# *TILSAM* – method
## – draft A of a technical protocol –

Edited by: Olav Werhahn (PTB)[1], Jan C. Petersen (DFM)

PTB:

Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

DFM:

Danish Fundamental Metrology Ltd., Matematiktorvet 307, 2800 Kgs. Lyngby, Denmark

[1] Corresponding author: olav.werhahn@ptb.de

**Preamble**

This document constitutes one of the results of a collaborative development process within the EUROMET project 934 (EURO 934). The participants of EURO 934 have approved this document. It is meant to be a recommendation. However, the EURO 934 partners suggest that this methodology description might serve as an underlying document for a documentary standard on traceable infrared laser-spectrometric amount fraction measurement (*TILSAM*) in the future.

Initially, this document is intended to present the basic principles of the measurement method used in a comparison on spectrometric amount fraction measurements of $CO_2$ conducted under EURO 934 in the year 2010.

All EURO 934 partners explicitly agree that this document shall be open for further improvements or changes, given that the described measurement process itself may undergo further optimization or standardization. This implies even the incorporation of suitable spectrometry techniques that are not part of this first edition.

**Introduction**

This document describes a method for measuring the amount-of-substance fractions in gas mixtures. The measurement is performed by infrared (IR) spectrometry. The measurand is the amount of substance fraction $x$ of a certain molecular species present in a mixture.

Infrared spectrometry techniques can be used in gas analysis applications to assign amount-of-substance fractions to species in gas mixtures of known constituents. The determination of the amount-of-substance fraction of a certain species without prior calibration of the spectrometric measurement instrument with calibration gas mixtures of a known composition leads to so-called calibration-free infrared spectrometry. In this context, calibration-free means allowing the quantity amount fraction to be measured in terms of the SI derived unit $mol \cdot mol^{-1}$ without referring to a standard or a measurement expressed in the same unit (s. also [1]). The method used, which is aiming at amount fraction results that are traceable to the SI units, is called traceable infrared laser-spectrometric amount fraction measurement (*TILSAM*) and is described in the following.

*TILSAM* has the potential of being a primary method [1] in gas metrology. However, it can also be used in field applications. This is depending on the assessed level of uncertainties of the respective results for a given analyte. The respective instrumentation and the implementation of the different methodological issues used in a certain *TILSAM* setup is thus governing the possible fields of application.

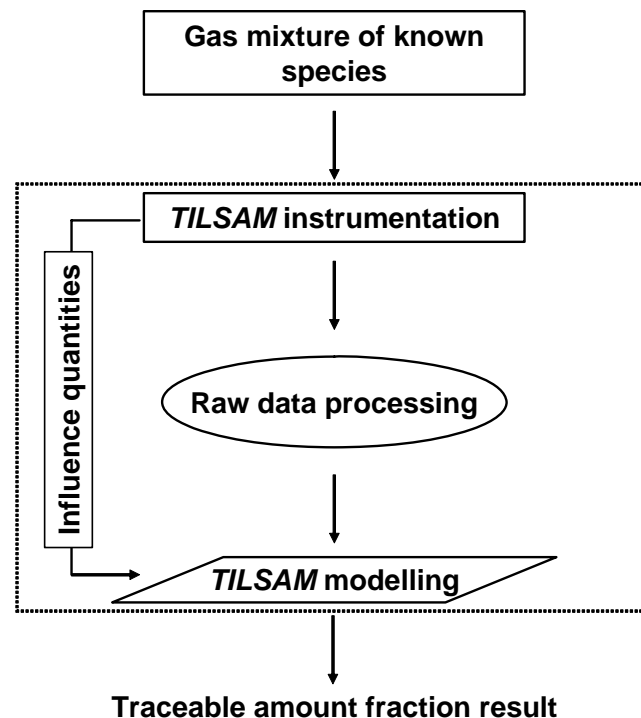In a schematic view, *TILSAM* works as sketched in Fig. 1.



**Fig. 1:** Sketch of the *TILSAM* method

## 1.    Scope

This protocol is a recommendation for using the principles of spectrometric methods to measure amount fractions of a known molecular species in a given gas mixture. The document itself is intended to be the first step of the standardization of spectrometric methods in gas analysis. This first version addresses only the simplest known spectrometry technique, i.e. direct laser absorption spectroscopy (LAS). However, more sophisticated, more sensitive techniques, e.g. cavity ring-down spectroscopy (CRDS) may also be candidates for developing a primary method. Future *TILSAM* protocol editions may, therefore, incorporate additional techniques as well.

This document defines the different terms used to describe the spectrometric measurement process, the model used to process the raw data and the subsequent estimation of uncertainties associated to the results of this method. This *TILSAM* protocol relies on a very basic experimental setup, that can be improved in reality wherever it might be suitable.

The *TILSAM* method is described for the analyte carbon dioxide ($CO_2$). It relies on the measurement of a spectrally isolated molecular ro-vibrational absorption line, the area of which is to be derived from the spectrometric measurement data. This protocol might not be usable where the analyte or the molecular spectrum is different from that. However, in addition to $CO_2$, there are other molecules to which the *TILSAM* method can be applied as well.

This protocol has been validated for amount fraction ranges between 100 µmol/mol and 100 mmol/mol of carbon dioxide in nitrogen. In ranges different from that, other influence quantities may have to be taken into account or the relative contribution of the considered quantities herein may change.

## 2.    Abbreviations, Terms, and Modelling of the Measurement

### *Abbreviations and Terms*

The abbreviations used within this document are summarized in Tab. 1, terms and quantities in Tab. 2.

**Tab. 1:** List of abbreviations.

| | | |
|---|---|---|
| LAS | direct laser absorption spectrometry | |
| CRDS | cavity ring-down spectrometry | |
| IR | infrared | |
| $CO_2$ | carbon dioxide | |
| $N_2$ | nitrogen | |
| molec | molecules | |
| $\tau$-1 | baseline, given by the experimental detector signal where no absorption occurs, representation of the transmission level $\tau = 1$ | |

| $\tau$-0 | 100-%-absorption, represented by $\tau = 0$ | |
| $r_{sweep}$ | laser sweep rate; units are defined by the experimental realization of the spectrum | |
| FWHM | quantity given as full width in x-direction at half of the maximum in y-direction | |

**Tab. 2:** Definitions of terms and quantities.

| Quantity | Symbol | Unit[a] | Notes |
|---|---|---|---|
| amount of $CO_2$ fraction | $x_{CO2}$ | mol·mol$^{-1}$ | |
| gravimetric amount of $CO_2$ fraction reference | $x_{CO2,grav}$ | mol·mol$^{-1}$ | |
| | | | |
| abundance of isotopologue $i$, $i = 1,2,3,…$ | $x_{iCO2}$ | 1 | given in the gas mixture |
| conventional abundance | $x_{iCO2,norm}$ | 1 | $x_{1CO2,norm} = 0.9842$ [2],[3] |
| isotopologue factor | $r_{iso}$ | 1 | $r_{iso} = x_{iCO2} / x_{iCO2,norm}$ |
| | | | |
| particle density (of species $j$) | $n$ ($n_j$) | molec·cm$^{-3}$ | $p = n \cdot k_B \cdot T$ |
| total gas pressure | $p$ | hPa | hPa = mbar |
| partial pressure of species $j$ | $p_j$ | hPa | $p_j = x_j \cdot p$ |
| gas temperature | $T$ | K | |
| norm gas temperature | $T_0$ | | $T_0 = 296$ K |
| Boltzmann's constant | $k_B$ | | $k_B = 1.3806505 \cdot 10^{-23}$ J/K |
| | | | |
| wavenumber | $\tilde{\nu}$ | cm$^{-1}$ | $\tilde{\nu} = 1/\lambda$ |
| line center wavenumber | $\tilde{\nu}_0$ | cm$^{-1}$ | specified by the probed transition |
| optical path length | $L$ | cm | interaction length with light |
| incident radiant power at $\tilde{\nu}$ | $\phi_0(\tilde{\nu})$ | W/m$^2$ | |
| radiant power at $\tilde{\nu}$ transmitted over length $L$ | $\phi(\tilde{\nu})$ | W/m$^2$ | |
| molecular line strength for $T_0$ | $S$ | cm/molec | $S = \int_{-\infty}^{\infty} \sigma(\tilde{\nu}) \mathrm{d}\tilde{\nu}$ |
| molecular line strength for $T$ | $S_T$ | cm/molec | |
| absorption line profile function centred at $\tilde{\nu}_0$ for a given $\tilde{\nu}$ | $g(\tilde{\nu} - \tilde{\nu}_0)$ | cm | $\int_{-\infty}^{\infty} g(\tilde{\nu} - \tilde{\nu}_0) \mathrm{d}\tilde{\nu} = 1$ |
| spectral transmission | $\tau(\tilde{\nu})$ | 1 | $\tau(\tilde{\nu}) = \phi(\tilde{\nu}) / \phi_0(\tilde{\nu})$ |
| spectral absorption | $1 - \tau(\tilde{\nu})$ | 1 | if scattering is neglected |
| natural spectral absorbance | $A(\tilde{\nu})$ | 1 | $A(\tilde{\nu}) = -\ln(\tau(\tilde{\nu}))$ |
| integrated absorption line area, defined by the integrated absorbances $A(\tilde{\nu})$ [b] | $A_{line}$ | cm$^{-1}$ | $A_{line} = \int A(\tilde{\nu}) \mathrm{d}\tilde{\nu}$ |
| absorption coefficient | $k(\tilde{\nu})$ | cm$^{-1}$ | $k(\tilde{\nu}) = \sigma(\tilde{\nu}) \cdot n$ |
| absorption cross section | $\sigma(\tilde{\nu})$ | cm$^2$ | $\sigma(\tilde{\nu}) = S \cdot g(\tilde{\nu} - \tilde{\nu}_0)$ |
| line width of the absorption line | $\Delta\tilde{\nu}$ | cm$^{-1}$ | FWHM |

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| Lorentzian line width | $\Delta\tilde{\nu}_L$ | cm$^{-1}$ | FWHM |
|---|---|---|---|
| Gaussian line width | $\Delta\tilde{\nu}_G$ | cm$^{-1}$ | FWHM |
| laser line width | $\Delta\tilde{\nu}_{laser}$ | cm$^{-1}$ | FWHM |
| | | | |
| laser sweep position | $\zeta$ | arb. units | often time units |
| detector signal at laser sweep position $\zeta$ | $I(\zeta)$ | arb. units | often in V |
| detector offset signal | $I_{offset}(\zeta)$ | arb. units | often in V |
| function to process measured raw data | φ | | |
| | | | |
| experimental parameter | $\Gamma$ | cm$^{-1}$ | $\Gamma = S_T \cdot p \cdot L / (k_B \quad T)$ |

[a] normally used in spectrometric practice; in some cases decimal powers have to be matched

[b] line areas can also be reported differently, e.g. based on integrated absorption coefficients $k$

In Tab. 2 there are also some relations that relate some of the spectrometric properties to each other. In the following modelling, only a few of them are further used for the description of the method.

### *Modelling*

*TILSAM* relies on the assumption that the spectrometric measurement can be completely modelled by the Beer-Lambert law as given in its following representation, bearing in mind that other formulations of the law are possible[2]

$$\phi(\tilde{\nu}) = \phi_0 \cdot \exp\{-S_T \cdot g(\tilde{\nu} - \tilde{\nu}_0) \cdot x_{CO2} \cdot \frac{p}{k_B \cdot T} \cdot L\} . \tag{1}$$

The representation given in (1) is subsequently used to define the measurand $A(\tilde{\nu})$ and its relation to the final measurement result $x_{CO2}$ by

$$A(\tilde{\nu}) = S_T \cdot g(\tilde{\nu} - \tilde{\nu}_0) \cdot \frac{p}{k_B \cdot T} \cdot L \cdot x_{CO2} . \tag{2}$$

Due to its larger reliability and less susceptibility to experimental errors, the integral form of (2) shall be used to calculate the amount fraction, which leads to

$$A_{line} = \int A(\tilde{\nu}) d\tilde{\nu} = S_T \cdot \frac{p}{k_B \cdot T} \cdot L \cdot x_{CO2} , \tag{3}$$

provided by the normalization of g($\tilde{\nu}$).This leads to the basic model equation for the amount fraction result follows as

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[2] For transferring other popular formulations based on cross section, absorption coefficient, particle density or partial pressure into (1), s. notes in Tab. 2.

$$x_{CO2} = \frac{k_B \cdot T}{S_T \cdot p \cdot L} \cdot A_{line} \cdot \qquad (4)$$

For a given experimental realization based on direct absorption spectrometry with an interaction length *L,* modelled by (1) and probing a given absorption transition with a known line strength *S*, the amount fraction result can be derived from the line area and the measured gas parameters *T* and *p*, simply by applying (4). However, the respective uncertainty of the resulting amount fraction value depends on various influence parameters resulting in modifications to (4). These modifications will be explained in sections 5 and 6.

## 3.    Basic Experimental Setup

A typical *TILSAM* setup is schown in Fig. 2. With this experimental realization of a two-channel regime it is possible to measure $\phi_0(\tilde{\nu})$ and $\phi(\tilde{\nu})$ simultaneously, or, by using a frequency marker, e.g. a Fabry-Perot etalon, $\phi(\tilde{\nu})$ and $r_{sweep}$ can be measured simultaneously.
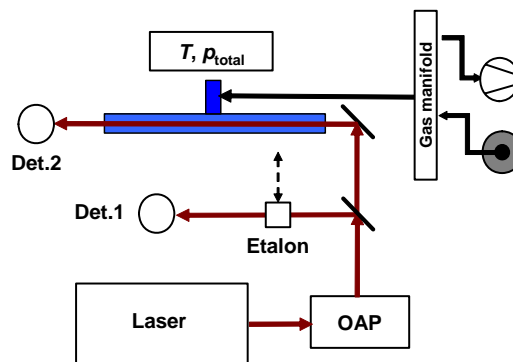


**Fig. 2:**      Basic setup used as *TILSAM* instrumentation. The two simultaneously measured signals from detectors Det. 1 and Det. 2 can be transferred to read measurement results for $\phi_0(\tilde{\nu})$ and $\phi(\tilde{\nu})$ or, by placing the etalon in the beam, $\phi(\tilde{\nu})$ and $r_{sweep}$. The OAP is used to collimate the diverging laser beam.

The length of the gas cell *L*, i.e. the interaction length of the molecules and the IR beanm, has to be measured independently. A gas manifold system is used to fill the absorption cell at with the gas mixture under test to the desired pressure *p*. The pressure *p* and the gas temperature *T* are measured inside the gas cell and on the cell wall surface, respectively.

It shall be stated that this document does not intend to exclusively promote or recommend a setup such as that presented in Fig. 2, but rather it intends to encourage the use of any suitable instrumentation setup for *TILSAM.*

## 4.    Measurement Policy

In order to perform the spectrometric amount fraction determination described by this document one has to ensure that the line width $\Delta\tilde{\nu}_{\text{laser}}$ of the applied IR laser is sufficiently narrow compared to the width $\Delta\tilde{\nu}$ of the probed molecular transition. The latter might be preset by varying *p* inside the gas cell, thus affecting the collisional broadening.

In addition to the spectrometric measurements themselves, *TILSAM* also relies on the measurement of the gas parameters *p* and *T*. The respective measurements have to be performed with calibrated devices in order to make the results traceable. The spectrometry has to be performed on the gas mixture under test. Therefore it must be ensured that no other gas or gas mixture from prior measurements interferes. In that respect it might be necessary to combine a vacuum system with the *TILSAM* instrumentation. In this way, the gas cell can be evacuated and the pressure of the gas mixture under test *p* may be preset. The latter enables also the performance of spectrometric measurements as a function of $\Gamma$ by varying *p*, with subsequent options for data retrieval (s. section 6).

The spectrometric measurement is carried out in a gas cell. In combination with the shape of the applied IR-laser beam, this cell provides a certain optical path length *L* which, for most gas cells, equals the interaction length of the gas molecules with the laser beam (which often is not true for the geometric length of the cell). There are different ways to measure this interaction length. However, the traceability of the final amount fraction result also relies on the traceability of *L*.

In order to derive the absorbance line area $A_{\text{line}}$, the spectrometric measurement has to be performed by sweeping the laser emission wavelength spectrally across the absorption line. The sweep width in relation to the line width has to be adjusted properly and shall be part of the documentation. To evaluate $A_{\text{line}}$, a measure to transfer the laser's sweep from any unit (often done in the temporal space) to the wavenumber domain has to be established for the *TILSAM* instrumentation. The resulting sweep rate (or sweep rate function) measurement shall also be part of the documentation.

The methods used to detect $\phi_0(\tilde{\nu})$ and $\phi(\tilde{\nu})$ for a single $A_{\text{line}}$ evaluation have to be reported in the documentation.

To ensure that $\tau$-1 and $\tau$-0 were properly established by the *TILSAM* instrumentation used, their respective control measurements are to be reported in the documentation. Due to possible side mode emissions of the laser, $\tau$-0 does often not correspond to *I* for a blocked laser beam. Therefore $\tau$-0 has to be measured instead by a respective molecular absorption, e.g. for the pure gas or high-concentration mixtures. Between $\tau$-1 and $\tau$-0 the linearity of any used detector has to be ensured.

The spectrometric measurements can be performed statically (off-line) or dynamically (in-line). In the first situation the gas mixture is filled into the gas cell at the desired pressure *p* and subsequently the gas cell is decoupled from the gas container. In the dynamic situation continuous flow of the gas mixture through the gas cell at a constant pressure *p* is established.

## 5.    Measurands and Influence Quantities

According to the modelling of the measurement given in section 2, the spectrometric measurand is the spectral absorbance $A(\tilde{\nu})$ measured across the molecular absorption line probed by the *TILSAM* instrumentation. By appropriate integration, the respective line area $A_{\text{line}}$ is then derived subsequently[3].

However, to apply equation (4) and/or to perform any further analysis, the following influence quantities have to be evaluated.

*Gas Temperature T:*

The temperature of the gas mixture under test is a measurand for any *TILSAM* procedure. In instrumental cases where the gas cell and, after thermal balancing, the gas itself, are temperature-stabilized, $T$ can be taken as equivalent to that of the temperature stabilizing system. Otherwise it is necessary to measure $T$ independently. Measurements of $T$ might be performed on the outer surface temperature of the gas cell, assuming a homogenous temperature along the interaction length $L$ and providing a thermal balancing of the gas with the outer cell walls ($T_{\text{wall}} = T$) or by some other options including internal cell wall temperature measurements.

Measurement options for $T$ shall, however, not be part of this document.

*Total pressure p:*

The total pressure of the gas mixture under test may serve as a varying parameter for the amount fraction determination, and influences the shape of the absorption profile $g(\tilde{\nu} - \tilde{\nu}_0)$. Therefore, it is recommended in this document to measure $p$ independently[4]. The pressure measurement must be performed directly at the gas cell, ensuring that no pressure gradient along $L$ is involved.

*Optical path length L:*

The optical path length which, in this document[5], is meant to equal the interaction length $L$ of the gas molecules and the IR beam is an influence quantity, experimentally realized in a given *TILSAM* instrumentation. Its value and related uncertainty can be taken from the specification documents of this instrumentation. In principle $L$ is affected by the shape of the IR beam and the in and out coupling of it, the mounting of the cell windows and the window material used. Even the gas pressure realized inside the gas cell may affect $L$.

However, neither options of measuring $L$ for a given *TILSAM* instrumentation nor design criteria for gas cells to be used for *TILSAM* shall be part of this document.

*Line Strength $S_T$:*

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[3] Due to section 2, $A_{\text{line}}$ is to be evaluated for each single laser sweep across the line. For improved statistics, very often $A(\tilde{\nu})$ is derived for accumulated laser scans averaging over the individual scans.
[4] Even though gas pressure measurements based on spectrometry itself are possible.
[5] For gas cells equipped with purged cell windows $L$ might be different from the optical path length.

Of all the influence quantities, the line strength *S* is probably the most important. The molecular line strength *S* serves to link the measured interaction of the photons and the molecules, as e.g., represented by the absorbance to the SI units. Thus, relying on the knowledge and usage of *S*, the methodology of *TILSAM* can be labelled as being calibration-free.

Line strength figures have been measured and published for a large number of molecules and molecular transitions. Various databases tabulate them, e.g. [3]. However, only recently line strengths of $CO_2$ have become available whose values are also assigned with uncertainty figures [4],[5],[6],[7]. For a number of transitions, line strengths with an impressive small uncertainty have been published as well [8]. However, a discrepancy between the two last publications is still to be clarified.

Due to a convention established by the majority of spectroscopists, line strengths are reported for the fixed norm temperature $T_0 = 296$ K. Furthermore, these respective line strengths *S* are given for a certain conventional isotopologic composition $x_{i,CO2}$ of the pure gas. The value of it for $CO_2$ is given in Tab. 2. The latter is necessary, because of the fact that by means of spectrometry and in particular by means of *TILSAM* the measurement is being performed on a single isotopologue, i.e. a transition belonging to a single isotopologue of the molecular species, whereas the final result, i.e. the amount fraction $x_{CO2}$ is meant to apply to the sum of all isotopologues being present in the mixture.

In order to apply the *TILSAM* method to any measurement temperature *T* the line strength S has to be transferred to the line strength $S_T$ by an appropriate specified approach. This might be done by the use of a line strength already reported/measured at the desired temperature *T*. Or alternatively *S* can be matched to *T* by applying a certain model function $\psi$ that explicitly describes the temperature dependence of *S* mathematically [4]

$$S_T = \psi(S, T) .$$

There is a common approximate model $\psi$ for *T* around room temperature given by

$$S_T = S \cdot \left(\frac{T_0}{T}\right)^j \cdot \exp\left[-\frac{h \cdot c \cdot E}{k_B} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \cdot \left[1 - \exp\left(\frac{h \cdot c \cdot \tilde{v}_0}{k_B \cdot T}\right)\right] \cdot \left[1 - \exp\left(\frac{h \cdot c \cdot \tilde{v}_0}{k_B \cdot T_0}\right)\right]^{-1} . \qquad (5)$$

Here *j* is related to the molecular structure, *h* is the Planck constant and *c* the speed of light whereas *E* denotes the ground state energy of the desired transition, that is tabulated in [3]. For $CO_2$ in the 2-μm combination band and the R(12) line centered at $\tilde{v}_0 = 4987.31$ cm$^{-1}$, the temperature dependence of $S_T$ can be described by $j = 1.25$ being in accordance with the temperature dependence of [3]. For that specific transition the line strength at 296 K has also been published in [7] as

$$S = (1.255 \pm 0.012) \cdot 10^{-21} \text{ cm/molec ,}$$

with the expanded uncertainty given for the coverage factor k = 2.  However, for the same $CO_2$ line another published figure is [8]

$$S = (1.2379 \pm 0.0014) \cdot 10^{-21} \text{ cm/molec .}$$

The ground state energy can be found in [3] as $E = 60.8709 \text{ cm}^{-1}$.

*Isotopologic composition $r_{iso}$:*

Typically, the demand in gas analysis is to report the measured amount of substance fraction of the desired species no matter which isotopologue abundance was present in the gas mixture under test. However, since *TILSAM* is based on a single molecular transition, it is isotopologue-selective. Measuring the spectrometric response of the gas mixture first gives a result based on one single isotopologue. In order to answer the typical question in gas analysis, line strengths are not given isotopologue-pure but for a certain abundance ($x_{iCO2,norm} \leq 1$) of the respective probed isotopologue.

In reality, for a given gas mixture, the present abundance of the probed isotopologue $x_{iCO2}$ may differ from the norm-abundance.Thereby, generally one has to correct for any given gas mixture by applying the isotopologic composition factor $r_{iso}$ .

In principle the isotopologic composition of the measured species ($CO_2$) in the present gas mixture has to be known or to be measured independently. However, in practice in many cases the latter will not be feasible. So, if or since $r_{iso}$ is not known exactly, its lack of knowledge has to be incorporated into the uncertainty budget. Taking $r_{iso} = 1$, its uncertainty has to cover the fact that it is not measured.


## 6.    Raw Data, Processing, and Data Retrieval

Raw data for the different experimental stages are given by the measured detector signals $I$ and $I_{offset}$ respectively. From the measured $I$ and $I_{offset}$ the different spectrometric quantities have to be processed. The order of the different experimental stages is specified in an independent measurement protocol document or is recommended as follows:

   a)  supporting measurement: establishing the wavenumber axis
   b)  supporting measurement: establishing $\tau$-1 and $\tau$-0
   c)  analytical measurement: measuring $\phi_0(\tilde{v})$ and $\phi(\tilde{v})$ for a preset $\Gamma$
   d)  analytical measurement: measuring $\phi_0(\tilde{v})$ and $\phi(\tilde{v})$ for a varied $\Gamma$
   e)  control measurement: establishing $\tau$-1 and $\tau$-0
   f)  control measurement: establishing the wavenumber axis

Single measurements may comprise multiple laser sweeps. In order to provide some statistics each analytical measurement should be performed under repeatability conditions at least ten times.

For each measurement the raw data processing $\varphi$ has to be applied providing the transformation from detector signals $I(\zeta)$, $I_{\text{offset}}(\zeta)$ via $\phi_0(\tilde{\nu})$ and $\phi(\tilde{\nu})$ towards $A(\tilde{\nu})$:

$$\phi_0(\tilde{\nu}) = \varphi(I(\zeta), I_{\text{offset}}(\zeta)) \text{ and } \phi(\tilde{\nu}) = \varphi(I(\zeta), I_{\text{offset}}(\zeta)) \,,$$

where the transfer from the measurement units for the laser sweep $\zeta$ into the desired wavenumber units is provided by the sweep rate function $r_{\text{sweep}}$ established and confirmed by the experimental stages a) and f):

$$\tilde{\nu} = r_{\text{sweep}}\left(\zeta\right) \,.$$

Here, it shall be noted that there are also experimental approaches where $\phi_0(\tilde{\nu})$ is not explicitly measured but derived from the wings of the measurement of $\phi(\tilde{\nu})$ by means of a fit. In addition, the methods to measure $\phi_0(\tilde{\nu})$ differ. A one channel regime will have to apply sequential measurements of $\phi_0(\tilde{\nu})$ and $\phi(\tilde{\nu})$, whereas a two or even more channel regime allows for simultaneous $\phi_0(\tilde{\nu})$ and $\phi(\tilde{\nu})$ measurements. None of these approaches shall be preferred by this document.

Assuming that the detectors are linear, the simplest case in a *TILSAM* instrumentation is where $I_{\text{offset}}$ is zero or negligible, $I(\zeta)$ is linear in the range defined by the signal levels for $\tau$-1 and $\tau$-0, and where $\varphi$ and $r_{\text{sweep}}$ are given by constant factors $\varphi^0$ and $r^0_{\text{sweep}}$, respectively. Then

$$\phi(\tilde{\nu}) = \varphi^0 \cdot I(r^0_{\text{sweep}} \cdot \zeta)$$

applies, and the same is true for $\phi_0(\tilde{\nu})$ with the same values for $\varphi^0$, $r^0_{\text{sweep}}$. In more complex systems this transformation can be different, e.g. where $I_{\text{offset}}$ has to be subtracted from $I(\zeta)$ or where some linearization correction has to be applied to the detector signals.

Finally the data processing has to evaluate the natural absorbance $A(\tilde{\nu})$, and in turn, the absorbance peak area $A_{\text{line}}$.

The latter action is crucial. More than one approach exists. Either a fit to $A(\tilde{\nu})$ can be applied by means of an appropriate line profile function $g^*(\tilde{\nu} - \tilde{\nu}_0)$ or a direct numerical integration of $A(\tilde{\nu})$ can be performed. From $g^*(\tilde{\nu} - \tilde{\nu}_0)$ the free fitting parameter *area* is derived and taken as $A_{\text{line}}$. Depending on the pressure $p$, $g^*(\tilde{\nu} - \tilde{\nu}_0)$ can be described by a Lorentzian, a Gaussian or a Voigt profile. In some cases, other line profiles, like Galatry or Rautian, may describe the spectral feature better with respect to reduced uncertainties [4],[8],[9] The Gaussian or so called Doppler line width $\Delta\tilde{\nu}_{\text{G}}$ can be kept fixed for the line fitting according to the measured gas temperature $T$ and the well-known relation between temperature and Doppler broadening [10][6]. However, even though the line width, i.e. the Lorentzian line width $\Delta\tilde{\nu}_{\text{L}}$, may serve as a quality check by plotting it versus $p$, the line width is not that

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[6] Here the question may arise of which mass determines the Doppler width, the molar mass of a isotopologue mixture of normal abundances and unknown composition or the mass of the probed isotopologue.

demanding at all. Therefore also the direct numerical integration approach has its benefits, e.g. no assumption of any certain line profile has to be made. Examples of that can be found in [11, 12]. In both approaches care has to be taken that the integration or the fit, respectively, is being performed on a sufficiently large spectral window with respect to the absorbance line width $\Delta \tilde{\nu}$ .

Once $A_{line}$ has been evaluated, the retrieval of the final result $x_{CO2}$ can be accomplished. By modifying equation (4) according to section 5, the model equation for an individual amount fraction measurement reads

$$x_{CO2} = \frac{k_B \cdot T}{r_{iso} \cdot S_T \cdot p \cdot L} \cdot A_{line} = \Gamma^{-1} \cdot A_{line} \qquad\qquad . \qquad (6)$$

For statistical reasons the retrieval of $x_{CO2}$ should be based on more than one measurement. Applying (6) and averaging individual measurements carried out under repeatability conditions or for varied experimental conditions $\Gamma$, e.g. varying $p$, $T$, or $L$, the final result is given as the mean of $N$ individual $x^i_{CO2}$ as

$$\bar{x}_{CO2} = \frac{1}{N} \cdot \sum_i^N x^i_{CO2} \qquad\qquad (7)$$

together with its respective standard deviation of the mean $s(\bar{x}_{CO2})$.

In addition to that, an alternative retrieval approach is based on the linear model given by reading (6) as

$$A_{line}(\Gamma) = x_{CO2} \cdot \Gamma \qquad\qquad (8)$$

and analysing the individually measured experimental $A_{line}$ values versus their respective $\Gamma$ figures by means of an appropriate linear regression type[7]. Through this, the final result of a measured data set can be reported from the slope of the regression line as *slope-evaluated amount fraction $x_{CO2}$*.

It should be noted that the slope-evaluated $x_{CO2}$ depends on the type of the regression model. Generally, its mathematical expression is different from (7), which may lead to two different amount fraction values for the same data set. However, both results have to be compared in awareness of their respective uncertainties[8].

The benefit of the linear model retrieval approach (8) is seen in the possibility of identifying hidden measurement errors. The model predicts a linear regression through the origin. For a free linear regression analysis, a resulting intercept that is not negligible compared to its own

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[7] There is an ongoing discussion in the literature on linear analysis/regression models (see [13. R. Willink, Metrologia **45**, 290 (2008)] and references therein.
[8] For this comparison the uncertainties may be based exclusively on statistics.

uncertainty, indicates some problems with the measurement. In that case it is recommended to report an analysis result containing three expressions:

i) the mean of the individual measurements $\overline{x}_{CO2}$
ii) the slope-evaluated $x_{CO2}$ together with the value and its uncertainty of the intercept
iii) the slope-evaluated $x_{CO2}$ given by a regression forced through the origin.


## 7. Uncertainty Estimation

The uncertainty figure $U(x_{CO2})$ and its respective budget for the final result of the measured amount fraction has to be GUM-compliant [14] or, at least GUM-based[9]. To make *TILSAM* results really traceable, all influence quantities have to be traceable. However, relying on quantities that have been taken from data bases, e.g. figures for $E$ and $\tilde{v}_0$ are needed in (5) to convert $S$ to $S_T$, traceability is not always provided. Nevertheless, this should be a very rare exception.

One open question is the best approach to estimate the uncertainty for $A_{line}$. Given the fact that there are some quite different methods to evaluate $A_{line}$, this document cannot provide a general recommendation for its uncertainty estimation. Generally speaking, the challenging task is to evaluate $A_{line}$ with uncertainties in both dimensions, i.e., the absorbance axis *and* the wavenumber axis. This gives rise to a certain correlation.

It should be noted that there are even some published concepts to evaluate the uncertainty $U$ in cases where an integral quantity has been evaluated from spectral measurements, taking into account uncertainties in the x- and the y-direction [12, 15, 16].

Once the uncertainty for the integrated absorbance line area $A_{line}$ has been evaluated, the respective propagation of it and of all other influence quantities to a combined uncertainty for the amount fraction $x_{CO2}$ has to be performed according to the ISO-GUM [14]. In cases where the slope evaluation approach (eq. (8)) has been applied, the linear regression of the measured data has to consider respective uncertainties for $A_{line}$ and $\Gamma$.


## 8. Possibilities of Validation

For any realized *TILSAM* instrumentation and its performance in terms of the reliability and the uncertainty of the measurement results, a validation with gravimetrically prepared gas standards is required. This does not mean that the *TILSAM* method is not free of calibration. Instead, the quality of being free-of-calibration with reference gas standards has been proved by this. This comparison of the spectrometrically evaluated $x_{CO2}$ with the gravimetric reference $x_{CO2,grav}$ also provides a test of the uncertainty budget for $x_{CO2}$.

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[9] The ISO standard in its first formulation [14.   ISO, Guide to the Expression of Uncertainty in Measurement, 1. International Organization for Standardization, Genevepp, 9267101889 9267101889] deals exclusively with linear model functions. The line shape profile and its respective line area $A_{line}$ fitting is not linear. Supplements to [14. ISO, Guide to the Expression of Uncertainty in Measurement, 1. International Organization for Standardization, Genevepp, 9267101889 9267101889] are underway.

An instrument-internal validation of *TILSAM* measurement results can be seen in the analysis of measured line widths $\Delta\tilde{\nu}_L$ as a function of pressure *p*. A linear relation between $\Delta\tilde{\nu}_L$ and *p* is expected as predicted by the theory of collisional broadening.

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## Appendix A: Example of a *Preliminary* Uncertainty Budget for a Measurement at PTB

| | TILSAM $CO_2$ | PTB |
|---|---|---|

### TILSAM $CO_2$

data 10% CO2/N2 from 06.08.2004

- purged with N2

- New T Testo-sensor in contact with cell

- calibrated manometer

**Model Equation:**

$$S_T = S_{T_0} * (T_0/T)^{\wedge}j$$
$$* \exp(-h*c*E/k_B*(1/T - 1/T_0)) * (1 - \exp(-h*c*v_0/(k_B*T))) / (1 - \exp(-h*c*v_0/(k_B*T_0)));$$

$$r_{sweep} = FSR/FSRSP;$$

$$A_{line} = r_{sweep} * Area;$$

$$r_{iso} = x_{12CO2}/x_{12CO2HITRAN};$$

$$x_{CO2} = A_{line} * 10^{\wedge}6 * k_B * T / (S_T * r_{iso} * p_{total} * 10^{\wedge}2 * L);$$

**List of Quantities:**

| Quantity | Unit | Definition |
|---|---|---|
| Area | SP | Area under the Voigt profile |
| $p_{total}$ | hPa | Total-Pressure in Gascell |
| T | K | Temperature in Gascell |
| L | cm | Cell Pathlength |
| FSR | $cm^{-1}$ | Free spectral range (FSR) of a Si - etalon |
| FSRSP | SP | FSR of a Si - etalon in SP digitized by the acquisition card |
| $k_B$ | J/K/molecule | Boltzmann constant |
| E | $cm^{-1}$ | Lower state energy |
| c | m/s | speed of light in vacuum |
| h | Js | Planck constant |
| $T_0$ | K | Norm temperature |
| $S_{T_0}$ | cm/molecule | Line strength for norm temperature To = 296 K |
| $v_0$ | $cm^{-1}$ | line center |
| $x_{12CO2}$ | | Amount of 12C fraction of the CO2 in the sample |
| $x_{12CO2HITRAN}$ | | Conventional 12CO2 abundance value given by HITRAN |
| $r_{iso}$ | | deviation of isotopomeric abundance in experiement from conventional value (HITRAN) |
| j | | |
| $S_T$ | cm/molecule | Line strength at temperature T |

| Date: 01/21/2009 | File: TILSAM_budget_2009-01-21 | Page 1 of 6 |
|---|---|---|

| | TILSAM $CO_2$ | | | | | PTB |

**Uncertainty Budget:**

| Quantity | Value | Standard Uncertainty | Degrees of Freedom | Sensitivity Coefficient | Uncertainty Contribution | Index |
|----------|-------|---------------------|--------------------|-----------------------|-------------------------|-------|
| Area | 28.7500 SP | 0.0219 SP | 900 | $3.6 \cdot 10^{-3}$ | $79 \cdot 10^{-6}$ mol/mol | 1.0 % |
| $p_{total}$ | 100.600 hPa | 0.100 hPa | 50 | $-1.0 \cdot 10^{-3}$ | $-100 \cdot 10^{-6}$ mol/mol | 1.7 % |
| T | 295.400 K | 0.200 K | 50 | $1.1 \cdot 10^{-3}$ | $220 \cdot 10^{-6}$ mol/mol | 7.5 % |
| L | 100.000 cm | 0.115 cm | infinity | $-1.0 \cdot 10^{-3}$ | $-120 \cdot 10^{-6}$ mol/mol | 2.2 % |
| FSR | $0.0484860$ $cm^{-1}$ | $77.6 \cdot 10^{-6}$ $cm^{-1}$ | 50 | 2.1 | $160 \cdot 10^{-6}$ mol/mol | 4.3 % |
| FSRSP | 43.4870 SP | 0.0230 SP | 5 | $-2.4 \cdot 10^{-3}$ | $-55 \cdot 10^{-6}$ mol/mol | 0.5 % |
| $k_B$ | $13.8065050 \cdot 10^{-24}$ J/K/molecule | $24.0 \cdot 10^{-30}$ J/K/molecule | 50 | $7.5 \cdot 10^{21}$ | $180 \cdot 10^{-9}$ mol/mol | 0.0 % |
| E | $60.8709$ $cm^{-1}$ | | | | | |
| c | $299.792458 \cdot 10^{6}$ m/s | | | | | |
| h | $662.606930 \cdot 10^{-36}$ Js | $110 \cdot 10^{-42}$ Js | 50 | $36 \cdot 10^{27}$ | $4.0 \cdot 10^{-12}$ mol/mol | 0.0 % |
| $T_0$ | 296.0 K | | | | | |
| $S_{To}$ | $1.25490 \cdot 10^{-21}$ cm/molecule | $7.20 \cdot 10^{-24}$ cm/molecule | 50 | $-82 \cdot 10^{18}$ | $-590 \cdot 10^{-6}$ mol/mol | 55.1 % |
| $\nu_0$ | $4987.30870$ $cm^{-1}$ | $4.00 \cdot 10^{-3}$ $cm^{-1}$ | 50 | 0.0 | 0.0 mol/mol | 0.0 % |
| $x_{12CO2}$ | 0.98420 | $4.00 \cdot 10^{-3}$ | 50 | -0.10 | $-420 \cdot 10^{-6}$ mol/mol | 27.6 % |
| $x_{12CO2HITRAN}$ | 0.9842 | | | | | |
| $r_{iso}$ | 1.00000 | $4.06 \cdot 10^{-3}$ | | | | |
| j | 1.250 | 0.144 | infinity | $-210 \cdot 10^{-6}$ | $-30 \cdot 10^{-6}$ mol/mol | 0.1 % |
| $S_T$ | $1.26034 \cdot 10^{-21}$ cm/molecule | $7.47 \cdot 10^{-24}$ cm/molecule | | | | |
| $r_{sweep}$ | $1.11495 \cdot 10^{-3}$ $cm^{-1}$/SP | $1.88 \cdot 10^{-6}$ $cm^{-1}$/SP | | | | |

| Date: 01/21/2009 | File: TILSAM_budget_2009-01-21 | Page 5 of 6 |

| | TILSAM $CO_2$ | | | | | PTB |
|---|---|---|---|---|---|---|
| **Quantity** | **Value** | **Standard Uncertainty** | **Degrees of Freedom** | **Sensitivity Coefficient** | **Uncertainty Contribution** | **Index** |
| $A_{line}$ | 0.0320549 $cm^{-1}$ | $59.3 \cdot 10^{-6}$ $cm^{-1}$ | | | | |
| $x_{CO2}$ | 0.10311 mol/mol | $797 \cdot 10^{-6}$ mol/mol | 130 | | | |

**Result:**      Quantity: $x_{CO2}$
                 Value: 0.1031 mol/mol
                 Relative Expanded Uncertainty: ±1.5 %
                 Coverage Factor: 2.0
                 Coverage: t-table 95%

| Date: 01/21/2009 | File: TILSAM_budget_2009-01-21 | Page 6 of 6 |
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