you should provide a converter to match VSL's types of plugs.

5. Reporting

When the measurement procedure has been completed, a report will be written by VSL containing:

- Equipment used for calibration
  (description of calibration equipment: type, calibration state of reference)
- Method of measurement
- Tables that summarise the results from each analyser (response time, amount fraction range, linearity, bias)
- The expanded measurement uncertainty (U k = 2).
- Conclusions
- General recommendations, statistics, etc.

- Overview of cited documents, guidelines, and publications.
- A description will also be provided of the applied statistics.

The report will be distributed to the participants. After approval the report will be made publicly available. The data can be reported anonymously if desired.

6. Confidentiality

The results of this comparison will be used for the report of the European project 21GRD06 MetCCUS. No other forms of dissemination and exploitation of the results are intended by VSL.

7. Schedule

VSL undertakes every reasonable effort to prevent delays during the comparison. Participants are kindly requested to send the equipment well before the agreed time schedule. In case of foreseeable delays, participants are kindly requested to report such delays to the comparison coordinator with an indication of when the equipment will arrive at VSL.

The schedule of this comparison is as follows:

Period:	**Event:**
August 2024	Draft protocol
	Reaching out to possible suppliers
	Protocol to be discussed with possible suppliers
December 2024	Equipment shipped to VSL
January 2025 – March 2025	Measurements of the equipment
March – April 2025	Discuss results with suppliers
May 2025	Return equipment to suppliers
June 2025	Draft report available
July 2025	Final report available

*) December and January is the time the equipment is expected to arrive at VSL in order to perform the measurements. Please make sure the equipment is sent to VSL during this time.

Logistics and Transport

The instrument should be shipped in a dedicated case to prevent the analyser from getting damaged during transport. The supplier is responsible for the shipment both to and from VSL. Opening hours for our Logistics department is Monday till Friday from 8:00 till 16:00.

Delivery address;
Noor Abdulhussain

Thijsseweg 11,
2629 JA Delft
the Netherlands

On arrival, the equipment will be inspected for damage and assessed for proper operation. In the case of an unexpected instrument failure, the supplier will be informed immediately.

Appendix B: Endress + Hauser

i. Linearity assassement data

Calibration set 2

Table 23 The table contains 7 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties

	x (µmol/mol)	ux (µmol/mol)	y	uy
1	0.700	0.320	0.009	0.000
2	10.692	0.372	6.595	0.029
3	20.684	0.507	16.576	0.022
4	30.675	0.675	26.533	0.011
5	40.666	0.858	36.425	0.025
6	50.248	1.038	45.913	0.024
7	60.165	1.228	55.724	0.041

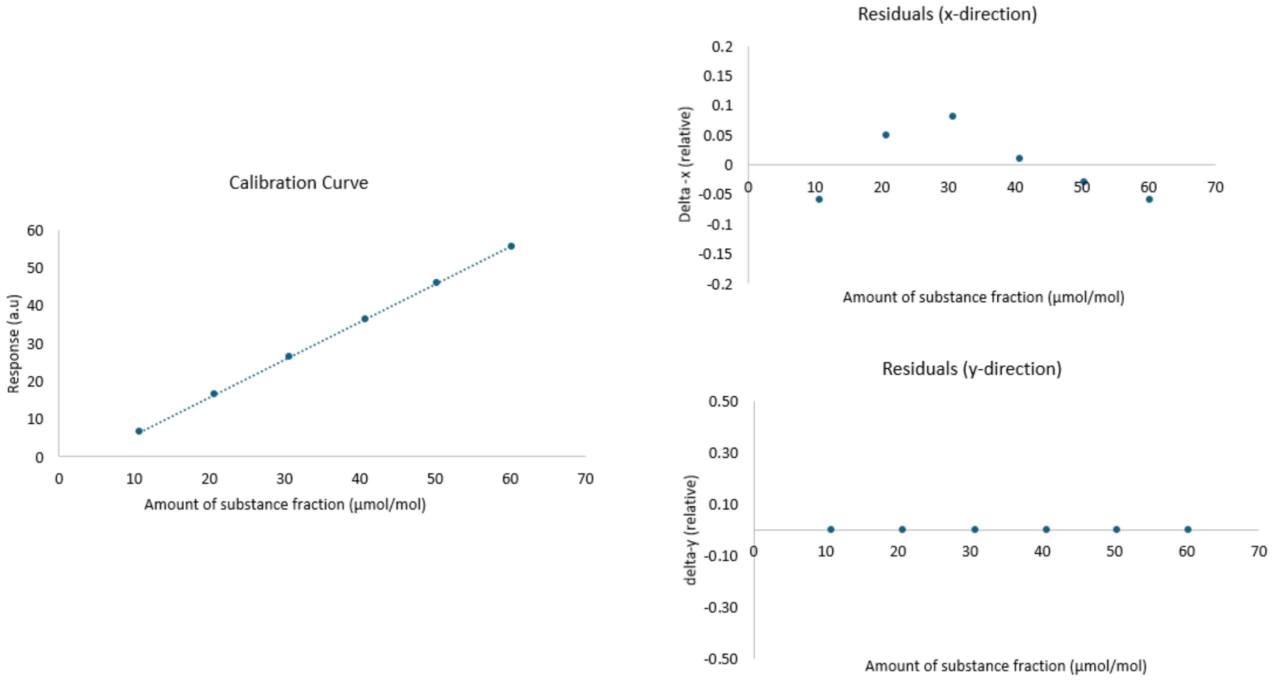


Figure 16 Calibration fit and residual analysis in x- and y-direction (set 2)

Calibration set 3

Table 24 The table contains 8 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties

	x (µmol/mol)	ux (µmol/mol)	y	uy
1	0.700	0.320	0.009	0.000
2	10.050	0.455	6.879	0.009
3	20.029	0.721	16.830	0.013
4	30.007	1.013	26.758	0.024
5	39.984	1.308	36.646	0.006
6	49.551	1.580	46.132	0.010
7	59.452	1.849	55.939	0.057

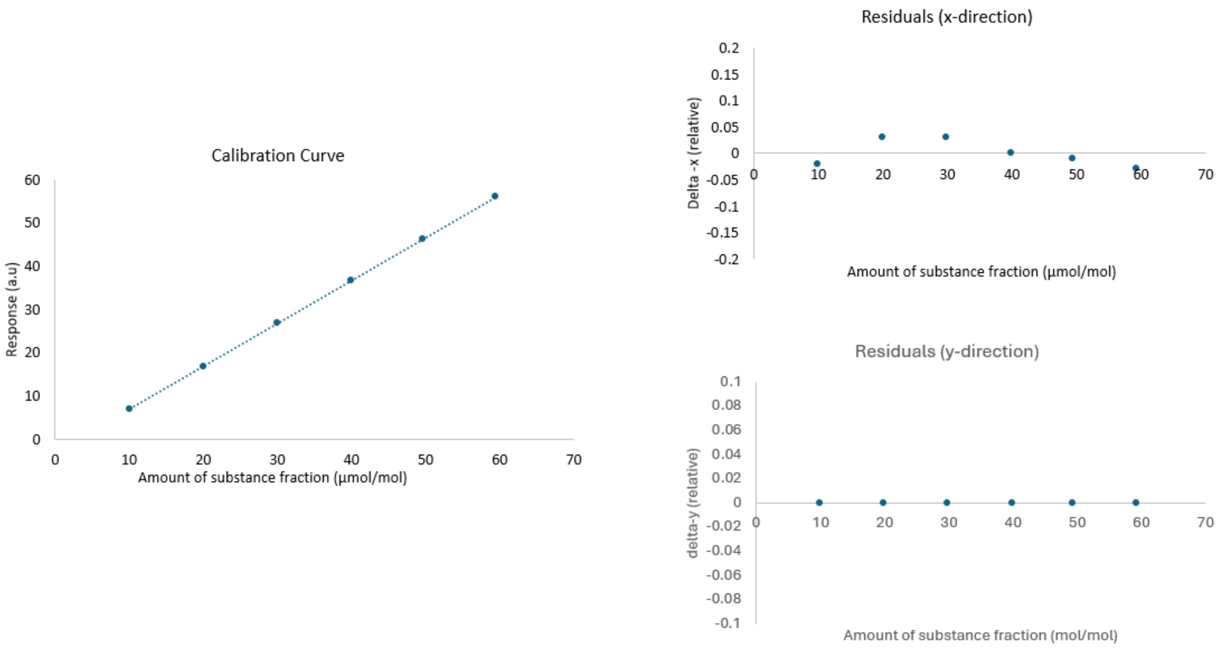


Figure 17 Calibration fit and residual analysis in x- and y-direction (set 3)

Calibration set 4

Table 25 The table contains 8 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties

	x (µmol/mol)	ux (µmol/mol)	y	uy
1	0.700	0.320	0.009	0.000
3	10.051	0.455	6.647	0.018
4	20.030	0.721	16.664	0.027
5	30.009	1.013	26.636	0.024
6	39.985	1.308	36.531	0.028
7	49.551	1.580	46.034	0.030
8	59.452	1.849	55.846	0.044

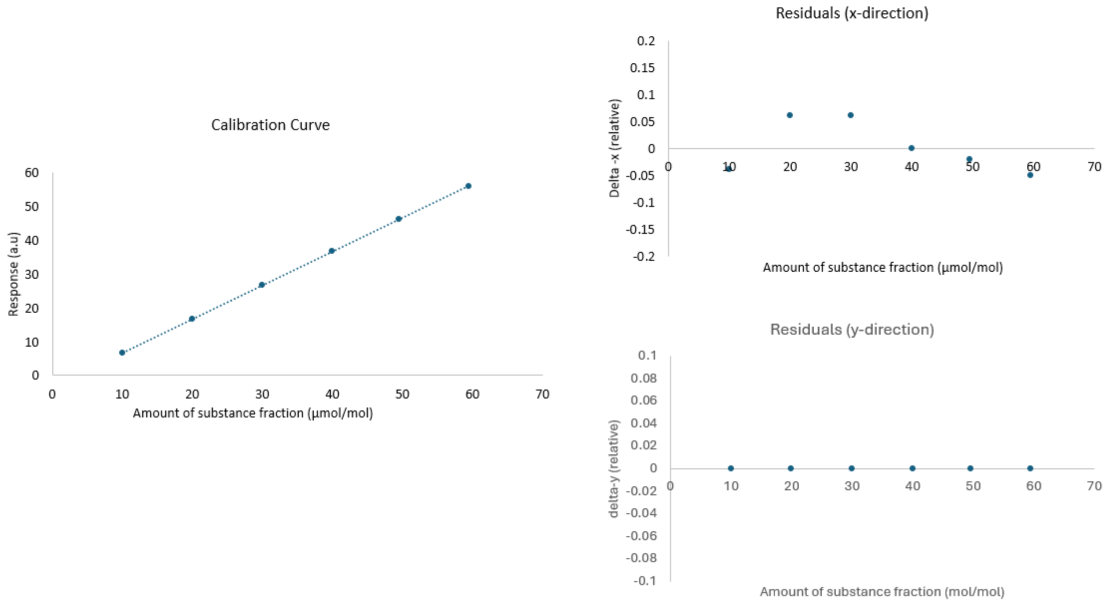


Figure 18 Calibration fit and residual analysis in x- and y-direction (set 4)

ii. Bias

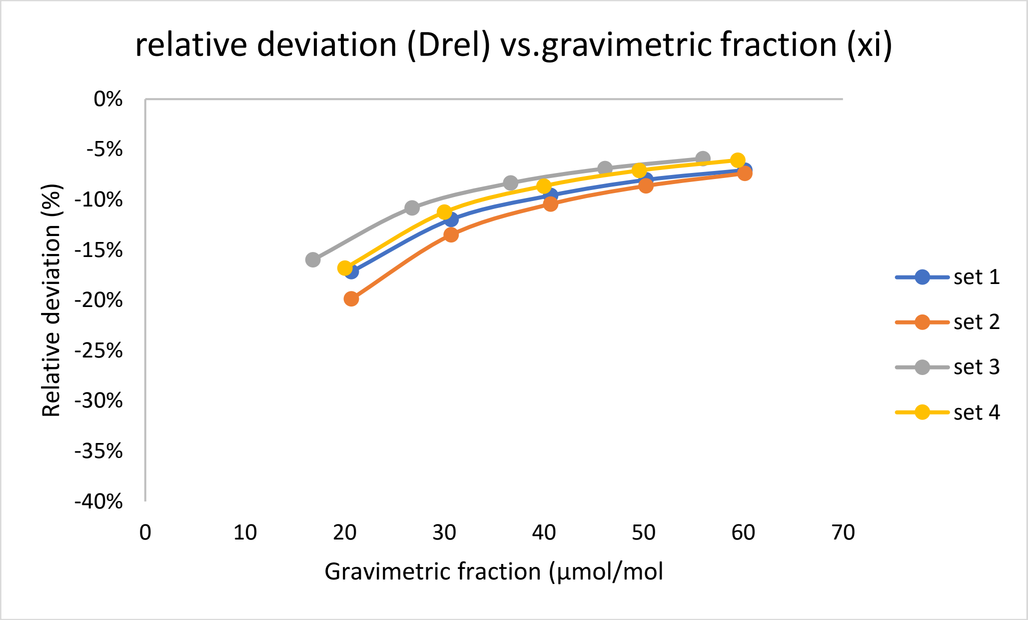


Figure 19 A visual plot showing the relative deviation (Drel%) vs gravimetric fraction (µmol/mol) for all four calibration sets in the range of 20 µmol/mol to 60 µmol/mol

Appendix C: MEECO

i. Linearity assassement data

Calibration set 2

Table 26 The table contains 8 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties

	x (µmol/mol)	ux (µmol/mol)	y	uy	
1	7.000040600E-01	3.1950844E-01	4.8387097E-01	7.4775650E-02	Fit
2	5.696732981E+00	3.3195543E-01	4.2806452E+00	8.0321933E-02	Fit
3	1.069199372E+01	3.7238208E-01	8.2806452E+00	8.0321933E-02	Fit
4	2.068370899E+01	5.0664730E-01	1.6590323E+01	6.0107431E-02	Fit
5	3.067479535E+01	6.7521008E-01	2.5167742E+01	9.5038193E-02	Fit
6	4.066586765E+01	8.5802592E-01	3.3790625E+01	7.8030184E-02	Fit
7	5.024809034E+01	1.0379643E+00	4.1996774E+01	8.1385846E-02	Fit
8	6.016548279E+01	1.2276201E+00	5.0362500E+01	9.8373875E-02	Fit

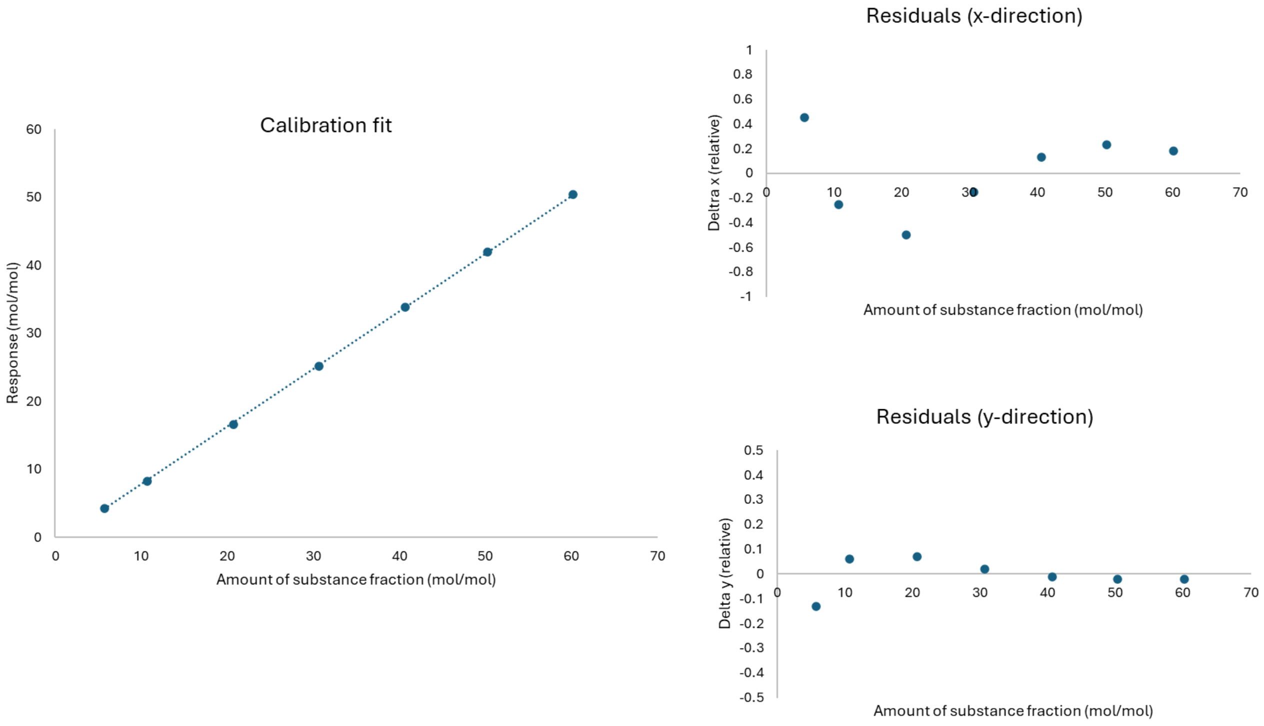
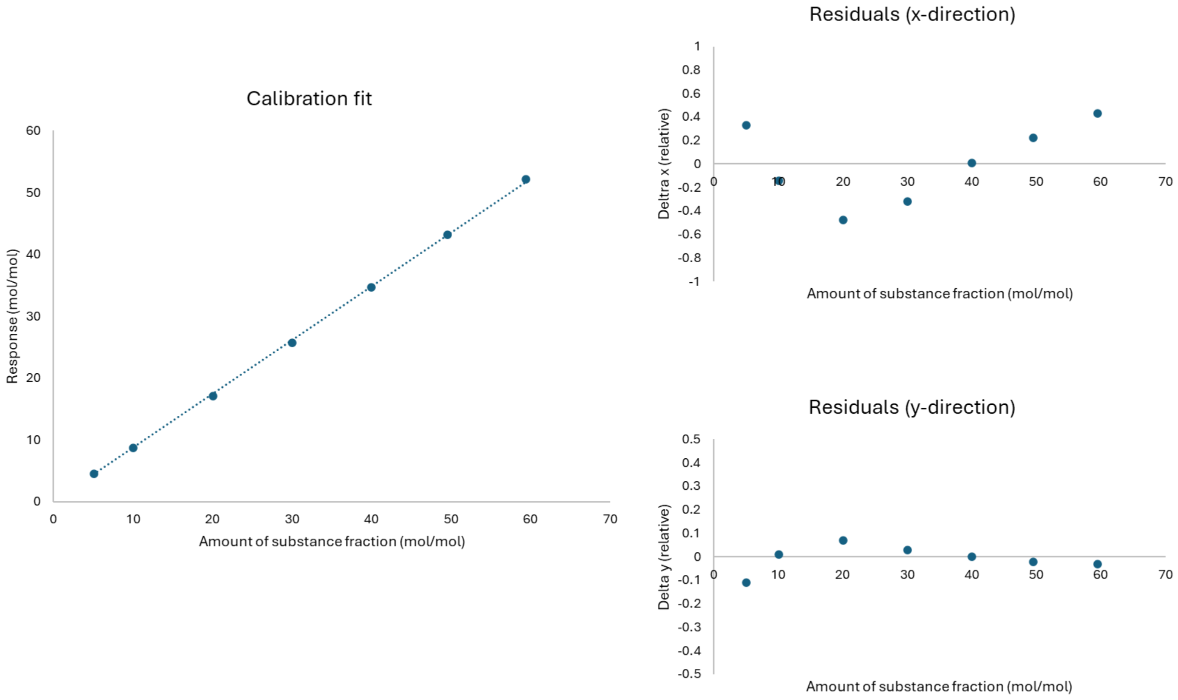


Figure 20 Calibration fit and residual analysis in x- and y-direction (set 2)

Calibration set 3

Table 27 The table contains 8 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties

	x (µmol/mol)	ux (µmol/mol)	y	uy	
1	7.000040600E-01	3.1950832E-01	5.0000000E-01	0.0000000E+00	Fit
2	5.061323467E+00	3.5728222E-01	4.5562500E+00	1.0080323E-01	Fit
3	1.005044937E+01	4.5516392E-01	8.6967742E+00	3.5921060E-02	Fit
4	2.002948659E+01	7.2142265E-01	1.7068750E+01	9.4185815E-02	Fit
5	3.000695409E+01	1.0133369E+00	2.5712903E+01	8.5509227E-02	Fit
6	3.998429706E+01	1.3084586E+00	3.4625000E+01	1.0160010E-01	Fit
7	4.955056059E+01	1.5799566E+00	4.3187097E+01	9.9892415E-02	Fit
8	5.945179474E+01	1.8487370E+00	5.2122581E+01	9.9460913E-02	Fit


Calibration fit

Residuals (x-direction)

Residuals (y-direction)

Figure 21 Calibration fit and residual analysis in x- and y-direction (set 3)

Calibration set 4

Table 28 The table contains 8 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties

	x (µmol/mol)	ux (µmol/mol)	y	uy	
1	7.000040600E-01	3.1950832E-01	4.0000000E-01	3.3839632E-16	Fit
2	5.061323467E+00	3.5728222E-01	4.3064516E+00	4.9946208E-02	Fit
3	1.005044937E+01	4.5516392E-01	8.5000000E+00	0.0000000E+00	Fit
4	2.002948659E+01	7.2142265E-01	1.7109375E+01	5.9228916E-02	Fit
5	3.000695409E+01	1.0133369E+00	2.5912903E+01	6.8155420E-02	Fit
6	3.998429706E+01	1.3084586E+00	3.4781250E+01	1.0701221E-01	Fit
7	4.955056059E+01	1.5799566E+00	4.3209677E+01	9.4584547E-02	Fit
8	5.945179474E+01	1.8487370E+00	5.1815625E+01	1.1482806E-01	Fit

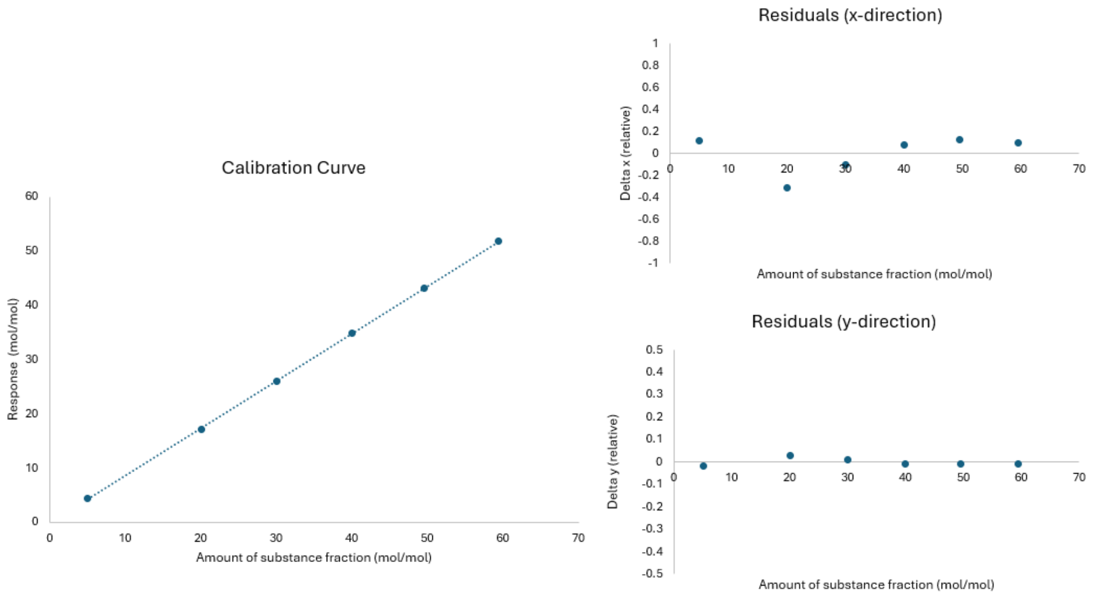


Figure 22 Calibration fit and residual analysis in x- and y-direction (set 4)

Appendix D: Endress + Hauser (Oxygen data)

i. Linearity assassement data

<u>Calibration set 2</u>

Table 29 The table contains 6 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties

	x (µmol/mol)	ux (µmol/mol)	Y	uy
1	10.24	0.0464	8.31	0.023
2	20.24	0.0630	18.99	0.026
3	30.24	0.0825	29.65	0.015
4	40.75	0.1006	40.88	0.028
5	50.88	0.1183	51.68	0.022
6	61.00	0.1371	62.68	0.025

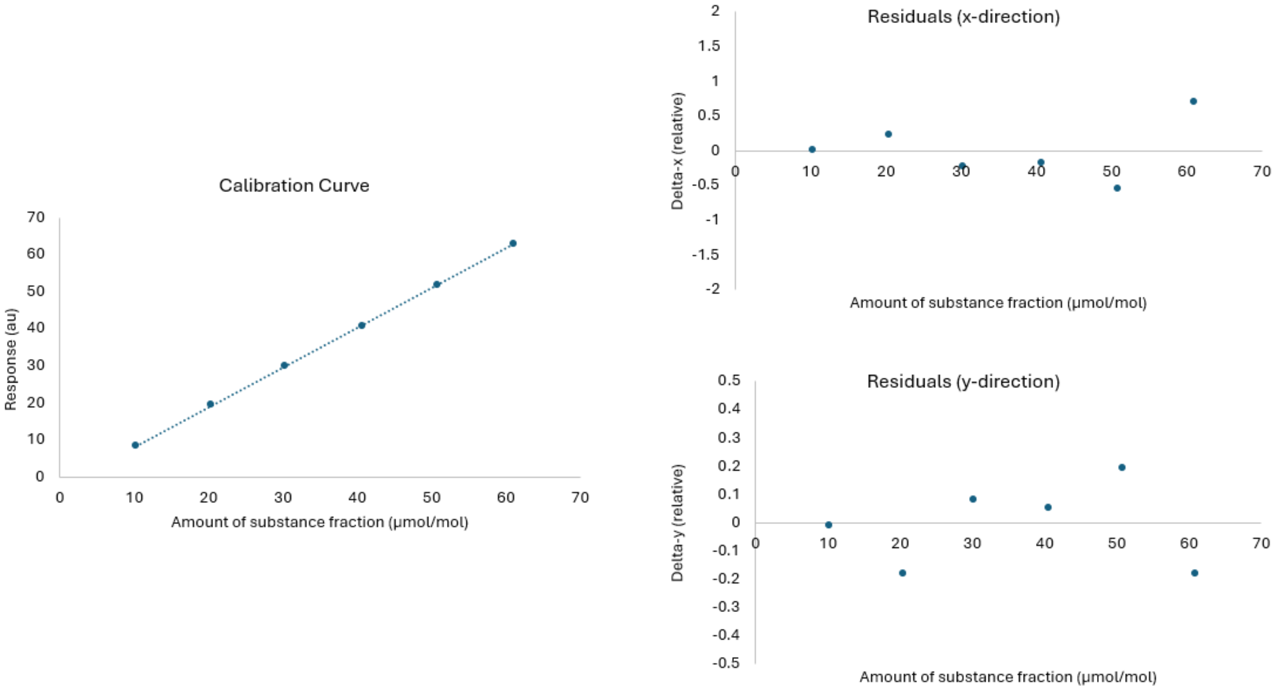


Figure 23 Calibration fit and residual analysis in x- and y-direction (set 2)

Calibration set 3

Table 30 The table contains 6 calibration points showing the measured signal response (y) versus the gravimetric values (x) of a compound. Each measurement includes associated uncertainties

	x (µmol/mol)	**ux (µmol/mol)**	**Y**	**uy**
1	10.24	0.0464	9.25	0.019
2	20.19	0.0630	19.83	0.025
3	30.23	0.0825	30.36	0.040
4	40.75	0.1006	41.58	0.047
5	50.86	0.1183	52.43	0.079
6	61.00	0.1371	63.44	0.010

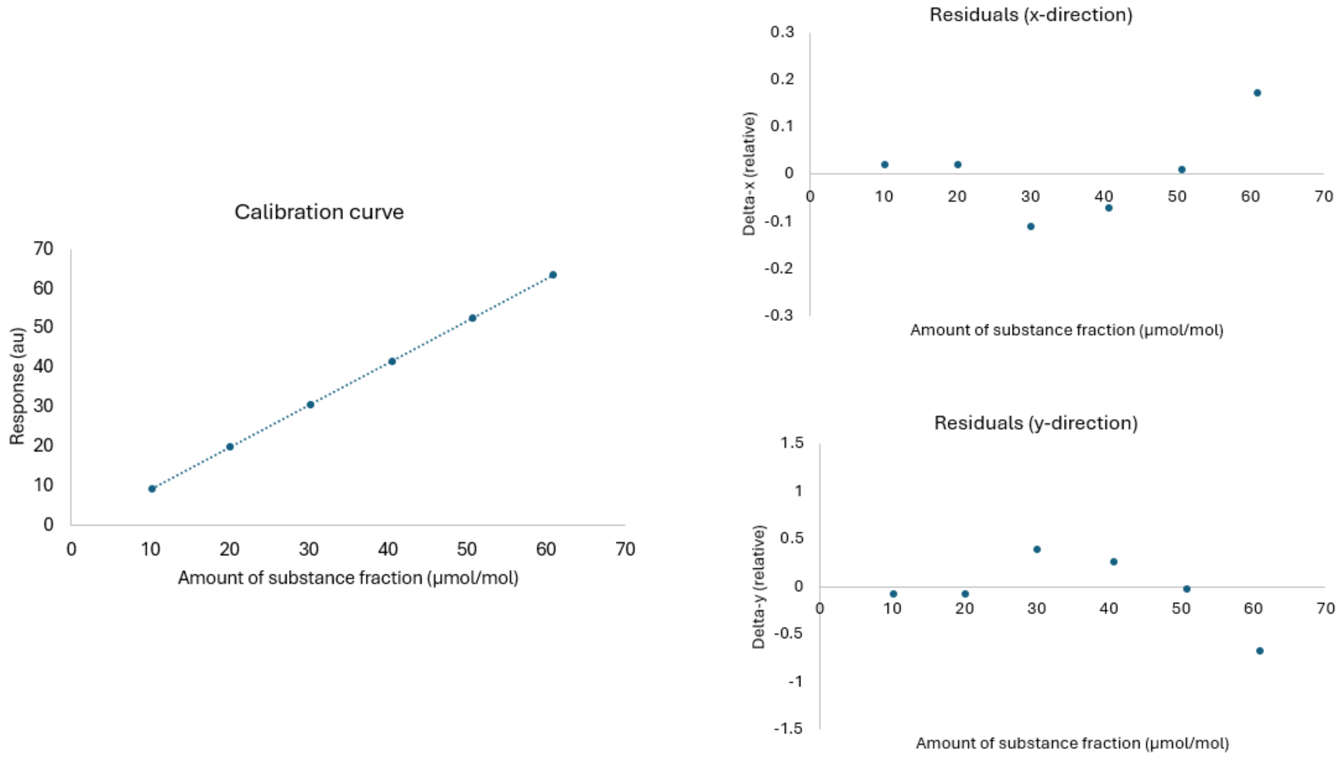


Figure 24Calibration fit and residual analysis in x- and y-direction (set 3)