

EURAMET Project 934
Comparison Report:
Carbon Dioxide (CO₂), 100 µmol/mol to 1000 µmol/mol, by means of the TILSAM method¹

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Abstract

Embedded in the EURAMET 934 project, a comparison on amount fraction measurements using the TILSAM method was conducted. Carbon dioxide (CO₂) mixtures with nitrogen, gravimetrically prepared at 300 and 500 µmol/mol CO₂ nominal levels, were analysed by two labs using the same type of laser-spectrometric amount fraction measurement method, probing the same CO₂ line at the 2 µm infrared spectral range. The reported results, based on three distinguished retrieval approaches for each participant, are agreeing with the comparison reference values to within 0.07 to 2.2 %. Relative expanded uncertainties of the TILSAM-based results are in the 1 to 3 % range ($k = 2$). The achieved comparability is expressed as degrees of equivalences of $D = 4$ to 16 µmol/mol for the 300 µmol/mol amount fraction level and $D = 0.3$ to 9 µmol/mol for the 500 µmol/mol level.

1. Introduction

Calibration-free infrared laser spectrometry can be used to assign amount of substance fraction values to certain species in gas mixtures. Calibration-free means, free of any calibration by means of certified reference gas mixtures. The method can be applied to get traceable infrared laser-spectrometric amount fraction measurements (TILSAM). This comparison was organized to evaluate the TILSAM method described in [1] by means of CO₂ measurements in the nominal range of $x_{\text{CO}_2} = 300$ µmol/mol and 500 µmol/mol. Participants were three NMIs, of which DFM and PTB were performing the analytical measurements. Cylinders were shipped to them by the NPL, who has communicated the nominal CO₂ amount fractions to DFM and PTB prior to shipment. The goal was to investigate the metrological comparability for this kind of measurement method.

The protocol for the comparison was based on the documentary description of the TILSAM method [1]. Therefore, both, the comparison protocol and the technical measurement description were to be used in order to participate in the comparison.

The comparison protocol and the documentary description of the TILSAM method are both results of the EURAMET project 934, which was aiming at the development of the method and the comparison [2].

Field: Amount of substance

¹ The method is described by the document TILSAM-method – technical protocol; available online: http://www.euramet.org/fileadmin/docs/projects/934_METCHEM_Interim_Report.pdf [1]

Subject: Spectrometric quantification of CO₂ in N₂, two cylinders with nominal carbon dioxide amount fractions of 300 μmol/mol and 500 μmol/mol, respectively, by means of *TILSAM*

Participants: DFM, PTB (spectroscopy), NPL (gas mixture)

Coordinating laboratory: PTB

Gas mixture preparation and provision: NPL

Quantities and units:

Among the numbers of quantities often used to express the composition of gas mixtures, for this comparison the results were to be given as amount of substance fractions. Referring to [1], the measurand was taken to be x_{CO_2} in units of mol·mol⁻¹ (or multiples thereof), denoting the carbon dioxide amount fraction in the mixtures.

2. Mixtures of CO₂ in N₂ and the reference values for the comparison (CRV)

A set of two CO₂ in N₂ mixtures was prepared gravimetrically by NPL and filled into cylinders. The composition of the mixtures was validated following NPL standard procedures. Details and specifications of each cylinder are denoted in Tab. 1.

Tab. 1: Details on sample gas mixtures.

mixture	A	B	Unit
cylinder no.	NPL 1263	NPL 1264	
cylinder size	10	10	L
nominal x_{CO_2}	300	500	μmol/mol
balance	Nitrogen	Nitrogen	
x_{CRV}	330.06±0.66	450.00±0.90	μmol/mol
$u_{\text{rel}}(x_{\text{CRV}})$	0.2	0.2	%

The comparison reference values (x_{CRV}) for each mixture were derived from the gravimetric preparation and subsequent verification as provided and communicated by NPL after returning the cylinders back to NPL and after reporting the results $x_{\text{CO}_2,i}$ of each participant to PTB. By that, the two x_{CRV} were formed independently from the $x_{\text{CO}_2,i}$ [3]. The x_{CRV} are also given in Tab. 1. Mixture A was prepared from pure CO₂ by a three-step dilution process with an uncertainty of 0.06 %, mixture B by single dilution with an uncertainty of 0.03 %. Due to the validation process against NPL primary standards followed after the preparation, the relative standard uncertainty $u_{\text{rel}}(x_{\text{CRV}})$ of both mixtures is given by 0.2 %

The analysis of the comparison data was performed by PTB referring to [3] and based on the technical *TILSAM* method description [1]

3. Design of the study

The two cylinders were sent by NPL to DFM first. After analysis, DFM circulated the two cylinders to PTB. After finishing the analysis at PTB, the cylinders were dispatched back to NPL.

The analysis of the two gas mixtures was to be performed referring to the *TILSAM* method according to the technical protocol [1] agreed on by the EURAMET 934 partners.

The spectrometry on each of the two mixtures was performed independently probing any suitable molecular absorption infrared ro-vibrational line of any isotopologue of CO₂ for which a certain line strength figure and ground state energy can be reported; examples were given in [1].

Referring to section 6 of [1], the analysis had to be based on analytical measurements carried out for different, at least two, values of the experimental parameter Γ (see experimental stages c) and d) in section 6 of [1].

The method to evaluate the absorbance line area A_{line} was selected by the participant.

Further referring to section 6 of [1], the data retrieval for each gas mixture had to be based on the linear model approach, yielding the so-called regression-based x_{CO_2} , and on averaging independent individual *TILSAM* results resulting to a directly retrieved x_{CO_2} . For the regression-based x_{CO_2} , two results were to report, one for a free regression and a second one forced through the origin.

The uncertainty estimation was to be comprised of a complete budget and as following the recommendations given in [4] and [1].

4. Results

As presented in detail in the Appendix, DFM and PTB reported their results according to the comparison protocol. Additionally, DFM has reported two sets of data on additional analysis processes, independent from the original one.

All measurements at both participating institutes were performed probing the same vibrational line of the main isotopologue of CO₂, the R(12) line at 4987.3 cm⁻¹, using the same line strength figure for this line, published in IEEE Trans. Instr. Meas., vol. 56(2), p. 529 (2007), $S_0 = 1.255 \times 10^{-21}$ cm/molecule.

Further on, the same type of laser was used at both institutes in TDLAS setups equipped with multi-pass cells to increase the sensitivity. DFM has worked in a Herriott-type cell of about 41 m optical path length, whereas PTB has used a 22 m optical path length White cell. Details of the used spectrometric setups are given in the individual report forms, attached in the Appendix.

According to the comparison protocol, the participants reported their results based on three different approaches, i.e. the direct retrieval, the regression-based retrieval, and a forced regression-based one. Those had to be based on the same data set, derived from measurements at different experimental parameters Γ . At both participants the variation of Γ was realized by means of a variation of the total pressure. DFM has realized 12 different pressures between 50 and 600 mbars to change Γ for each of its three sets of data on the two mixtures. PTB has realized 9 pressure settings between 100 and 900 mbars for the 300 $\mu\text{mol/mol}$ and 8 different pressure steps in between 70 and 780 mbars for the 500 $\mu\text{mol/mol}$ data. Gas temperatures were measured in both participating labs by means of PT100 surface resistances in the range of 296 to 298 K. Spectroscopic measurement parameters for both laboratories were checked, a) with respect to the wavenumber axis before and after the analytical measurements by means of a free-space mirror etalon at DFM

and by means of a removable solid Si-etalon at PTB, and b) with respect to the absorbance axis by means of simultaneous measurements of the detector signals before and behind the sample gas cell by both participants. Detectors used at DFM were NewFocus 2033 detectors succeeded by digital lock-in amplification of the chopped laser beam. This combination was necessary due to the low sensitivity of the detectors in the 2- μm range. Detectors used in PTB's setup were room temperature XInGaAs detectors suitable to measure up to 2.4 μm equipped with pre- and main amplifiers.

The reported analysis results of DFM and PTB are summarized in Tab. 2, together with their computed degrees of equivalence, $D = x_{\text{CO}_2} - x_{\text{CRV}}$ with respect to the CRV, the normalized error $E_n = D / U(D)$, and the relative deviation from the CRV. The expanded uncertainty of the degree of equivalence $U(D)$ was computed from the standard uncertainties of the analysis result $u(x_{\text{CO}_2})$ and that of the CRV denoted as $u(x_{\text{CRV}})$ by means of

$$U(D) = 2 \times \sqrt{u(x_{\text{CO}_2})^2 + u(x_{\text{CRV}})^2} .$$

Tab. 2: Reported analysis results including standard uncertainties ($k = 2$) from DFM and PTB for three different retrieval approaches, computed degrees of equivalences D , normalized errors E_n , as well as rel. deviations from the comparison reference value CRV.

Retrieval	Direct	Degrees of equivalence		norm. Error	
	$x_{\text{CO}_2} / \mu\text{mol/mol}$	$D / \mu\text{mol/mol}$	$U(D) / \mu\text{mol/mol}$	$E_n / 1$	rel. Dev. from CRV / %
DFM300_2	345.7 \pm 4.7	15.64	9.4922284	1.64766368	4.738532388
DFM500_1	459.7 \pm 5.8	9.7	11.7388245	0.82631783	2.155555556
PTB300	321.6 \pm 4.3	-8.46	8.70071261	-0.97233415	-2.563170333
PTB500	447.1 \pm 6.0	-2.9	12.134249	-0.23899295	-0.644444444
Retrieval	Regression				
		D	$U(D)$	$E_n / 1$	rel. Dev. from CRV / %
DFM300_2	345.7 \pm 5.4	15.64	10.8803676	1.43745143	4.738532388
DFM500_1	453.9 \pm 6.4	3.9	12.8	0.3046875	0.866666667
PTB300	325.9 \pm 2.2	-4.16	4.59373486	-0.90558122	-1.260376901
PTB500	449.7 \pm 3.1	-0.3	6.45600496	-0.04646837	-0.066666667
Retrieval	Reg. forced				
		D	$U(D)$	$E_n / 1$	rel. Dev. from CRV / %
DFM300_2	345.4 \pm 4.7	15.34	9.4922284	1.61605888	4.647639823
DFM500_1	457.2 \pm 5.8	7.2	11.7388245	0.61334932	1.6
PTB300	321.5 \pm 1.4	-8.56	3.09554519	-2.76526411	-2.593467854
PTB500	447.0 \pm 1.2	-3.00	3.00	-1.00000	-0.666666667

Degrees of equivalence D for the 300 $\mu\text{mol/mol}$ and 500 $\mu\text{mol/mol}$ mixtures are compared in Fig. 1 and 2, respectively. The first two data points in both figures represent the reported results from PTB and the final results from DFM (DFM300_2 and DFM500_1). The remaining two DFM results for the 300 and 500 $\mu\text{mol/mol}$ mixtures are presented as some further

information to support the discussion below. Each figure is representing results on the respective mixture due to the three requested data retrieval approaches, i.e. the direct retrieval, the regression-based, and when the regression was forced through the origin.

DFM has chosen its results DFM300_2 and DFM500_1 to be the final comparison results based on the criteria that those have the smallest intercept figures, when looking at the regression-based retrieval. In order to demonstrate the level of consistency with the model equation, which does not predict any intercept at all, Fig. 3 displays the intercept value of all results reported for this study together with its standard uncertainty.

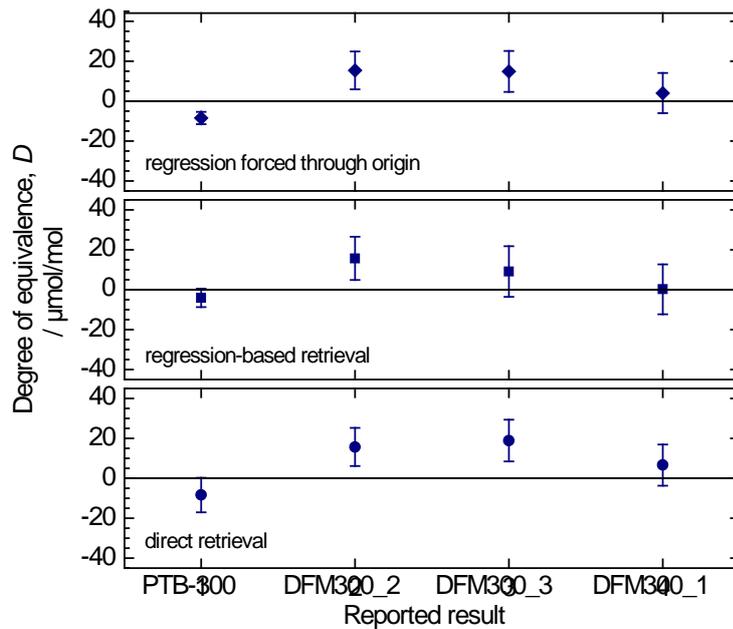


Fig. 1: Comparison results on the 300 μmol/mol mixture, expressed as degree of equivalence *D*. For *D* expanded uncertainties are given with $k = 2$.

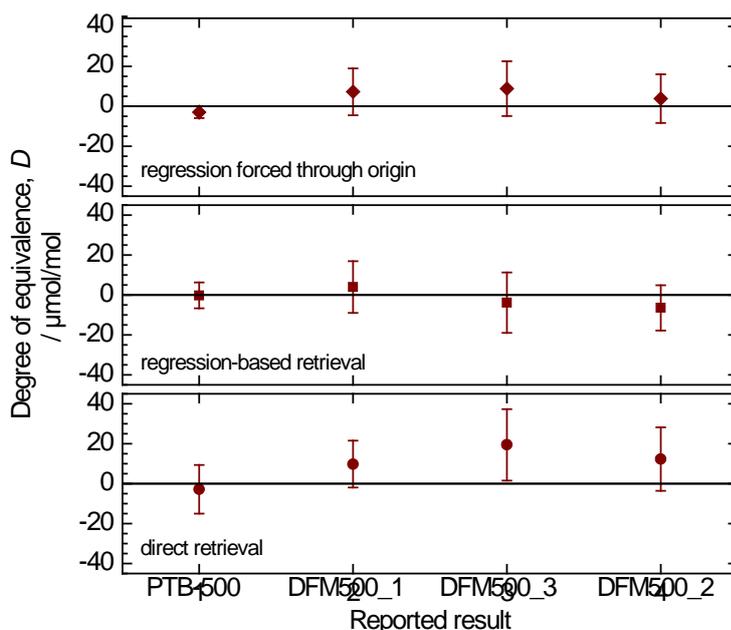


Fig. 2: Comparison results on the 500 µmol/mol mixture, expressed as degree of equivalence D . For D expanded uncertainties are given with $k = 2$.

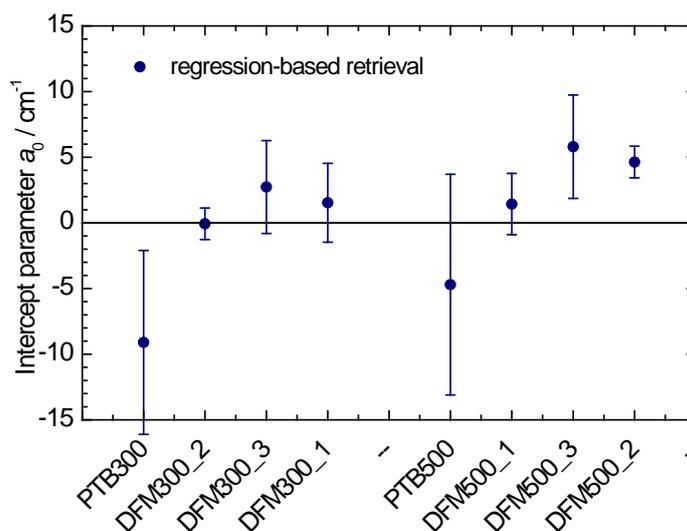


Fig 3: Regression-based retrieval: intercept parameters and respective uncertainties ($k = 1$) from the linear model approach, $A_{\text{line}} = x_{\text{CO}_2} \cdot \Gamma + a_0$, where a_0 was predicted to be zero.

5. Discussion

The results of the present study reveal that spectroscopy by means of the *TILSAM* method provides some comparability level which is significant lower than that of established techniques in gas metrology.

At the 500 µmol/mol level the reported results over all three retrieval approaches agree with the CRV within 0.07 to 2.2 %. The level of relative deviations is covered by the respective

measurement uncertainties, yielding degrees of equivalences that are all smaller than their uncertainty figures.

However, at the 300 $\mu\text{mol/mol}$ level the picture is somewhat more complicated. Here, looking at the reported final analysis results PTB300 and DFM300_2, only the PTB result agrees with the CRV for the most interesting direct and regression-based retrievals. Forcing the regression through zero, neither PTB300 nor DFM300_2 agrees with the CRV, for which relative deviations from CRV were found to be 2.6 and 4.6 %, respectively. While PTB's results agree with each other regarding the different retrievals, they exhibit decreasing uncertainties from the direct to the forced regression approach (bottom to top panel of Fig. 1). The latter is causing the fact that PTB's forced-regression results at the 300 $\mu\text{mol/mol}$ level does not agree with the CRV. DFM's results come with similar levels of uncertainties across the three retrieval approaches.

By looking at DFM's additional informative results, the 300 $\mu\text{mol/mol}$ picture changes slightly. Now, DFM300_1 agrees with the CRV for all three retrievals. In contrast, for the other additional result DFM300_3, only the regression-based result yielded an agreement with the CRV.

Within the two labs, the results from the different retrievals agree with each other within the stated uncertainties. This holds for both amount fraction levels and for all results, including DFM's additional two sets. However, if one is looking for the best agreement of all results, the regression-based retrieval yielded the most robust and comparable amount fractions, at both, the 500 $\mu\text{mol/mol}$ and the 300 $\mu\text{mol/mol}$ level. The fact that DFM's results on the lower level seem to be less consistent with the CRV, might be attributed to the experimental problems with sensitivity due to weak signal strengths achievable with the used detectors as mentioned in DFM's report (s. Appendix).

The protocol of the comparison and the technical document on the *TILSAM* method required to report the three retrieval approaches. Next to the most evident direct retrieved results (indicated in the report form as "averaging" method), the regression-based retrieval was recommended as a measure to check better for quality issues with the measurements. This is based on the linear model of the measured absorption line areas versus the experimental parameter (i.e. total gas pressure), $A_{\text{line}} = x_{\text{CO}_2} \times \Gamma$, derived from the Beer-Lambert law, which does not contain any constant coefficient, i.e. an intercept parameter. The regression-based retrieval, based i.e. on a free generalized linear regression, however, is yielding an intercept parameter, which could either be significant or not. Not-significant means that its uncertainty is larger than its value component. In Fig. 3 the resulting intercept parameters from the reported regression-based retrievals are compared together with their expanded uncertainties ($k = 2$). Except of DFM500_3 and DFM500_2, DFM's intercept parameters of the regression-based retrievals on both mixtures were insignificant, and by that, in accordance with the model equation. However, as visible in Fig. 1, they are not automatically agreeing with the CRV. In contrast, PTB300 showed a significant intercept parameter for the 300 $\mu\text{mol/mol}$ data and an insignificant intercept for the 500 $\mu\text{mol/mol}$ result. The significance of the intercept parameters does not correlate with the level of comparability as given by the degree of equivalence for the presented results. This shows some inconsistency with the expectation, expressed in the *TILSAM* technical protocol [1], due to which the regression-based retrieval would be superior with respect to the other two retrieval strategies because of its additional measurement quality identifier given by the intercept parameter. This observation, on the other hand, conforms to the *TILSAM* description requirement to report results of all three retrieval approaches.

Regarding the reported uncertainties it is interesting to note that, first of all, the level of precision as expressed by the standard uncertainties is in the same range for both

participants, looking at the direct retrieval. As well, there is not much of variation comparing both amount fraction levels, as both participants reported standard uncertainties around 5 $\mu\text{mol/mol}$. This transforms to relative expanded uncertainties ($k = 2$) at the 500 $\mu\text{mol/mol}$ of 2.6 % and 2.7 % for DFM500_1 and PTB500, respectively. The relative expanded uncertainties at the 300 $\mu\text{mol/mol}$ level read 2.8 % and 2.7 % for the DFM300_2 and PTB300 data. These similar uncertainty levels confirm that both laboratories used experimental setups of comparable quality and accessed their measurement uncertainties in a similar type of estimation. This is worthwhile to note, because, looking at PTB's uncertainty budgets, the most influencing parameter at both amount fraction levels was the determination of the line area A_{line} .

Regarding the other two retrievals, the situation is slightly different. Whereas PTB's results gain in terms of smaller uncertainties when moving to the regression-based retrievals, DFM's results stay at the same level of uncertainty.

PTB states that the reported uncertainty of the direct retrieved result is based on a combined uncertainty from individual uncertainties of the individual measurements. This combined uncertainty was computed conservatively, taking just the square root of the number of individual measurements in the denominator (s. e.g. p. 7, Tab. 5 of PTB's report form in the Appendix). In contrast, the regression-based retrieval was computed using a generalized linear regression, which accounted for correlations due to the linear model of Beer-Lambert's law, such decreasing the resulting uncertainty of PTB's data with respect to the direct retrieval. However, for the regression analysis forced through the origin, PTB just took an ordinary linear regression approach, taking uncertainties of pressure, temperature and the other experimental condition parameters not into account. Consequently, the uncertainty decreased even further, however, as evidenced by the fact that the respective forced-regression result of PTB300 is not in accordance the CRV, fairly underestimating the uncertainty.

DFM was computing the uncertainty of the direct-retrieved results, according to a combined uncertainty based on the standard deviation of the mean of the individuals summed up with some smaller contribution from experimental parameters of the individual measurements (s. e.g. p. 4, Tab. 4 of DFM's report form in the Appendix). This standard deviation-based approach yields similar results as what is expected from a regression-based analysis. Since DFM performed the latter one using the same type of generalized regression for both regression-based retrievals, their results does not exhibit a large variation of uncertainties across the three retrievals.

From the spectroscopic point of view, the comparison results are showing that both institutes were reaching almost the limit of what was possible in terms of measurement uncertainty. At the very end, the limiting factor of achievable measurement uncertainty is set by the accuracy of which the line strength of the probed transition is known. For the R(12) line, this figure was taken by both institutes from [5] to be 0.5 %, relative. Combining the line strength uncertainty with that of the other experimental parameters, i.e. optical path length, gas pressure, and temperature, there is not that much left for the uncertainty of the derived line area arriving at the final 1 % combined uncertainty range. As mentioned above, the line area is the most contributing quantity to the final uncertainty, looking at the reported budgets of PTB. To go a step further, improving the final result by spectroscopic means, were possible enhancing the optical path length. This measure would increase the signal-to-noise of the absorbance feature, and by that, finally decrease the uncertainty of the line area.

To conclude, one has to note that this comparison was the first organized in the gas metrology community by means of infrared spectroscopy, and really focused to a specific analytical method. Accordingly, the level of demonstrated comparability was not as high as it

is normally found in gas metrology comparisons. Also, the number of participants was rather limited, most likely because gas metrology groups mainly rely on more established measurement techniques. However, the results are showing that gas spectroscopy labs can demonstrate a very promising comparability as their computed relative deviations from the CRV are on a few percentage level, which in turn, is better than spectroscopic results typically reported in scientific literature.

6. References

- [1] TILSAM technical protocol; pdf-file
- [2] EUROMET 934 project; website
- [3] CCQM document: CCQM09_03.pdf equivalent to GAWG document GAWG/09-15
- [4] GUM; JCGM 100:2008
- [5] IEEE Trans. Instr. Meas., vol. 56(2), p. 529 (2007)

APPENDIX**Report Form PTB****Report Form EUROMET 934, comparison on CO₂ by means of *TILSAM***1 General information:

institute	PTB				
contact	Olav Werhahn				
tel./fax	+49 531 592 3123 / +49 531 592 69 3123				
e-mail	olav.werhahn				
date receiving cylinders	2011-02-25	from NMI:	DFM		
date sending cylinders off	2011-06-10	to NMI:	NPL		
linked nat. institute	none	dating from:	–	to:	–

2 Results on mixture A (nominal 300 µmol/mol CO₂, cylinder no. NPL 1263):

Parameters of the *TILSAM* instrumentation used to analyse mixture A are given in the following Tab. 2 (missing parameters may be added)

Tab. 2: Parameters of the *TILSAM* instrumentation used to analyse mixture A.

instrument type	custom made setup, Nanoplus DFB	
spectrometric measurement mode	1-channels	
wavenumber axis evaluation	solid FPI, FSR 0.05 cm ⁻¹	before and after analytical measurements
spectrometric detector type (s)	1 RT-XInGaAs	
absorbance evaluation mode	sequentially measured sample and reference signals	reference base line fitted to analytical data
molecular absorption line probed	¹² C ¹⁶ O ₂ R(12) in 2-µm band	4987.31 cm ⁻¹
spectral coverage probed by a single laser sweeps	1.2 cm ⁻¹	
laser tuning by	current	
laser modulation frequency	140 Hz	
number of scans (laser sweeps) per absorbance curve	50	
gas sampling mode	static	
gas pressure measured by	1000 torr MKS baratron type 626A	
gas temperature measured by	PT100 surface resistance	

gas pressure (range) used for analysis	100 to 900 mbars	
gas temperature (range) used for analysis	296 to 297 K	
type of gas cell used for analysis	multipass White-type	
optical path length (range)	(21.84±0.11) m	
number of different exp. parameters Γ processed for the slope-evaluated x_{CO_2}	9	
Γ varied by variation of	p	
type of regression for slope evaluation	GLS / BLeast	ref. ISO 6143

In Tab. 3 below the respective measured data on mixture A are summarized:

Tab. 3: Measurement result on mixture A. Retrieval methods include averaging N individual measurements, applying linear models $A_{\text{line}} = x_{\text{CO}_2} \cdot \Gamma + a$, with a being either a free parameter or a fixed one, forced to zero.

cylinder pressure as received	100	bar		
cylinder pressure as sent off	100	bar		
$x_{\text{CO}_2} / \mu\text{mol}\cdot\text{mol}^{-1}$	$u(x_{\text{CO}_2}) / \mu\text{mol}\cdot\text{mol}^{-1}$	retrieval method	info	data set name
321.6	4.3 (1.35% rel.)	averaging	$N = 9$	BLeast300ppmNPL_2011-04-12.dat
321.5	1.4 (0.4% rel.)	slope evaluation	intercept: $a = 0$	"
325.9	2.2 (0.7% rel.)	slope evaluation	$a = (-9.1 \pm 3.5) \cdot 10^{-5} \text{ cm}^{-1}$	"

The respective results on averaged and slope-evaluated x_{CO_2} can be supported by sending in the respective data sets as ascii data with columns for A_{line} , $u(A_{\text{line}})$, Γ , $u(\Gamma)$, specified by the names given in Tab. 3.

The uncertainty estimation for x_{CO_2} is based on budgets for individual spectrometric measurements. Tab. 4 summarizes the uncertainty estimation for an individual *TILSAM* result on mixture A, an example with quantitative figures is also presented in the appendix of [1].

Tab. 4: Uncertainty budget for an individual *TILSAM* result; to be added by missing quantities or changed to any desired units.

model equation:	see section 6 of [1]		
list of quantities:			
quantity	unit	definition	type (proposal [1])
$X_{12\text{CO}_2\text{HITRAN}}$	1	conventional isotopomeric abundance	constant
$X_{12\text{CO}_2}$	1	sample isotopomeric abundance	rect.
r_{iso}	1	$r_{\text{iso}} = x_{12\text{CO}_2} / x_{12\text{CO}_2\text{HITRAN}}$	int. result

ν_0	cm ⁻¹	line center wavenumber	normal	
S_0	cm/molec.	line strength at 296 K	normal	
E	cm ⁻¹	lower state energy	constant	
T	K	gas temperature	normal	
S_T	cm/molec	line strength at T	interim result	
j	1	partition func. approx. $(T_0/T)^j$	rect.	
p	hPa	sample pressure	normal	
L	cm	optical path length	normal	
Γ	cm ⁻¹	$\Gamma = S_T \cdot p \cdot L / (k_B \cdot T)$	normal	
A_{line}	cm ⁻¹	absorbance line area	normal	
budget:				
quantity	value	standard u	sens. coeff.	u-contribution / mol/mol
$X_{12\text{CO}_2\text{HITRAN}}$	0.98420	-	-	-
$X_{12\text{CO}_2}$	0.98420	$4.00 \cdot 10^{-3}$	$-330 \cdot 10^{-6}$	$-1.3 \cdot 10^{-6}$
f_{iso}	1	$4.06 \cdot 10^{-3}$	-	-
ν_0	4987.308 cm ⁻¹	$4 \cdot 10^{-3}$ cm ⁻¹	0	0
S_0	$1.25500 \cdot 10^{-21}$ cm/molecule	$6.28 \cdot 10^{-24}$ cm/molecule	$-260 \cdot 10^{15}$	$-1.6 \cdot 10^{-6}$
E	60.8709 cm ⁻¹	-	-	-
S_T	$1.25500 \cdot 10^{-21}$ cm/molecule	$6.28 \cdot 10^{-24}$ cm/molecule	$-260 \cdot 10^{15}$	$-1.6 \cdot 10^{-6}$
j	1.250	0.144	$630 \cdot 10^{-9}$	$90 \cdot 10^{-9}$
L	2184.0 cm	11.0 cm	$-150 \cdot 10^{-9}$	$-1.6 \cdot 10^{-6}$
p	506.8770 hPa	0.0280 hPa	$-640 \cdot 10^{-9}$	$-18 \cdot 10^{-9}$
T	296.570 K	0.500 K	$2.1 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$
Γ	33.9 cm ⁻¹	0.3 cm ⁻¹	-	-
A_{line}	0.0110300 cm ⁻¹	$11 \cdot 10^{-5}$ cm ⁻¹	0.030	$3.2 \cdot 10^{-6}$
X_{CO_2}	$325.7 \cdot 10^{-6}$ mol/mol	$4.3 \cdot 10^{-6}$ mol/mol	-	-

The propagation of the uncertainties of the individual *TILSAM* results towards the reported CO₂ amount fractions given in Tab. 3 is described in Tab. 5.

Tab. 5: Uncertainty propagation of individual *TILSAM* results (to be added/changed/matched by the participant).

Retrieval	Uncertainty propagation	Combined uncertainty
averaging individual i	calculating combined u from u_i	$u_c = 1/\sqrt{N} \cdot (\sum u_i^2)^{1/2}$
regression-based, $a = 0$	OLS weighted with $u(A_{\text{line}})$	standard "error" from Origin7.5 OLS
regression-based	GLS / BLEast	slope standard uncertainty BLEast

3 Results on mixture B (nominal 500 $\mu\text{mol/mol}$ CO_2 , cylinder no. NPL 1264):

For reporting on mixture B the same structure as for mixture A is used.

Parameters of the *TILSAM* instrumentation used to analyse mixture B are given in the following Tab. 6 (missing parameters may be added)

Tab. 6: Parameters of the *TILSAM* instrumentation used to analyse mixture B.

instrument type	custom made setup, Nanoplus DFB	
spectrometric measurement mode	1-channels	
wavenumber axis evaluation	solid FPI, FSR 0.05 cm^{-1}	before and after analytical measurements
spectrometric detector type (s)	1 RT-XInGaAs	
absorbance evaluation mode	sequentially measured sample and reference signals	reference base line fitted to analytical data
molecular absorption line probed	$^{12}\text{C}^{16}\text{O}_2$ R(12) in 2- μm band	4987.31 cm^{-1}
spectral coverage probed by a single laser sweeps	1.2 cm^{-1}	
laser tuning by	current	
laser modulation frequency	140 Hz	
number of scans (laser sweeps) per absorbance curve	50	
gas sampling mode	static	
gas pressure measured by	1000 torr MKS baratron type 626A	
gas temperature measured by	PT100 surface resistance	
gas pressure (range) used for analysis	80 to 780 mbars	
gas temperature (range) used for analysis	295 to 296 K	
type of gas cell used for analysis	multipass White-type	
optical path length (range)	(21.84 \pm 0.11) m	
number of different exp. parameters Γ processed for the slope-evaluated x_{CO_2}	8	
Γ varied by variation of	p	
type of regression for slope evaluation	GLS / BLeast	ref. ISO 6143

In Tab. 7 below the respective measured data on mixture B are summarized:

Tab. 7: Measurement result on mixture B. Retrieval methods include averaging N individual measurements, applying linear models $A_{\text{line}} = x_{\text{CO}_2} \cdot \Gamma + a$, with a being either a free parameter or forced to zero.

cylinder pressure received	as	115	bar		
cylinder pressure as sent off		113	bar		
$x_{\text{CO}_2} / \mu\text{mol}\cdot\text{mol}^{-1}$	$u(x_{\text{CO}_2}) / \mu\text{mol}\cdot\text{mol}^{-1}$	retrieval method	info	data set name	
447.1	6 (1.35% rel.)	averaging	$N = 8$	BLeast500ppmNPL_2011-04-05.dat	
447.0	1.2 (0.3% rel.)	slope evaluation	intercept: $a = 0$	"	
449.7	3.1 (0.7% rel.)	slope evaluation	$a = (-4.7 \pm 4.2) \cdot 10^{-5} \text{ cm}^{-1}$	"	

The respective results on averaged and slope-evaluated x_{CO_2} can be supported by sending in the respective data sets as ascii data with columns for A_{line} , $u(A_{\text{line}})$, Γ , $u(\Gamma)$, specified by the names given in Tab. 7.

The uncertainty estimation for x_{CO_2} is based on budgets for individual spectrometric measurements. Tab. 8 summarizes the uncertainty estimation for an individual *TILSAM* result on mixture B, an example with quantitative figures is also presented in the appendix of [1].

Tab. 8: Uncertainty budget for an individual *TILSAM* result; to be added by missing quantities or changed to any desired units.

model equation:	see section 6 of [1]			
list of quantities:				
quantity	unit	definition	type (proposal [])	
$X_{12\text{CO}_2\text{HITRAN}}$	1	conventional isotopomeric abundance	constant	
$X_{12\text{CO}_2}$	1	sample isotopomeric abundance	rect.	
r_{iso}	1	$r_{\text{iso}} = X_{12\text{CO}_2} / X_{12\text{CO}_2\text{HITRAN}}$	int. result	
ν_0	cm^{-1}	line center wavenumber	normal	
S_0	$\text{cm}/\text{molec.}$	line strength at 296 K	normal	
E	cm^{-1}	lower state energy	constant	
T	K	gas temperature	normal	
S_T	cm/molec	line strength at T	interim result	
j	1	exponent for the partition func. approx.	rect.	
p	hPa	sample pressure	normal	
L	cm	optical path length	normal	
Γ	cm^{-1}	$\Gamma = S_T \cdot p \cdot L / (k_B \cdot T)$	normal	
A_{line}	cm^{-1}	absorbance line area	normal	

budget:				
quantity	value	standard u	sens. coeff.	u-contribution
$X_{12\text{CO}_2\text{HITRAN}}$	0.98420			
$X_{12\text{CO}_2}$	0.98420	$4.00 \cdot 10^{-3}$	$-330 \cdot 10^{-6}$	$-1.3 \cdot 10^{-6}$
r_{iso}	1	$4.06 \cdot 10^{-3}$	-	-
ν_0	4987.308 cm^{-1}	$4 \cdot 10^{-3} \text{ cm}^{-1}$	0	0
S_0	$1.25500 \cdot 10^{-21} \text{ cm/molecule}$	$6.28 \cdot 10^{-24} \text{ cm/molecule}$	$-260 \cdot 10^{15}$	$-1.6 \cdot 10^{-6}$
E	60.8709 cm^{-1}	-	-	-
S_T	$1.25500 \cdot 10^{-21} \text{ cm/molecule}$	$6.28 \cdot 10^{-24} \text{ cm/molecule}$	$-260 \cdot 10^{15}$	$-1.6 \cdot 10^{-6}$
j	1.250	0.144	$630 \cdot 10^{-9}$	$90 \cdot 10^{-9}$
L	2184.0 cm	11.0 cm	$-150 \cdot 10^{-9}$	$-1.6 \cdot 10^{-6}$
p	487.704 hPa	0.0280 hPa	$-920 \cdot 10^{-9}$	$-26 \cdot 10^{-9}$
T	295.650 K	0.500 K	$3 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$
Γ	32.79 cm^{-1}	0.28 cm^{-1}	-	-
A_{line}	0.01470 cm^{-1}	$15 \cdot 10^{-5} \text{ cm}^{-1}$	0.031	$4.6 \cdot 10^{-6}$
x_{CO_2}	$448.4 \cdot 10^{-6} \text{ mol/mol}$	$5.8 \cdot 10^{-6} \text{ mol/mol}$	-	-

The propagation of the uncertainties of the individual *TILSAM* results towards the reported CO₂ amount fractions given in Tab. 7 is described in Tab. 9.

Tab. 9: Uncertainty propagation of individual *TILSAM* results (to be added/changed/matched by the participant).

averaging individuals i	calculating combined u from u_i	$u_c = 1/\sqrt{N} \cdot (\sum u_i^2)^{1/2}$
regression-based, $a = 0$	OLS weighted with $u(A_{\text{line}})$	standard "error" from Origin7.5 OLS
regression-based	GLS / BLeast	slope standard uncertainty BLeast

Report Form DFM**Report Form EUROMET 934, comparison on CO₂ by means of TILSAM**1 General information:

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date receiving cylinders	December 2009	from NMI:	NPL
date sending cylinders off		to NMI:	PTB
linked nat. institute	none	dating from:	– to: –

2 Results on mixture A (nominal 300 µmol/mol CO₂, cylinder no. NPL 1263):

Parameters of the *TILSAM* instrumentation used to analyse mixture A are given in the following Tab. 2 (missing parameters may be added)

Tab. 210: Parameters of the *TILSAM* instrumentation used to analyse mixture A.

instrument type	custom made setup, 42 m multipass cell and 2 µm diode laser borrowed from PTB	
spectrometric measurement mode	1-channels	
wavenumber axis evaluation	Simple free-space FPI, mirror separation determined with laser distance meter and double-checked with HITRAN spectra.	before and after analytical measurements
spectrometric detector type (s)	New Focus 2033 detectors followed by lock-in amplifiers (SR 850)	lock-in detection with chopped laser beam required due to low sensitivity of detectors at 2 µm.
absorbance evaluation mode	Signal (power after cell) and reference (power before cell) measured simultaneously.	signal/reference fitted to Voigt profiles taking into account incoherent/non- resonant contribution.

molecular absorption line probed	$^{12}\text{C}^{16}\text{O}_2$ R(12) in 2- μm band	4987.31 cm^{-1}
spectral coverage probed by a single laser sweeps	28 GHz (0.93 cm^{-1})	
laser tuning by	current	
laser modulation frequency	50 mHz	
number of scans (laser sweeps) per absorbance curve	1	
gas sampling mode	static	
gas pressure measured by	Balzers BG G15 000 (Pirani gauge)	
gas temperature measured by	PT100 surface resistance	
gas pressure (range) used for analysis	50 to 600 mbars	
gas temperature (range) used for analysis	296 to 298 K	
type of gas cell used for analysis	Astigmatic multipass absorption cell (New Focus / Aerodyne design)	
optical path length (range)	(41.88 \pm 0.02) m	Measured with laser distance meter (Bosch).
number of different exp. parameters Γ processed for the slope-evaluated x_{CO_2}	12	
Γ varied by variation of	p	
type of regression for slope evaluation	GLS (DFM-LSQ Analyzer)	L.Nielsen, Metrologia 35 , 115 (1998).

In Tab. 3 below the respective measured data on mixture A are summarized:

Tab. 311: Measurement result on mixture A. Retrieval methods include averaging N individual measurements, applying linear models $A_{\text{line}} = x_{\text{CO}_2} \cdot \Gamma + a$, with a being either a free parameter or a fixed one, forced to zero.

cylinder pressure as received	100	bar		
cylinder pressure as sent off	100	bar		
$x_{\text{CO}_2} / \mu\text{mol}\cdot\text{mol}^{-1}$	$u(x_{\text{CO}_2}) / \mu\text{mol}\cdot\text{mol}^{-1}$	retrieval method	info	data set name
336.5	5.1 (1.5% rel.)	Averaging	$N = 12$	NPL 300ppm analysis 20110113.xls
345.7	4.7 (1.4% rel.)			NPL 300ppm analysis 20110114.xls
348.9	5.2 (1.5% rel.)			NPL 300ppm analysis 20110115.xls

334.0	5.0 (1.5 % rel.)	Slope evaluation	intercept: $a = 0$	"
345.4	4.7 (1.4 % rel.)			
344.9	5.1 (1.5 % rel.)			
330.2	6.2 (1.9% rel.)	Slope evaluation	$a = (4.6 \pm 4.5)$ MHz	"
345.7	5.4 (1.6% rel.)		$a = (-0.2 \pm 1.8)$ MHz	
339.1	6.3 (1.8 % rel.)		$a = (8.2 \pm 5.3)$ MHz	

Tab. 4 summarizes the uncertainty estimation for an individual *TILSAM* result on mixture A. For slope evaluation data, the uncertainty is calculated with the DFM-LSQ analyser software using input data as in Tab. 4.

Tab. 4: Uncertainty budget for an individual *TILSAM* result; to be added by missing quantities or changed to any desired units.

model equation:				
		$x_{co2} = \frac{k_B T A_i f}{r_{iso} L S (1 + S_{T,corr} (296 - T)) \times (cp_0 + cp_1 p_i + cp_2 p_i^2)} \quad i = 1, 2, \dots, 12$		
list of quantities:				
quantity	unit	definition	type (proposal [])	
$X_{12CO2HITRAN}$	1	conventional isotopomeric abundance	constant	
X_{12CO2}	1	sample isotopomeric abundance		
r_{iso}	1	$r_{iso} = X_{12CO2} / X_{12CO2HITRAN}$	normal	
S	cm/molec.	line strength at 296 K	normal	
T	K	gas temperature	normal	
$S_{T,corr}$	K ⁻¹	line strength temp. dependence	normal	
p	hPa	pressure gauge reading	normal	
cp_1	1	pressure gauge calibr. - scale factor	normal	
L	cm	optical path length	normal	
A_{line}	MHz	absorbance line area	normal	
f	1	frequency scale calibration factor	normal	
cp_0	hPa	pressure gauge calibration const.	normal	
cp_2	hPa ⁻¹	pressure gauge calibration const.	normal	
budget:				
quantity	value	standard u	sens. coeff.	relative u -contribution / %
r_{iso}	1	$4.00 \cdot 10^{-3}$	-	0.40
S	$1.25500 \cdot 10^{-21}$ cm/molecule	$6.20 \cdot 10^{-24}$ cm/molecule	-	0.49
$S_{T,corr}$	-0.0852 K ⁻¹	0.09 K ⁻¹	-	~ 0
L	4188.0 cm	2.0 cm	-	0.05
cp_1	1	$3.1 \cdot 10^{-3}$	-	0.31

cp_2	$-6.0 \cdot 10^{-6} \text{ hPa}^{-1}$	$3.0 \cdot 10^{-6} \text{ hPa}^{-1}$	-	~ 0
cp_0	$7.3 \cdot 10^{-5} \text{ hPa}$	$1.0 \cdot 10^{-1} \text{ hPa}$	-	~ 0
f	1	0.01	-	1.00
T	296.71 K	0.1 K	-	0.03

Total relative uncertainty, excluding contribution from A_{line} and p , is 1.22 %

The uncertainty contribution from A_{line} and p is mainly of type A and is included as described in Tab 5. Tab 5 describes the propagation of the uncertainties of the individual *TILSAM* results towards the reported CO₂ amount fractions given in Tab. 3. When averaging individual measurements, the type A uncertainty from Tab. 5 is added in quadrature to the 1.22 % relative uncertainty from Tab. 8. When using DFM-LSQ Analyzer, the uncertainties of the individual $A_{\text{line},i}$ and p_i are adjusted for overall consistency.

Tab. 512: Uncertainty propagation of individual *TILSAM* results (to be added/changed/matched by the participant).

Retrieval	Uncertainty propagation	Combined uncertainty
averaging individuals i	calculating combined u	$u_A = 1/\sqrt{N} \cdot \text{stdev}(x_{\text{CO}_2,i})$ $u_B = 1.22 \% \cdot \langle x_{\text{CO}_2,i} \rangle$ $u = (u_A^2 + u_B^2)^{1/2}$
regression-based, $a = 0$	GLS / DFM-LSQ analyzer	GLS / DFM-LSQ analyser
regression-based	GLS / DFM-LSQ analyzer	GLS / DFM-LSQ analyser

3 Results on mixture B (nominal 500 $\mu\text{mol/mol}$ CO₂, cylinder no. NPL 1264):

For reporting on mixture B the same structure as for mixture A is used.

Parameters of the *TILSAM* instrumentation used to analyse mixture B are given in the following Tab. 6 (missing parameters may be added)

Tab. 6: Parameters of the *TILSAM* instrumentation used to analyse mixture B.

instrument type	custom made setup, 42 m multipass cell and 2 μm diode laser borrowed from PTB	
spectrometric measurement mode	1-channels	
wavenumber axis evaluation	Simple free-space FPI, mirror separation determined with laser distance meter	before and after analytical measurements

	and double-checked with HITRAN spectra.	
spectrometric detector type (s)	New Focus 2033 detectors followed by lock-in amplifiers (SR 850)	lock-in detection with chopped laser beam required due to low sensitivity of detectors at 2 μm .
absorbance evaluation mode	Signal (power after cell) and reference (power before cell) measured simultaneously.	signal/reference fitted to Voigt profiles taking into account incoherent/non-resonant contribution.
molecular absorption line probed	$^{12}\text{C}^{16}\text{O}_2$ R(12) in 2- μm band	4987.31 cm^{-1}
spectral coverage probed by a single laser sweeps	28 GHz (0.93 cm^{-1})	
laser tuning by	current	
laser modulation frequency	50 mHz	
number of scans (laser sweeps) per absorbance curve	1	
gas sampling mode	static	
gas pressure measured by	Balzers BG G15 000 (Pirani gauge)	
gas temperature measured by	PT100 surface resistance	
gas pressure (range) used for analysis	50 to 600 mbars	
gas temperature (range) used for analysis	296 to 298 K	
type of gas cell used for analysis	Astigmatic multipass absorption cell (New Focus / Aerodyne design)	
optical path length (range)	(41.88 \pm 0.02) m	Measured with laser distance meter (Bosch).
number of different exp. parameters Γ processed for the slope-evaluated x_{CO_2}	12	
Γ varied by variation of	p	
type of regression for slope evaluation	GLS (DFM-LSQ Analyzer)	L.Nielsen, Metrologia 35 , 115 (1998).

In Tab. 7 below the respective measured data on mixture B are summarized:

Tab. 7: Measurement result on mixture B. Retrieval methods include averaging N individual measurements, applying linear models $A_{\text{line}} = x_{\text{CO}_2} \cdot \Gamma + a$, with a being either a free parameter or forced to zero.

cylinder pressure received	as	115	bar		
cylinder pressure as sent off		115	bar		
$x_{\text{CO}_2} / \mu\text{mol}\cdot\text{mol}^{-1}$	$u(x_{\text{CO}_2}) / \mu\text{mol}\cdot\text{mol}^{-1}$	retrieval method	info	data set name	
459.7	5.8 (1.3% rel.)	averaging	$N = 12$	NPL 500ppm analysis 20110113.xls	
462.2	7.9 (1.7% rel.)			NPL 500ppm analysis 20110114.xls	
469.4	8.9 (1.9% rel.)			NPL 500ppm analysis 20110115.xls	
457.2	5.8 (1.3% rel.)	slope evaluation	intercept: $a = 0$	"	
453.8	6.0 (1.3% rel.)				
458.8	6.8 (1.5% rel.)				
453.9	6.4 (1.4% rel.)	slope evaluation	$a = (4.3 \pm 3.5) \text{ MHz}$	"	
443.5	5.6 (1.3% rel.)		$a = (13.9 \pm 1.8) \text{ MHz}$		
446.1	7.5 (1.7% rel.)		$a = (17.4 \pm 5.9) \text{ MHz}$		

Tab. 8 summarizes the uncertainty estimation for an individual *TILSAM* result on mixture B. For slope evaluation data, the uncertainty is calculated with the DFM-LSQ analyser software using input data as in Tab. 8.

Tab. 8: Uncertainty budget for an individual *TILSAM* result; to be added by missing quantities or changed to any desired units.

model equation:	$x_{\text{CO}_2} = \frac{k_B T A_i f}{r_{\text{iso}} L S (1 + S_{T,\text{corr}} (296 - T)) \times (c p_0 + c p_1 P_i + c p_2 P_i^2)} \quad i = 1, 2, \dots, 12$			
list of quantities:				
quantity	unit	definition	type (proposal [])	
$X_{12\text{CO}_2\text{HITRAN}}$	1	conventional isotopomeric abundance	constant	
$X_{12\text{CO}_2}$	1	sample isotopomeric abundance		
r_{iso}	1	$r_{\text{iso}} = X_{12\text{CO}_2} / X_{12\text{CO}_2\text{HITRAN}}$	normal	
S	cm/molec.	line strength at 296 K	normal	
T	K	gas temperature	normal	
$S_{T,\text{corr}}$	K^{-1}	line strength temp. dependence	normal	

p	hPa	pressure gauge reading	normal	
cp_1	1	pressure gauge calibr. - scale factor	normal	
L	cm	optical path length	normal	
A_{line}	MHz	absorbance line area	normal	
f	1	frequency scale calibration factor	normal	
cp_0	hPa	pressure gauge calibration const.	normal	
cp_2	hPa ⁻¹	pressure gauge calibration const.	normal	
budget:				
quantity	value	standard u	sens. coeff.	
			relative u-contribution / %	
r_{iso}	1	$4.00 \cdot 10^{-3}$	-	0.40
S	$1.25500 \cdot 10^{-21}$ cm/molecule	$6.20 \cdot 10^{-24}$ cm/molecule	-	0.49
$S_{\text{T,corr}}$	-0.0852 K^{-1}	0.09 K^{-1}	-	~ 0
L	4188.0 cm	2.0 cm	-	0.05
cp_1	1	$3.1 \cdot 10^{-3}$	-	0.31
cp_2	$-6.0 \cdot 10^{-6} \text{ hPa}^{-1}$	$3.0 \cdot 10^{-6} \text{ hPa}^{-1}$	-	~ 0
cp_0	$7.3 \cdot 10^{-5} \text{ hPa}$	$1.0 \cdot 10^{-1} \text{ hPa}$	-	~ 0
f	1	0.01	-	1.00
T	296.71 K	0.1 K	-	0.03

Total relative uncertainty, excluding contributions from A_{line} and p , is 1.22 %

The uncertainty contribution from A_{line} and p is mainly of type A and is included as described in Tab. 9. Tab. 9 describes the propagation of the uncertainties of the individual *TILSAM* results towards the reported CO₂ amount fractions given in Tab. 8. When averaging individual measurements, the type A uncertainty from Tab. 7 is added in quadrature to the 1.22 % relative uncertainty from Tab. 8. When using DFM-LSQ Analyzer, the uncertainties of the individual $A_{\text{line},i}$ and p_i are adjusted for overall consistency.

Tab. 9: Uncertainty propagation of individual *TILSAM* results (to be added/changed/matched by the participant).

Retrieval	Uncertainty propagation	Combined uncertainty
averaging individuals i	calculating combined u	$u_A = 1/\sqrt{N} \cdot \text{stdev}(x_{\text{CO}_2,i})$ $u_B = 1.22 \% \cdot \langle x_{\text{CO}_2,i} \rangle$ $u = (u_A^2 + u_B^2)^{1/2}$
regression-based, $\sigma = 0$	GLS / DFM-LSQ analyzer	GLS / DFM-LSQ analyser
regression-based	GLS / DFM-LSQ analyzer	GLS / DFM-LSQ analyser