Typical uncertainty of dTDLAS measurements

A 4.1.14

Jan 2020

Typical uncertainty of dTDLAS measurements

16ENV08 JRP protocol: A4.1.14 'A guidance document will be launched describing the typical uncertainty of dTDLAS measurements (Task 1.4). ….'

In IMPRESS 2 project, PTB (AG3.42) task is to test HCl monitoring optical spectrometer for the future underpinning of technique development. PTB validates the dTDLAS method in absorption cells and investigate the influence of heterogeneous effects on amount fraction measurements. This document focuses on describing the typical uncertainty of dTDLAS measurements.

1. Direct tunable diode laser absorption spectroscopy (dTDLAS)

In dTDLAS, the wavelength λ of a tunable laser is rapidly scanned across a narrow region of the optical spectrum covering one or several absorption lines. The intensity of the light, $I(\lambda)$, impinging on a photodetector after passing a sample with absorbers can be described by Lambert-Beer equation according to

$$I(\lambda) = E(t) + I_0(\lambda) \cdot Tr(t) \cdot \exp[\alpha(\lambda)], \tag{1}$$

$$\alpha(\lambda) = S(T) \cdot g(\lambda - \lambda_0) \cdot N \cdot L, \tag{2}$$

with $\alpha(\lambda)$ the absorbance at wavelength λ, the background emission $E(t)$ at time t, initial laser intensity $I_0(\lambda)$, and the broadband transmission losses $Tr(t)$ which are synchronously derived from the individual raw signals and absorption profiles. For the application in a stack it is important to correct for any changes in the effective transmission of the complete light path between laser and detector. These changes can be caused by the quickly fluctuating dust load of the flue gases, optical window degradation by dust, heat, or chemical effects, vibrations, and thermal lensing effects. The exponential term embraces the absorption line strength $S(T)$ at gas temperature T, the normalised (area=1) line shape function $g(\lambda - \lambda_0)$ (centred at the wavelength λ_0), the absorber number density N and the optical

path *L*. Molecular line data e.g. absorption line strength and its temperature dependence, self or foreign broadening coefficients can be obtained from the HITRAN database or our own dedicated measurements.

By combining Eq(1) and the ideal gas law, the gas amount fraction amount fraction $x_{species}$ is

$$x_{species} = \frac{k_B \cdot T}{S(T) \cdot r_{iso} \cdot L \cdot p_{total}} \int \ln(\frac{I(\lambda) - E(t)}{I_0(\lambda) \cdot Tr(t)}) \frac{d\lambda}{dt} dt = \frac{k_B \cdot T \cdot A_{line}}{S(T) \cdot r_{iso} \cdot L \cdot p_{total}},\qquad(3)$$

where k_B is the Boltzmann constant, p_{total} is the total pressure of the gas sample, r_{iso} is a correction factor for the isotopic composition in the gas sample, and A_{line} is the line area determined by spectral integration of the measured absorption line over the wavenumber axis. $d\lambda/dt$ describes the dynamic wavelength tuning coefficient of the laser, which has to be determined experimentally.

A typical experimental schematic of dTDLAS measurements is shown in Figure 1: Principal of a TDLAS setupFigure 1. The laser driver, which includes temperature and current controllers, drives the diode laser. A function generator is used to scan the laser injection current and thus tune the wavelength of the laser across the desired absorption features.
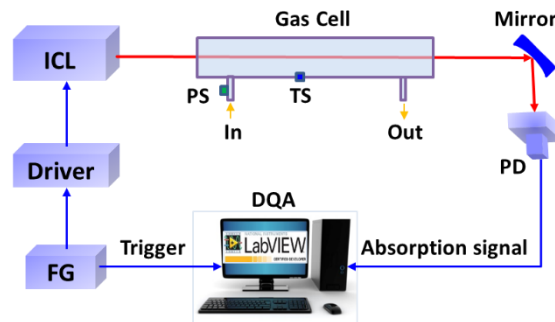

Figure 1: Principal of a TDLAS setup, PS-pressure sensor, TS-temperature sensor, PD-photodetector, FG-function generator, DQA-data acquisition card.

2. Uncertainty of adTDLAS measurement

The general rules of calculating uncertainty are summarized in an ISO standard (Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement (GUM)). This means that following the GUM would ensure reliability and comparability of the measurement results, based on transparently and reproducibly derived measurement uncertainties. Expanded uncertainty is calculated from standard uncertainty "uncertainty of the result of a measurement expressed as a standard deviation" by multiplying it with the so-called coverage factor (*k*), typically in the range of 2 to 3, depending on the type of distribution and the confidence interval. Here we give expanded uncertainties, which refer to a confidence interval of 95 %, and *k* = 2.

In dTDLAS, absolute spectrometric gas amount fraction measurements as shown in Eq(3) include measurements of gas sample properties (e.g. temperature and pressure) and requires the independent measurement of some other quantities, such as optical path length (interaction path length of laser beam with gas sample), line area which based on laser tuning behavior.

First, we discusses the individual input quantities in Eq.(3) and estimate expanded uncertainties (k = 2). The gas temperature T is measured independently with a sensor placed in the measurement volume, such as PT100 or thermal couple. For example, temperature in the range of 290 – 300 K, the expanded uncertainty of the measured values was 0.5 K (relative uncertainty 0.17 %). The uncertainty originates from the calibration uncertainty, the resistance/ measurements, as well as long-term stability of the sensors.

The gas pressure p_{total} is measured with a pressure sensor - capacitance diaphragm gauges. Uncertainty of pressure is determined by taking into account the calibration uncertainty, and long-term stability of the sensor. In our case (gas cell in Laboratory), the pressure uncertainty is found to be about relative uncertainty 0.2 % (2 mbar at 1000 mbar).

Similarly, the path length L can be determined using e.g. mechanical measurements or interferometry. The uncertainty of the path length result depends on the measurement method. Here for our Brewster angle cell, we used the results of mechanical measurements, which yielded a path length of 774 mm with an expanded uncertainty of 2 mm, corresponding to 0.26 % relative uncertainty (including uncertainty contribution from imperfect alignment, i.e., the light beam being unparallel to the symmetry axis of the cell).

Line parameters such as the line strength $S(T)$ of a probed species absorption line can be measured in separate experiments or taken from spectroscopy databases, e.g. HITRAN. The line strength of the probed transition is the most important influence parameter. Its temperature dependence expressed by means of an exponent j is important for amount fraction measurements at gas temperatures different from 296 K. For example, the line strength uncertainty of the HCl transition line we used in IMPRESS2 project is in the range of 2 - 4 % (k = 2) from literature and HITRAN database.

In dTDLAS amount fraction measurements, a single absorption line from an isotopologue is probed but the amount fraction is reported for the sum of all isotopologues of this gas species. Line strength values for isotopologue absorption lines in HITRAN, are not reported for the pure isotopologue, but for a certain "natural" conventional abundance value. For a gas sample, the abundance of the probed isotopologue could differ from this conventional value at which the line strength value was reported. Therefore, $r_{iso} = x_{iso,sample}/x_{iso,convention}$ is introduced to correct for this deviation. If r_{iso} is unknown and no other sample information is available, it is computed from assumptions on the conventional value while its uncertainty is conservatively estimated using information on natural isotopic composition of elements.

The line area A_{line} is determined by fitting a Voigt profile to the measured absorbance spectrum. This gives a value with an associated uncertainty based on the line fitting residual. Another contribution to the line area uncertainty is wavenumber axis - the dynamic laser tuning coefficient which is determined separately. Normally, the wavenumber axis is generated from the Fabry-Perot etalon measurement. Results of this measurement are used to convert the x-axis of the measured spectra from the time domain to wavenumbers. Another common source of uncertainty of the line area might be detector nonlinearity - a nonlinear relation between light intensity and the measured detector signal.

As an example from Ref [4], table 1 summarizes the expended uncertainty for each input parameter in Eq(3). Considering the uncertainty contributions described above, these components yield 2.2 % uncertainty for amount fraction measurements. The line strength has 1.3% expended uncertainty. It is

concluded that the uncertainty of the line strength of the probed transition delivers the second largest contribution to the amount fraction uncertainty, while the most significant contributor is the uncertainty of the line area A_{line}. The listed uncertainty components in Table 1 are not of statistical origin and originate from sources, which cannot be suppressed by averaging results of multiple measurement sequences.

Table 1: Typical uncertainty budget for the amount fraction measurements. [4]

Uncertainty component	Value	Relative expanded uncertainty (%)	Relative contribution to the uncertainty of the amount fraction (%)
p	200 hPa	0.24	1.22
T	296.4 K	0.16	0.54
L	76.643 m	0.05	0.05
S_0	1.981×10^{-20} cm/molecule	1.3	35.82
A_{line}	3.392×10^{-3} cm^{-1}	1.7	61.26
K_T	0.998	0.21	0.94
r_{iso}	1	0.09	0.17
x	100.72 µmol/mol	2.2	

3. Uncertainty from other sources

In section 2, we discussed the typical uncertainty of dTDALS amount fraction measurements, which are done with a gas cell in a well-controlled environment- laboratory. Here we give a brief discussion on the uncertainties which come from other sources when using dTDALS in other environment, for instance, cross-stack monitoring, combustion diagnostics. In field applications, the dTDLAS spectrometer normally works with a so-called open-path configuration, which means that the laser light is not directed through a confined measurement cell which is flushed with a sample of gas flow, but directed directly through gas flow, either by using a retro-reflector, or through separation of a laser and a detector module. The spectral evaluation for an open-path system suffers from several drawbacks: The gas properties are less well defined than in a closed measurement cell (less stable and less homogeneous), and spectral measurements have to be done at ambient pressure. The latter causes a poorer separation of absorption lines through pressure-broadening (larger line width of absorption lines), which in turn may lead to stronger cross-interference. The choice of the probed absorption line of a TDLAS spectrometer is of central importance, because this choice greatly affects how much measurements may be perturbed by cross-interference, and how strong changes in pressure and temperature of the probed gas sample will affect the measurement signal. The temperature and pressure measurements uncertainty budgets shown in Table 1 can be much worse than 0.2 % for hot flue gases, e.g. > 2 %. If so, the temperature and pressure uncertainties dominate the results, rather than spectroscopic data. Along the laser path, e.g. cross the stack, the distributions of temperature, species compositions might be heterogeneous. This will also increase the measurement uncertainty as Eq. (3) is based on homogeneous gas conditions.

4. References

[1] International Organization for Standardization. Guide to the Expression of Uncertainty in Measurement. 1. ISO Guide 98-3 2008, ISBN 9267101889.

[2] International Organization for Standardization. Supplement 1 to the Guide to the Expression of Uncertainty in Measurement: Propagation of distributions using a Monte Carlo method. ISO Guide 98-3 Supplement 1.

[3] Andrea Pogány, Oliver Ott, Olav Werhahn, and Volker Ebert. "Towards traceability in CO2 line strength measurements by TDLAS at 2.7 μm." *Journal of Quantitative Spectroscopy and Radiative Transfer* 130 (2013): 147-157.

[4] Andrea Pogány, Steven Wagner, Olav Werhahn, and Volker Ebert. "Development and metrological characterization of a tunable diode laser absorption spectroscopy (TDLAS) spectrometer for simultaneous absolute measurement of carbon dioxide and water vapor." *Applied spectroscopy* 69, no. 2 (2015): 257-268.

[5] Javis A. Nwaboh, Zhechao Qu, Olav Werhahn, and Volker Ebert. "Interband cascade laser-based optical transfer standard for atmospheric carbon monoxide measurements." *Applied optics* 56, no. 11 (2017): E84-E93.

[6] Zhechao Qu, Olav Werhahn, and Volker Ebert. "Thermal Boundary Layer Effects on Line-of-Sight Tunable Diode Laser Absorption Spectroscopy (TDLAS) Gas Concentration Measurements." *Applied spectroscopy* 72, no. 6 (2018): 853-862.