Gas sensing in industry by tunable diode laser spectroscopy (TDLS)

Review on state-of-the-art metrology for demanding species concentration, temperature and pressure measurement tasks

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Preface

Dear Reader,

Gas sensing has been an important issue since the existence of mankind. Before highly efficient sensors have been developed gas sensing was done with the human sense of smell which is still very important. The human sense of smell can detect NH\textsubscript{3} and warns from its inhalation. However there are strict limitations to the human nose, e.g. CO cannot be sensed and is a very harmful gas formed during combustion.

In industry gas sensing is an important issue in order to protect from harmful gaseous species and of the same importance to optimize the production process. Tunable diode laser sensors can be used for fast in-situ measurements, inside the production process. Therefore almost instantaneous feedback of important process operating parameters (e.g. species concentration) is given and the process control system can react accordingly. This fast response saves significant amounts of material and energy which is especially important when energy costs increase dramatically and resources are tight.

The importance of tunable diode laser spectroscopy (TDLS) has increased significantly due to its increase in robustness and availability of high quality laser diodes. Tunable diode lasers are versatile tools and already new and extended methods and diodes (e.g. MEMS-tunable VCSELs) are in development and will find their way to application.

Finally, I want to thank my dear friend and colleague Dr. Maximilian Lackner for giving such a comprehensive overview of tunable diode laser spectroscopy from its background to its various applications ranging from the steel making industry to power plants and pharmaceutical industry.

TDLS is a very versatile tool and has a very high potential for process optimization and production safety. I look very much forward to see its increasing application in industry.

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1 Introduction

In the process industries, accurate and reliable measurements of numerous parameters are vital for optimum plant performance. Often, these measurements have to be carried out in harsh environments. Therefore, rugged, robust sensors are needed. Besides temperatures, pressures and flow, species concentrations are often relevant parameters, but they cannot always be measured easily. Optical methods have the inherent advantage of operating in contact-less mode. Several of them work in-situ, thereby yielding timely results without interfering with the system under investigation. An optical method for industrial applications is tunable diode laser absorption spectroscopy (TDLAS). TDLAS is the most common variant of tunable diode laser spectroscopy (TDLS). The focus of this book lies in TDLAS with reference to derived techniques.

By TDLAS, multiple gas flow properties can be measured: These are species concentrations, temperature, pressure and velocity, and derived there from, flux and residence time distribution.

Absorption spectroscopy using diode lasers has been used for measuring gas temperatures and concentrations for at least 25 years [1] - [2]. Recently, with increasing maturity and broader availability of laser light sources and peripheral electro-optical components, TDLAS has found use in numerous applications in industrial process plants. It is assumed that 5-10% of all infrared-based gas sensors that are sold every year are already based on TDLAS [3] - [4], showing that TDLAS has matured [5] and become an established technique [6] which, for several key applications as outlined in this book, has been accepted as the best available technology [7].

This book presents the principles and possibilities of TDLAS and highlights several applications in the process industries with other industries being touched upon. The focus is on the measurement of flow properties in gases.

Additional introductory and review articles on TDLAS can be found in [8] - [14] and [342]. Textbooks on laser spectroscopy are [367] - [369]. Lasers in chemistry are covered in [341]. The intention of this book is to provide the reader with an updated overview on TDLAS in industrial applications. How this book is structured: In the first section, the principles of the technology are reviewed, covering aspects of detection limits, laser sources and advanced detection techniques. Related technologies are presented alongside a comparison of TDLAS to conventional techniques. The main part of the book is dedicated to applications of TDLAS in the process industries. After general remarks, the measurement of important species such as O₂, HCl, CH₄, H₂O, NH₃, HF, alkali atoms and temperature is reviewed besides a section on handheld and open path applications. Then, several industries are addressed, ranging from steel and aluminium production to the semiconductor, pharmaceutical, automotive, petrochemical and other industries. Finally, an outlook on TDLS-based gas sensing for industrial applications is presented in this book.
Lasers bear certain risks, therefore it is of utmost importance to familiarize oneself with the device before starting to use it. This is equally valid for equipment in the lab and off-the-shelf industrial sensors, some of which are completely eye safe, but others are not. For the user of commercial equipment, handbooks dealing with safety aspects are available from the manufacturers. Also, most instruments will have appropriate provisions and interlocks against wrong use. Scientists and developers who operate with new lasers need to pay very close attention to safety hazards that they might be exposed to. For a textbook on laser safety, see e.g. [375].
2 Principles of TDLS

2.1 General

Spectral analysis was developed by R.W. Bunsen and G.R. Kirchhoff in the middle of the 19th century \cite{15}. Many important gases show absorption in the infrared spectral region. Fig. 1 shows the corresponding absorption bands in the near infrared (NIR) and mid infrared (MIR).

![Absorption lines of CO\(_2\), CO, H\(_2\)O, HCl, CH\(_4\) and NH\(_3\) in the infrared. Data for CO\(_2\), CO and CH\(_4\) are taken from the spectroscopic database GEISA \cite{16}, data for H\(_2\)O, HCl and NH\(_3\) are taken from the spectroscopic database HITRAN \cite{17}.](image_url)

The absorption lines in gases are narrow so that by using a highly monochromatic light source, isolated peaks can be probed individually, see an example of isolated N\(_2\)O lines in the presence of H\(_2\)O and CO\(_2\) in Fig. 2.
Fig. 2: Because of their narrow line width, absorption lines can be accessed individually. Which lines can be used for spectroscopy depends on gas concentrations, temperature and pressure, as not all lines are interference-free. The marked N₂O line can be probed without disturbing interference from CO₂ and H₂O.

The absorption spectra in the NIR contain lines in several overtone and combination bands. There are, for instance, > 50,000 transitions at 1000 K for H₂O between 1 and 2 μm [18]. Those are tabulated in spectral databases such as HITRAN [17] or GEISA [16]. The molecules are rovibrationally excited in the mid infrared spectral region (2.5-30 μm); Rovibrationally means that rotations and vibrations of the molecules are induced as they absorb the laser light. In the near IR (0.8-2.5 μm), overtone and combination bands are situated. From Fig. 1 it can be seen that the fundamental bands in the MIR are stronger than the overtone and combination bands in the NIR, compare e.g. the bands for water or carbon dioxide as they decrease in strength as the wavelength decreases.

As outlined in this book, the laser sources in the MIR are rather difficult to operate, they mostly require cryogenic (liquid nitrogen) cooling for cw (continuous wave) operation. Room-temperature operated diode lasers in the near infrared spectral region are therefore much more commonly used. However, a higher measurement sensitivity of the sensor is needed because the transitions are weaker (compare Fig. 1). By looking up the position of absorption lines in spectral databases such as HITRAN [17] or GEISA [16], absorption lines that are isolated can be selected for interference-free measurements. Note, however, that although an absorption line is separated from absorption lines of other gases that are present, it is not truly unperturbed by the other gases in the measurement volume because of influences on the line shape (broadening effects, see later).

For small molecules, the absorption bands are composed of individual lines, which can be investigated by spectroscopic techniques. Species with more than four atoms generally have complex rovibrational spectra where the assignment of individual spectral lines is not possible any more, except under certain experimental conditions such as extreme cooling or Doppler-free diagnostics. In tunable diode laser absorption spectroscopy, individual absorption lines as depicted in Fig. 1 are probed.

To this end, a diode laser with an emission frequency (wavelength) matched to a suitable absorption line is used. The experimental setup, which essentially consists of the laser and the detector with a probed absorption volume in between, is simple and is depicted in Fig. 3. I₀ is the initial light intensity (before the sample, also called the baseline), and I is the penetrated light intensity (after the sample).
A diode laser is a handy light source for spectroscopists because it is compact, rugged, room-temperature operated and offers bright, monochromatic light. The diode lasers that are used in TDLAS can be tuned in their emission wavelength. This wavelength-tuning or wavelength-scanning is done by altering temperature or injection current of the laser. The laser wavelength \( \lambda \) [\( \mu \text{m} \)] can also be expressed as a frequency \( \nu \) [\( \text{cm}^{-1} \)]. \( \lambda \) is easily converted into \( \nu \) by \( \nu = \frac{1}{\lambda} \). Wave numbers [\( \text{cm}^{-1} \)] are frequently used by spectroscopists because they are directly proportional to the energy.

In TDLAS, the laser wavelength is scanned over the entire absorption peak in order to record the full spectral feature. This is illustrated in the following Fig. 4.

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**Fig. 3:** Experimental setup for TDLAS. 1: Monochromatic light source; 2: sample volume; 3: detector; \( I_0 \) is the initial light intensity (also termed the baseline) and \( I \) the transmitted light intensity.

**Fig. 4:** Pressure broadening and shift of an HF absorption line by Ar gas. Reprinted from [25] with permission from Elsevier.
Diode lasers can be wavelength-tuned in a narrow range by either varying the temperature [K] or the drive current [mA]. Usually, the temperature is adjusted so that the laser wavelength coincides with the wavelength of the transition of the target molecule. It is then fixed to typically +/- 1 mK. The drive current is modulated. In Fig. 4, a linearly rising ramp is used as drive current modulation. Temperature control can be done thermoelectrically by a Peltier element. This modulation causes a continuous and repetitive change in the laser wavelength.

It has proven convenient to apply a linearly rising current ramp to the laser as shown in Fig. 4 (a) (dotted line). As soon as the threshold current at the given temperature is reached, the device starts lasing. The output power ($I_0$), termed “baseline” in Fig. 4, then scales approximately linearly with current. At the same time, the emission wavelength shifts. As the current increases, the laser wavelength increases. In Fig. 4 (b), an absorption peak can be seen as a dip on the transmitted light intensity ($I$), termed “signal” in Fig. 4, at the resonance frequency $\nu$ (resonance wavelength $\lambda$). In Fig. 4 (c), the absorbance $\alpha(\nu)$ has been plotted. The absorbance $\alpha(\nu)$ is derived from the ratio of initial and transmitted laser light intensity. It is defined as follows (equation 1):

$$\alpha(\nu) = \ln(I_0(\nu)/I(\nu))$$

**Equation 1**

Equation 1 is called Lambert-Beer’s law. The line integrated absorbance is directly proportional to the number density of the absorbing species between laser and detector (number density = concentration x path length). The width of the absorption peak is determined by the ambient temperature and pressure, the area and the height of the peak, expressed as absorbance, by the number density of the absorbing species. The width is also influenced by the composition of the gas matrix via the species dependent pressure broadening coefficient.

The absorption is defined as $A = I/I_0$, the transmittance $T$ as $T = 1 - A$. In contrast to the absorbance $\alpha$, the absorption $A$ is not directly proportional to the number density of the gas under investigation.

It has proven advantageous to work with absorption values between 1 and 50%, corresponding to 99-50% transmission, although signal evaluation is typically possible even with less than 1% of laser light transmission, which can occur in particle-laden gas flows. Instead of using the peak height, one can also determine the area of the absorption peak, which, in contrast to the maximum peak height, is independent from broadening mechanisms. The above-given relation of Lambert Beer can be further refined;

The absorbance is linearly proportional to the mole fraction $x_i$ of species $i$ with $n_i$ overlapping absorption lines as described by equation 2:

$$a(n) = P x_i * \sum_{j=1}^{n_i} S_{i,j}(T) * f_{i,j}(n-n_0, i, j, \alpha_i, j)$$

**Equation 2**

In equation 2, $P$ is the total pressure [atm], $l$ the path length [cm], $S_{i,j}$ the temperature-dependent line strength [atm$^{-1}$*cm$^{-1}$] of line $j$ and species $i$ and $\phi$ the line shape function [cm] [19] - [20]. For details, the reader is referred to [17], [19] - [20].
The line shape function $\phi(\nu)$ is normalized according to equation 3 (see [21] for a description):

$$\int_{-\infty}^{\infty} f(n)dn = 1$$

**Equation 3**

$\phi(\nu)$ describes the broadening of the lines by thermal motion (Doppler broadening) and by intermolecular collisions (collisional or pressure broadening). Doppler broadening is caused by the motion of the gas molecules, pressure broadening is caused by perturbation of the gas molecules.

At low pressures, typically below 0.1 bar, the line shapes are best described by a Gaussian function. The contribution of the natural line width in the NIR and MIR is insignificant. At moderate pressures at around ambient, the line shape is a convolution of Doppler [19] and collisional contributions, which is described by a Voigt [22] profile. At high pressures, the line shape can be described by a purely Lorentzian function. The molecular line shape is a convolution of Gaussian and Lorentzian components, which can be described by a Voigt profile. If collisional narrowing effects (Dicke narrowing) have to be taken into account, the Galatry [23] and the Rautian [24] profiles are more suitable. The Voigt profile, which can be computed easily, is often used for modelling at around ambient pressure, where it yields adequate results. The observed line shape also includes instrument broadening due to the finite laser line width. More information on this can be found in [25]. The instrument response function and its minimization are discussed in [26].

The following Fig. 5 shows an example for spectral line broadening [343] and shifting.

![Fig. 5: Recording of an individual absorption line. (a) shows the current ramp applied to the laser and the baseline ($I_0$), (b) gives the transmitted signal ($I$). In (c), the absorbance $\alpha = \ln(I_0/\nu)$ is shown.](image)

The speed (frequency) of the current ramps applied to the laser determines the time resolution of the absorption spectroscopic measurements (compare Fig. 4). If the ramps are applied at 1 kHz, the time resolution will be 1 ms, provided that no spectra are averaged.
Signal $I$ and baseline $I_0$ can be recorded simultaneously (using a beam splitter), but also consecutively. It is also possible to determine the baseline mathematically by applying a fitting procedure. The following Fig. 6 illustrates the need for recording the absorbance not only at the centre of the absorption peak, but also in the wings where no resonant absorption occurs (\(\equiv\) tuning of the wave length).

**Fig. 6:** TDLAS without (a) and with (b) interferences. The absorbance $\alpha(\nu)$ in (c) and (d) is the same. Non-specific attenuation and the offset can be removed by scanning over the entire absorption feature (here: double peak). The wavelength scan of the line is achieved by tuning the laser current (temperature held constant). Reprinted from [27] with permission from Elsevier.

In Fig. 6, a TDLAS measurement on a double peak is shown. In the left frame (a), there are no interferences. One can see the baseline $I_0$ (no absorption by the target species) and the transmitted signal $I$. In (c) the derived absorbance $\alpha(\nu)$ is shown. The right frame in Fig. 6 (b) incorporates several interferences, everything else left equal. Fig. 6 (a) constitutes an ideal laboratory measurement, Fig. 6 (b) is representative of a real-world application like in a furnace or chimney. Compared to Fig. 6 (a), the whole signal in Fig. 6 (b) has been reduced in its intensity, and has also lifted off. The reduction in intensity stems from non-specific beam attenuation. The laser light beam travelling through the sample volume might be subjected to partial blocking (e.g. by soot and ash particles passing the beam path), scattering (particles and particulates like smoke) and beam steering. In non-homogeneous media where strong temperature gradients are encountered (such as in turbulent, non-premixed flames), the laser beam will not travel along a straight path, but instead be constantly redirected by refractive index gradients. This effect is known as beam steering. The offset might stem from emissions caused by a flame, thermal radiation emitted by hot walls or luminosity of glowing soot particles.
The specific absorption of the laser light by the target molecule is extremely dependent on the wavelength (narrow peaks). The non-specific attenuation and the luminosity hitting the detector, on the other hand, are far less wavelength specific.

As stated above, $I_0$ can be calculated by fitting the far wings of the absorption peak on the transmitted intensity $I$ by e.g. a polynomial function. The absorbance trace can be converted from the time domain (as shown in Fig. 6) into the frequency or wavelength domain by using an etalon [28] or a calculated reference spectrum. An etalon consists of two parallel surfaces where interference effects lead to a periodic intensity oscillation of the transmitted light. The spacing of the peaks is determined by the free spectral range of the etalon (FSR). By counting the number of peaks, the tuning range can be determined.

The following Fig. 7 shows the data evaluation process in a TDLAS measurement in an illustrative way.

**Fig. 7**: Illustration of how the absorbance is extracted from the raw data (a). In (b), the offset was removed, in (c), the individual ramps were rescaled (removal of beam steering and similar effects). In (d), the absorbance $\alpha(\nu)$ is shown (double peak from Fig. 6). From the rising absorbance $\alpha(\nu)$ in (d), an increasing concentration of the measured species over time can be inferred. Reprinted from [27] with permission from Elsevier.

Fig. 7 shows the data evaluation in the 4 subfigures (a) – (d) where (a) represents the raw data (laser ramps + offset) as seen by the detector. In (b), the offset was removed (data processing unit). In (c), all ramps were rescaled and in (d), the extracted absorbance can be seen (data processing unit). In a final step, one has to convert the absorbance into a concentration.

It can be inferred from Fig. 7 that the frequency of the current ramp applied to the laser, i.e. the tuning speed or the duration of an individual measurement, has to be shorter than the time scale of the fluctuations. Neither the amount of light from flames or glowing soot particles hitting the photo detector nor the extent of non-specific beam attenuation by partial blocking of the beam and scattering are constant. They fluctuate strongly over time. These effects will distort the signal; To compensate these effects and to obtain undistorted absorption peaks, the tuning of the laser must be faster than these transient processes to measure under quasi-stationary conditions.

This is illustrated in Fig. 8 for the measurement of $\text{H}_2\text{O}$ in an ignition experiment.
Fig. 8: Raw data obtained during a measurement of H\textsubscript{2}O during the ignition of CH\textsubscript{4} in air (signal at the photo detector). The latter is a superimposition of emissions from the flame and the laser signal. The transmission of the laser signal fluctuates strongly over time. The insert shows a magnification from the indicated location of the curve. One can see the laser-induced combustion of a stochiometric methane/air mixture (air equivalence ratio = 1.06, initial pressure 3 MPa (30 bar), initial temperature 473K, ignition by a laser pulse with 20 mJ energy from a Nd:YAG laser). The repetition rate of the diagnostic laser was 5 kHz (corresponding to a 0.2 ms time resolution). The total recorded time is 264 ms, the insert is 4.6 ms long (23 times 0.2 ms). Reprinted from [29] with permission from Elsevier.

Typically, the output power of the tunable diode lasers is in the order of 1-10 mW. Approx. 1 % of transmission is still enough to record absorption spectra.

The dependency of the absorbance on temperature and pressure (compare equation 2) is shown in Fig. 9 and Fig. 10 for NH\textsubscript{3}.

Fig. 9 depicts spectra of NH\textsubscript{3} at pressures ranging from 9.6 to 1000 mbar (0.44 m path length, 296 K).