TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY (TDLAS) IN THE PROCESS INDUSTRIES– A REVIEW

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ABSTRACT

The availability of new lasers in the near and mid infrared spectral region has led to the development of sensors for gas measurements that are now applied extensively in the process industries. Based on tunable diode laser absorption spectroscopy (TDLAS) molecules like O_2, CH_4, H_2O, CO, CO_2, NH_3, HCl and HF can be detected *in-situ* with high selectivity and sensitivity in continuous, real time operation. Using sensitive detection techniques like wavelength modulation spectroscopy (WMS), often low ppb and ppm concentration measurements with 1s integration time are feasible. Detection limits can be improved by using extractive sampling and a long multi-pass cell.

TDLAS has become an accepted technique in the process industries for difficult measurement tasks, because it is compatible with high temperatures, pressures, dust levels and corrosive media. Gas concentrations, temperatures, velocities and pressures can be determined. TDLAS is used widely for continuous emission monitoring and process control with over 1,000 field instruments worldwide. In this article, after an introduction to the basics of TDLAS, several interesting applications and installations in various process industrial units with some examples from other industries are reviewed.

Keywords: Tunable diode laser absorption spectroscopy, TDLAS, TDLS, review, process industry, process control, gas temperature, pressure, concentration, flow

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). By this technique, 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 paper, has been accepted as the best available technology [7].

This review article 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]. The intention of this review article is to provide the reader with an update on TDLAS in industrial applications. How this article 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 paper is dedicated to applications of TDLAS in the process industries. After general remarks, the measurement of O_2, HCl, CH_4, H_2O, NH_3, 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 TDLAS in the process industries is presented.

2 PRINCIPLE OF TDLAS

2.1 General

Spectral analysis was developed by R.W. Bunsen and G.R. Kirchhoff in the middle of the 19th century [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).

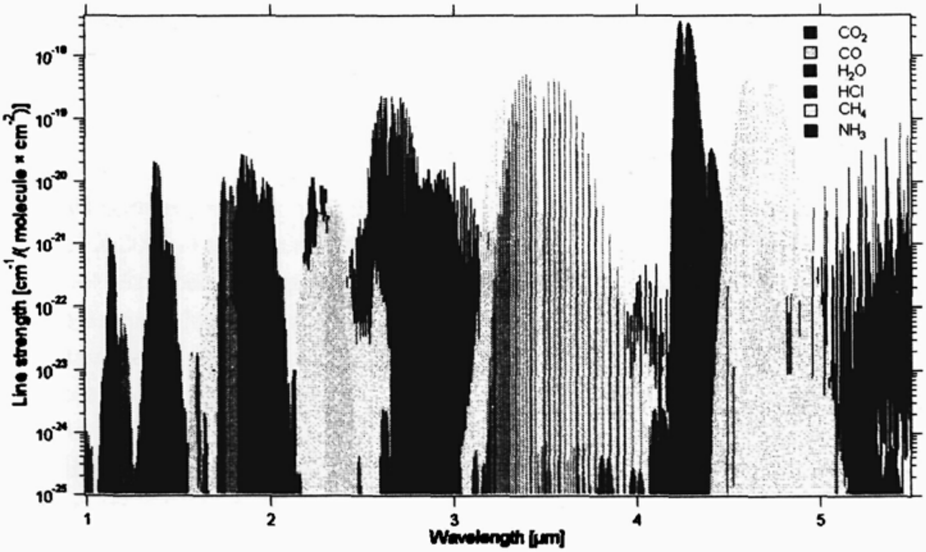

Fig. 1: Absorption lines of CO_2, CO, H_2O, HCl, CH_4 and NH_3 in the infrared. Data for CO_2, CO and CH_4 are taken from the spectroscopic database GEISA [16], data for H_2O, HCl and NH_3 are taken from the spectroscopic database HITRAN [17].

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_2O lines in the presence of H_2O and CO_2 in Fig. 2.

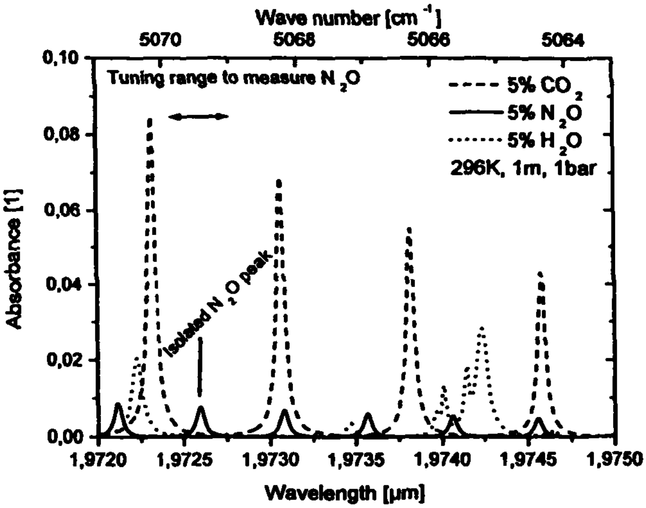

Fig. 2: Because of their narrow line width, absorption lines can be accessed individually. Which lines can be used for spectroscopy depends on gas concentrations, temperature and pressure, as not all lines are interference-free. The marked N_2O line can be probed without disturbing interference from CO_2 and H_2O.

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 H_2O 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 becomes shorter. As outlined in this paper, 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. I_0 is the initial light intensity (before the sample, also called the baseline), and I is the penetrated light intensity (after the sample).

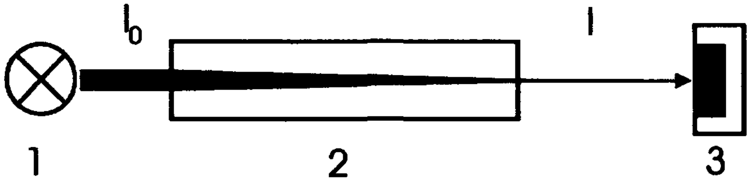

Fig. 3: Experimental setup for TDLAS. 1: Monochromatic light source; 2: sample volume; 3: detector; I_0 is the initial light intensity (also termed the baseline) and I the transmitted light intensity.

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 λ [μm] can also be expressed as a frequency ν [cm^{-1}]. λ is easily converted into ν by $\lambda = 1/\nu$. Wave numbers [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.

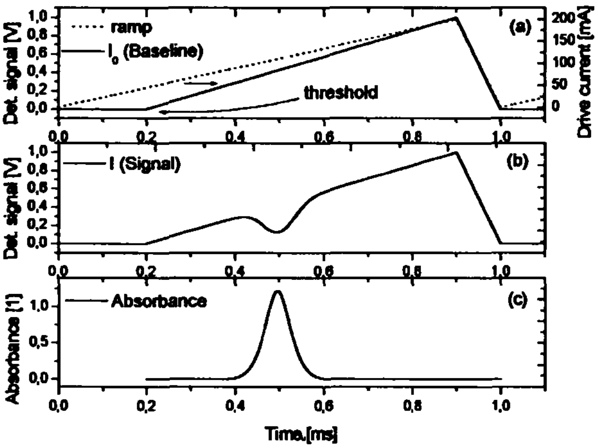

Fig. 4: Recording of an individual absorption line. (a) shows the current ramp applied to the laser and the baseline (I_0), (b) gives the transmitted signal (I). In (c), the absorbance $\alpha=\ln(I_{0(\nu)}/I_{(\nu)})$ is shown.

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 ν (resonance wavelength λ). In Fig. 4 (c), the absorbance α(ν) has been plotted. The absorbance α(ν) is derived from the ratio of initial and transmitted laser light intensity. It is defined as follows (equation 1):

$$\alpha(\nu) = \ln(I_{0(\nu)}/I_{(\nu)}) \tag{1}$$

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 α, 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 of 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:

$$\alpha(\nu) = P * x_i * l * \sum_{j=1}^{n_i} S_{i,j}(T) * \phi_{i,j}(\nu - \nu_{0,i,j}, a_{i,j}) \tag{2}$$

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 ϕ 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):

$$\int_{-\infty}^{+\infty} \phi(\nu) d\nu = 1 \tag{3}$$

$\phi(\nu)$ 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 and shifting.

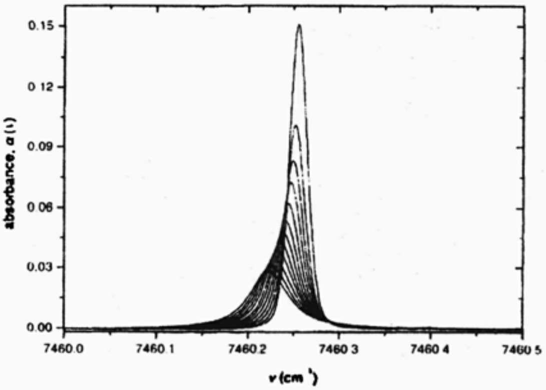

Fig. 5: Pressure broadening and shift of an HF absorption line by Ar gas. Reprinted from [25] with permission from Elsevier.

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 (= *tuning of the wave length*).

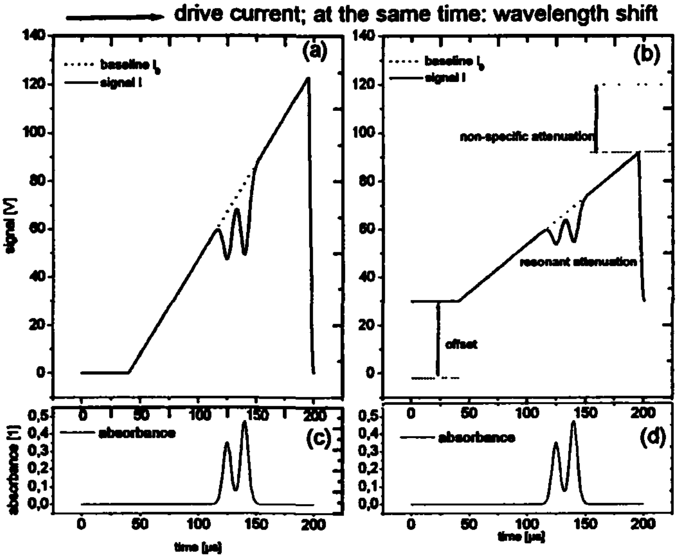

Fig 6: TDLAS without (a) and with (b) interferences. The absorbance α(ν) in (c) and (d) is the same. Non-specific attenuation and the offset can be removed by scanning over the entire absorption feature (here: double peak). The wavelength scan of the line is achieved by tuning the laser current (temperature 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 α(ν) 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 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 H_2O in an ignition experiment.

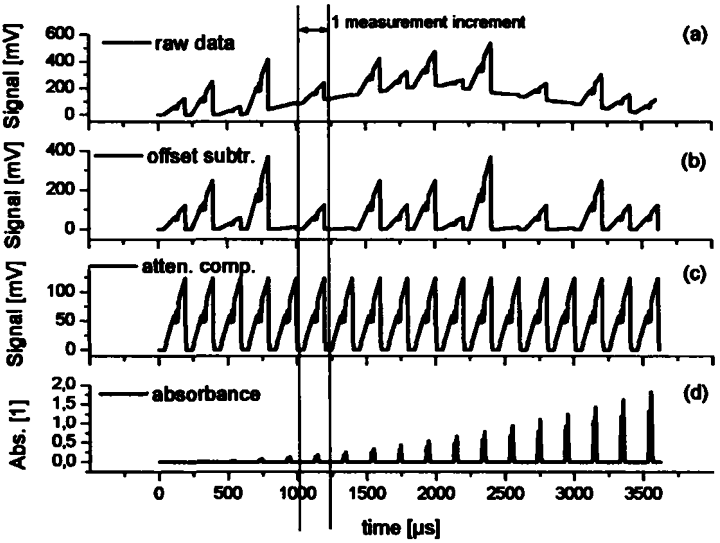

Fig. 7: Illustration of how the absorbance is extracted from the raw data (a). In (b), the offset was removed, in (c), the individual ramps were rescaled (removal of beam steering and similar effects). In (d), the absorbance $\alpha(\nu)$ is shown (double peak from Fig. 6). From the rising absorbance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

Typically, the output power of the tunable diode lasers is in the order of 1-10 mW. Approx. 1 % of transmission is sill 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_3.

Fig. 9 depicts spectra of NH_3 at pressures ranging from 9.6 to 1000 mbar (0.44 m path length, 296 K).

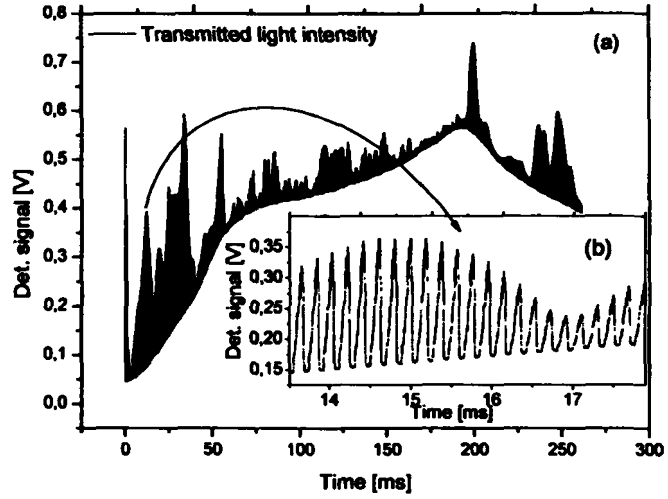

Fig. 8: Raw data obtained during a measurement of H_2O during the ignition of CH_4 in air (signal at the photo detector). The latter is a superimposition of emissions from the flame and the laser signal. The transmission of the laser signal fluctuates strongly over time. The insert shows a magnification from the indicated location of the curve. One can see the laser-induced combustion of a stoichiometric 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.

Pressure broadening effects can be seen. In Fig. 10, spectra of NH_3 at temperatures ranging from 296 to 1173K (0.44 m path length, 40 mbar) are shown.

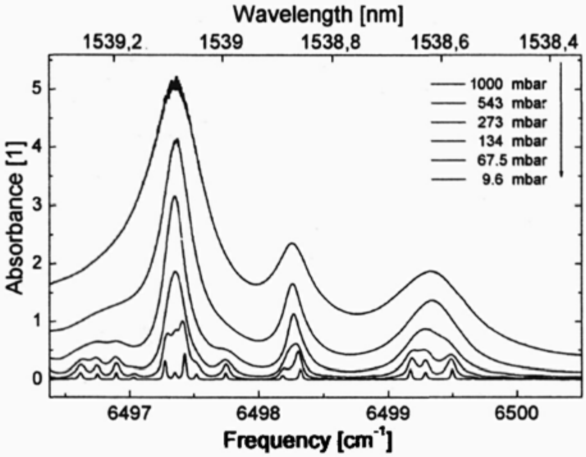

Fig. 9: Spectra of pure NH_3 measured for gas pressures of 9.6, 67.5, 134, 273, 543 mbar and 1000 mbar at 296 K and 44 cm path length (order: bottom to top of graph). Reprinted from [30] with permission from Springer.

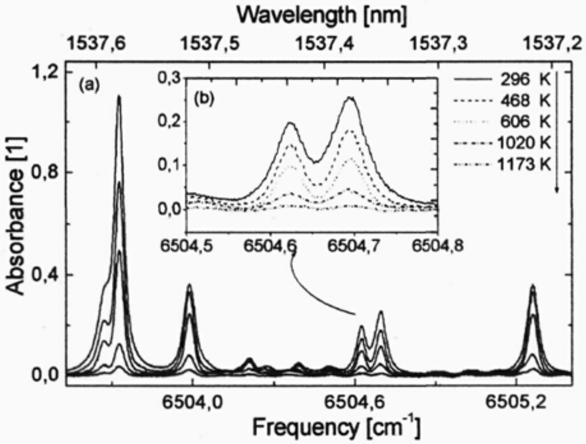

Fig. 10: Spectra of 40 mbar pure NH_3 at temperatures of 296, 468, 606, 1020 and 1173 K (order: top to bottom of graph). The insert (b) shows a magnification. Reprinted from [30] with permission from Springer.

In Figs. 9 and 10, two axes are plotted: wavelength λ [nm] and frequency ν $[cm^{-1}]$.

TDLAS measurements can be carried out in 2 ways:

1) ***In-situ* measurements:** The laser is sent directly through the system under investigation. This approach is particularly suited to probe harsh environments and to avoid altering the system. Also, timely measurements can be obtained.
2) **Extractive sampling:** The gas sample is measured in a special multi-pass cell [31] where the laser beam is reflected multiple times in order to obtain a long effective path length. Common cells are of the Herriot [32], White [33] or Chermin [34] type. A path length of 100 m (100 reflections in a 1 m long cell) is common. This approach is particularly suited to measure trace concentrations.

For industrial applications, Herriot-type cells are often preferred because they are less critical towards miss-alignment than the White-type cells [35]. Gas velocities can be measured by TDLAS based on the Doppler shift of the absorption lines as the gas is in motion [5], [36-37]. For a review on gas velocity measurements, see also [38]. More work on velocity sensing by TDLAS can be found in [39-40].

Generally, for each gas species to be measured, one laser is needed. This is due to the limited tuning range of the lasers, typically 1-2 nm for DFB lasers and 5-10 nm for a VCSEL (see later). If multiple gas concentrations have to be measured, multiplexing can be applied. This means that the beams of several diode lasers are combined before and separated after the sample volume. One can distinguish between time-division multiplexing and frequency-division multiplexing [41]. For an instrument with multiple lasers, see e.g. [42]. A setup where several DFB lasers were multiplexed to probe a C_2H_4/air flame for the simultaneous measurement of CO, CO_2, H_2O and temperature is described in [43].

Under certain circumstances, if the laser tuning range can cover undisturbed absorption lines of several species, multiple species can be measured with a single laser, see e.g. in [44] for simultaneous CO and CH_4 measurements or [45] for simultaneous CO and CO_2 measurements with a single laser.

Often, optical fibres are used to facilitate handling, see [46-47] as examples in combustion diagnostics and [48] for a review of fibre-optic chemical sensors. A review on fibre optics can be found in [49].

For any application, the absorption lines to be measured have to be carefully selected depending on expected temperature, pressure and concentration range of the target and any interfering species. Line selection should primarily be based on the transition strength and isolation from interfering species. The temperature sensitivity should also be taken into account. Line selection is discussed in [20].

Fringes due to etaloning often pose an experimental problem in TDLAS. They can be minimized by avoiding parallel reflecting surfaces in the laser beam path, e.g. by using wedged windows. [50] describes a method of etalon fringe suppression.

Measuring the peak area is more robust than determining the peak height because of line broadening effects [51].

TDLAS is essentially calibration-free, meaning that no calibration in the field has to be done prior to instrument commissioning and later in the use of the instrument;

For line locking purposes, the laser beam can be split and a portion be directed through a reference cell (the laser temperature can then be controlled by a thermoelectric cooler (TEC)) to centre the absorption peak in the laser tuning window.

The production of representative calibration standards for (trace) gases in discussed in [52-53]. In [54], advances in data acquisition are described. A calibration algorithm to carry out species concentration measurements under conditions of varying or unknown pressure or temperature is discussed in [55].

2.2 Detection limits

Detection limits for several target species as measurable with commercial TDLAS instruments are given in [6], [51], [56-57]. Note that these limits depend on the matrix. For most cases, a minimum detectable absorbance of 10^{-5} is assumed. The detection limit is often governed by etalon fringes. By using wedged windows, the etaloning effect [28] can be minimized. Table 1 shows typical detection limits [58].

Detection limits for these gases at an absorbance of 10^{-6} are given in [35]. A comparison of the achievable detection limit in the MIR and in the NIR is also given in [59]. Modulation techniques (see below), in conjunction with long path lengths, have made possible the detection of many species in the ppb and ppt concentration range, e.g. 2.7 ppt NO_2 at atmospheric pressure and 0.75 ppt NO_2 at reduced pressure [60].

Table 1

Typical detection limits in TDLAS, assuming an absorbance of 10^{-5}, a bandwith of 1 Hz and a path length of 1m. Reproduced from [58].

Molecule		MIR				NIR			
water	H_2O	2	ppb	5940	nm	60	ppb	1390	nm
carbon dioxide	CO_2	0.13	ppb	4230	nm	3000	ppb	1960	nm
carbon monoxide	CO	0.75	ppb	4600	nm	30000	ppb	1570	nm
						500	ppb	2330	nm
nitric oxide	NO	5.8	ppb	5250	nm	60000	ppb	1800	nm
						1000	ppb	2650	nm
nitrogen dioxide	NO_2	3	ppb	6140	nm	340	ppb	680	nm
nitrous oxide	N_2O	0.44	ppb	4470	nm	1000	ppb	2260	nm
sulphur dioxide	SO_2	14	ppb	7280	nm		ppb		nm
methane	CH_4	1.7	ppb	3260	nm	600	ppb	1650	nm
acetylene	C_2H_2	3.5	ppb	7400	nm	80	ppb	1520	nm
hydrogen fluoride	HF					10	ppb	1310	nm
hydrogen chloride	HCl	0.83	ppb	3400	nm	150	ppb	1790	nm
hydrogen bromide	HBr	7.2	ppb	3820	nm	600	ppb	1960	nm
hydrogen iodide	HI					2100	ppb	1540	nm
hydrogen cyanide	HCN	12	ppb	6910	nm	290	ppb	1540	nm
hydrogen sulfide	H_2S					20000	ppb	1570	nm
ozone	O_3	11	ppb	9500	nm		ppb		nm
ammonia	NH_3	0.8	ppb	10300	nm	800	ppb	1500	nm
formaldehyde	H_2CO	8.4	ppb	3550	nm	50000	ppb	1930	nm
phosphine	PH_3	6.2	ppb	10100	nm	1000	ppb	2150	nm
oxygen	O_2					78000	ppb	760	nm

2.3 Alternatives to TDLAS

Absorption-based optical methods stand in contrast to emission-based techniques such as laser-induced fluorescence (LIF).

A comparison of TDLAS to other methods is given in [61-64]. In [65], TDLAS is compared to chemiluminescence for NO_x measurements. A comparison of 4 *in-situ* techniques can be found in [66]. In [67], TDLAS is compared to Fourier Transform Infrared (FTIR) spectroscopy for CO_2 measurements. FTIR spectroscopy has wide spectral coverage and is the method of choice for multi-component gas analysis. The sensitivity and selectivity is not as good as in TDLAS because the spectral resolution is lower. FTIR spectrometers are less easy to integrate into a production process than TDLAS, which is compatible to optical fibre-coupling [68]. Scanned- and fixed-wavelength absorption diagnostics for combustion measurements are discussed in [69]. Clearly, the scanned wavelength technique is more robust. Optical and *in-situ* diagnostics are a wide field, see e.g. [70] for a review on this subject. Other laser-based techniques that can be used instead of TDLAS or that yield complementary information –and some of which deploy infrared radiation as well-are emission spectroscopy, Raman spectroscopy [71] (Stokes, Anti-Stokes, Rayleigh scattering [72]), non-dispersive infrared (NDIR) spectroscopy [73], [74], attenuated total reflection (ATR) [75], thermography and pyrometry. Rayleigh scattering and CARS are described in [76-77]. Photoacoustic spectroscopy (PAS) [78-80] and variable pressure infrared diode laser spectroscopy [81] are two other alternative techniques to TDLAS. Laser-induced-fluorescence (LIF) spectroscopy is an emission-spectroscopic technique that can also be carried out with tunable diode lasers, [82]. DOAS (differential absorption optical spectroscopy), LIDAR (light detection and ranging) and DIAL (differential absorption LIDAR) can also be carried out with tunable diode lasers [83]. A microspectrometer is described in [84]. A review on infrared spectroscopy can be found in [85]. In [73], an application in combustion control where NDIR is more cost-effective than TDLAS is discussed. TDLAS is a useful tool for path-averaged, line-of-sight measurements. It can be used when no point measurement is required. Often, path-averaged results are more useful than point measurements, for instance to assess the overall efficiency of a process or to screen a large volume for a certain gas leak.

2.4 TDLAS in research and development

Tunable diode laser absorption spectroscopy has been used in research and development extensively. Out of the broad array of applications, examples include fundamental spectroscopy, optical remote sensing [86] of trace gas concentrations and the *in-situ* measurement of transient species, e.g. the CH_3 radical [87] and the OH radical [88-89]. Note that the measurements in [89] were carried out at 308 nm. Isotope ratios can also be determined using TDLAS [90-92]. Species concentration measurements in plasmas are described in [93-94].

Tunable diode lasers have been used in several laboratory, ground-based and airborne instruments [95-96]. For such measurements aboard balloons or stratospheric aircraft, the instruments must work in an unattended fashion and withstand vibrations. This is outlined in [97] where an instrument to detect 30 ppb CH_4 with 1 s integration time in a high altitude aircraft is described.

Tunable diode laser atomic absorption spectroscopy (DLAAS) allows element-selective detection by diode laser atomic absorption in combination with separation techniques [98-100]. Atomic absorption spectroscopy (AAS) is typically carried out in a graphite furnace with hollow cathode lamps (HCL) as light sources. In [101], the detection of Pb using a tunable laser light source (frequency doubling and sum frequency mixing of two semiconductor lasers to yield 283 nm radiation) is described with the target of improved signal/noise ratio compared to HCL.

Reviews on and introductions to TDLAS can be found in [8-12], [14], [97, [102]. Textbooks detailing on lasers in combustion research are [103]-[104]. A review on diode lasers in analytical chemistry can be found in [105], and a review on laser spectroscopy in analytical chemistry in [106-107]. The latter two articles describe the use of lasers in absorption and emission-based, stand-alone or hyphenated spectroscopic techniques in the liquid and gaseous phase. Also, the use of lasers for sample introduction by ablation is discussed. Lasers are used in a great number of different applications in analytical chemistry, going down even to single molecule detection [105]. Their acceptance as analytical tools has been a comparatively slow process [108].

2.5 Laser sources

A laser [109] as a light source for industrial gas sensing applications must be compact, rugged, stable and long-lived. Favourably, it is operated at room-temperature. In order to probe individual absorption lines, the wavelength of the light must be narrower than the absorption peak. These requirements can be tackled by diode lasers, which were first reported in 1962 [110]. A diode laser essentially consists of a p/n junction of a semiconductor crystal, where light is emitted upon recombination of electrons and holes as electrical current flows across the junction. The description of diode lasers is not in the scope of this article. For more information on laser principles, the interested reader is referred to a textbook on diode lasers, for instance [111]. Conventional diode lasers that are used in consumer electronics and data communication emit light in multiple modes. For TDLAS, a tunable laser [112-113] in single mode operation is needed. Tuning of the laser is achieved by either varying the laser temperature or current. Wavelength tuning by current modulation is faster. Tuning rates of up to 5 MHz have been reported for a 1.68 µm VCSEL [28].

The following Fig. 11 shows the wavelength range accessible with certain material combinations in diode lasers.

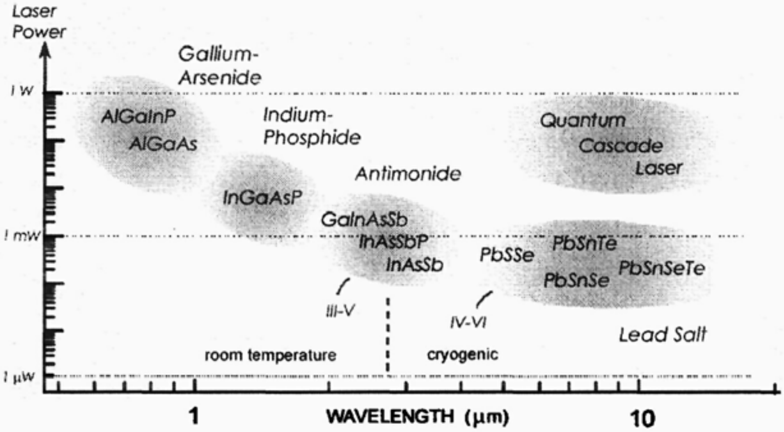

Fig. 11: Materials for certain laser wavelengths. Reprinted from [114] with permission from the Optical Society of America.

Based on the material combinations depicted above, there are several types of single mode diode lasers, the most important ones being DFB lasers (DFB = distributed feedback), DBR lasers (DBR = distributed Bragg reflector) and VCSELs (vertical-cavity surface-emitting laser). These lasers contain a wavelength-selective element (e.g. a grating) so that only a specific wavelength is emitted.

DBR and DFB lasers are of the Fabry Perot type; they are so-called edge emitting lasers (EEL) because the laser light is emitted perpendicularly to the pump direction from the cleaved lateral surface (edge) of a semiconductor crystal. Typically, EEL have the disadvantage of showing mode hops as they are wavelength-tuned (no continuous tuning possible).

Special lasers are external cavity diode lasers (ECDL or ECL) where a mechanically operated grating outside the laser cavity is used to tune the laser wavelength. One can distinguish between the Littman and the Littrow setup. ECDL can scan wide wavelength ranges, e.g. 90 nm (1490-1580 nm) as reported in [115]. The detection of CO and CO_2 using an ECL is described in [116].

Liquid nitrogen cooled lead salt diode lasers [117] became available for spectroscopists in the 1970's with wavelengths between 3 and 30 μm [118]. Because the lead salt laser and its detector require cryogenic cooling, the application of these devices is mostly restricted to laboratory environments, although the strong, fundamental rovibrational transitions in the MIR are probed and hence better lower detection limits than in the NIR are feasible. The typical tuning range of single-mode distributed feedback (DFB) diode laser is 1 cm^{-1} [18]. DFB lasers have become available within the entire wavelength range from 730 nm to 2800 nm with output powers between 10 - 150 mW [119-121].

Another interesting type of lasers for TDLAS is the vertical-cavity-surface-emitting laser (VCSEL). In contrast to EELs like DFB and DBR lasers, the light of a VCSEL is emitted from the surface of the laser and not perpendicularly to the pump direction. This offers several advantages such as low divergence, on-wafer testing and on-chip integration possibility.

Long-wavelength VCSELs have become available from 1.4 to 2.3 μm [122-125]. The typical continuous, single mode tuning range of a VCSEL is one order of magnitude wider than for EEL, it is approx. 5 nm (approx. 10-30 cm^{-1}, depending on wavelength).

The following Table 2 shows the characteristics of a few DFB lasers and VCSELs with respect to their wavelength tuning properties. A comparison of VCSELs and EELs for TDLAS can be found in [128-130]. The characteristics of several tunable diode lasers are compared in [119]. It is stated there that an external cavity laser (ECL) is well suited for laboratory instruments for multiple species detection, however, it is considered unsuitable for industrial applications because of mechanical and thermal stability limitations. The DFB laser, which has a limited tuning range, can be used in field applications.

Table 2

Tuning properties of EEL and VCSEL lasers.

Laser	$\Delta\lambda/\Delta I$	$\Delta\lambda/\Delta I$	$\Delta\lambda/\Delta T$	$\Delta\lambda/\Delta T$	Threshold current	Source
760 nm VCSEL	0.29 nm/mA	- 5.0 cm^{-1}/mA	0.05 nm/K	-0.86 cm^{-1}/K	2.3 mA (298 K)	[126]
1540 nm VCSEL	0.11 nm/mA	- 2.96 cm^{-1}/mA	0.11 nm/K	-0.46 cm^{-1}/K	0.93 mA (293 K)	[126]
1680 nm VCSEL	0.86 nm/mA	- 3.05 cm^{-1}/mA	0.11 nm/K	-0.40 cm^{-1}/K	0.75 mA (288 K)	[126]
1810 nm VCSEL	0.9 nm/mA	- 2.75 cm^{-1}/mA	0.125 nm/K	-0.38 cm^{-1}/K	0.9 mA (303 K)	[126]
760 nm DFB laser	0.0047 nm/mA	- 0.081 cm^{-1}/mA	0.0597 nm/K	-1.03 cm^{-1}/K	~ 30mA (298 K)	[127]
1580 nm DFB laser	0.003 nm/mA	- 0.012 cm^{-1}/mA	0.15 nm/K	-0.60 cm^{-1}/K	~ 30 mA (298 K)	[128]

Single mode DFB lasers and VCSELs typically have a narrow line width of a few tens of MHz (kHz is possible [131]) and a typical side mode suppression ratio of > 30 dB. Instrument broadening effects due to the finite line width can be determined by using the delayed heterodyne method [132]. In [25], the laser line width was determined to be 11 and 24 MHz for a 1.31 and a 1.34 µm DFB laser, respectively.

Quantum cascade lasers (QCL) are interesting, single mode light sources in the MIR [133-135]. They can be fabricated at any wavelength from 4.5 – 17 µm [136] to access the strong, fundamental rovibrational transitions (see Fig. 1). QCL can be operated in cw (continuous wave) mode at cryogenic conditions and in pulsed mode at room temperature. Using thermoelectric cooling, quasi-room temperature operation can be achieved. CW operation of a QCL with thermoelectric cooling emitting at 9.3 µm was demonstrated in [137]. QCLs have not found as widespread a use in industry as DFB and VCSEL lasers. Gas sensing with QCLs is described in [138] for industrial gas process stream analysis. For trace pollutant measurement in combustion flows, the reader is referred to [136], and for atmospheric CO detection to [139]. CO and NO measurements in combustor exhaust flows are described in [140].

Novel, promising lasers are the so-called MEMS-VCSELs. A continuous, single mode tuning range of up to 60 nm has been demonstrated. [141]. Such a MEMS-VCSEL has been applied to molecular spectroscopy [142] recently, see Fig. 12 for a 27 nm (110 cm^{-1}) wide spectrum of CO with more than 30 absorption lines.

Diode laser development has been driven by the telecommunications industry. Since SiO_2 fibres, which are widely used, have the least signal attenuation at 1.3 and 1.55 µm, this is where many laser sources are available. Meanwhile, several lasers are especially produced for spectroscopic applications.

For field use, long-term stability of any given sensor is a prerequisite. Laser frequency stability can be analyzed by Allan plots [143] and is discussed in [51]. Frequency drifts need to be avoided. By readjusting the laser temperature, slight drifts can be compensated for, provided that a reference gas cell is use to check the laser wavelength position (line locking).

If a desired wavelength is not readily available, frequency doubling can be used as demonstrated in [89] for the detection of the OH radical at 308 nm. Another method is difference-frequency generation (DFG) as described in [144].

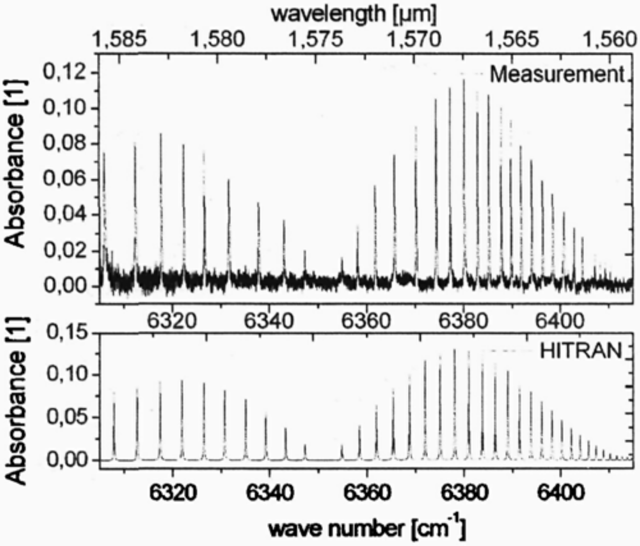

Fig. 12: Spectrum of CO (top) and model calculation (bottom). Experimental conditions: 291K, 43.5 cm, 1bar, pure CO. The depicted tuning range is 27 nm (110 cm^{-1}). Reprinted from [142] with permission from the Optical Society of America.

As detectors, photodiodes are typically used. For the MIR, lead salt detectors made from HgCdTe (MCT) are commonly deployed. They require liquid nitrogen cooling. For shorter wavelengths in the NIR, room-temperature operated devices based on InGaAs can be used. Since the laser beam is divergent, collimating optics have to be employed in the setup.

2.6 Advanced detection techniques

In absorption spectroscopy, a small attenuation of an essentially large signal has to be measured. Emission spectroscopy, on the other hand, benefits from a virtually non-existing background signal and is hence intrinsically more suitable for sensitive trace concentration determination. As shown above, the signal strength for TDLAS is considerably weaker in the NIR than in the MIR, however, it is the near IR where a broad selection of suitable, cost-effective lasers is available. Under optimum conditions, an absorbance of 10^{-2} can be detected and evaluated in a single laser scan (direct absorption). By averaging multiple spectra, one can reach approx. 10^{-3} in direct TDLAS. In order to determine even smaller absorbancies down to 10^{-6} and less, special detection techniques can be used, the most common ones being wavelength modulation spectroscopy (WMS) [145-146] and frequency modulation spectroscopy (FMS) [147-148].

The principle of WMS and FMS is that detection is shifted to a higher frequency where noise is less. In WMS, the modulation frequency (f) which is imposed on the current tuning ramp is typically below 100 kHz. In FMS, the modulation frequency is on the order of several MHz or GHz, which is comparable to the absorption peak line width. Large modulation depth WMS is outlined in [149-150]. The photo detector output is processed by phase-sensitive detection (PSD) with reference to the fundamental frequency f or the second harmonic (2f) [151]. This can be achieved with a lock-in amplifier. 2nd harmonic detection is detailed in [152-153]. The detection of absorbancies as low as 10^{-6} with 1 s integration time has been reported [12]. A special approach in FMS is two tone frequency modulation spectroscopy (TTFM) [97], [154]. Heterodyne detection is described in [155].

The Hobbs' auto balancing technique [156-158] is an electronic circuit where I and I_0 are divided before amplification. This prevents uncorrelated noise in I and I_0 from being amplified and hence lowers the minimum detectable absorbance. The Hobbs' auto balancing technique is often referred to as balanced ratiometric detection (BRD), see also [159].

The following Fig. 13 shows the signal shape in direct absorption, 1st and 2nd harmonic detection.

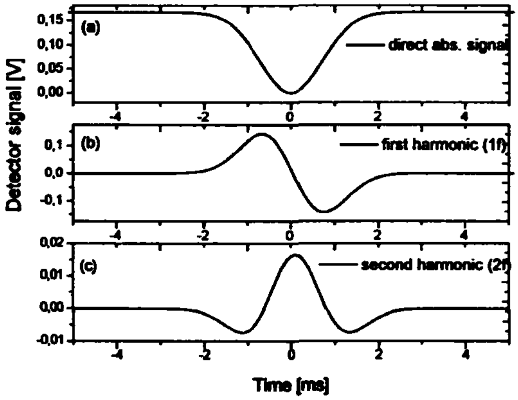

Fig. 13: Signal shape in 1st and 2nd harmonic detection compared to direct absorption spectroscopy (sloping background not shown).

Signal processing in TDLAS is discussed in a review article in [53]. Commercial TDLAS instruments often use 2f WMS detection. Typically, the laser is scanned at kHz rates and several 10 or 100 spectra are averaged so that with 1s integration time, absorbancies of 10^{-5} can be detected. In [160], the laser was wavelength-scanned at 2 kHz and 400 spectra were averaged for every output value for a measurement in a boiler.

2.7 Related techniques

There are several techniques which are based on or similar to TDLAS. Cavity ring-down spectroscopy (CRDS) is a slight modification of direct absorption spectroscopy. In CRDS, the intensity decay of narrow line width light in a resonant cavity filled with the (trace) gas to be determined is measured. The technology is described in [161] – [163]. Since the light is reflected in the high finesse cavity numerous times, very long effective optical path lengths (up to tens of km) are obtained. The faster the light decay, the higher is the analyte concentration. Compared to traditional TDLAS, CRDS is a very sensitive technology. The long path length permits the spectroscopy on weaker, more isolated absorption lines and small cell volumes for rapid gas exchange [163]. However, CRDS is sensitive to mirror misalignment and changes in mirror reflectivity.

Cavity enhanced absorption spectroscopy (CEAS) [164-165], integrated cavity output spectroscopy (ICOS) [166] and intracavity laser absorption spectroscopy (ICLAS) [167] are similar techniques.

The lowest absorbencies can be determined by combining the advantages of FMS and CRDS. This can be done in a technique called noise-immune cavity enhanced-optical heterodyne molecular spectroscopy (NICE-OHMS) [168]. Minimum absorbencies of ~ 10^{-14} can be detected. NICE-OHMS, due to the complex setup, is currently only a laboratory technique.

A technique to measure broadly absorbing species by TDLAS has been developed in [169-170].

2.8 Comparison of TDLAS to conventional techniques

Non-optical techniques like gas chromatography (GC) or mass spectrometry (MS) require the sample to be extracted from the process and often to be preconditioned. The intrusive probes are subjected to fouling, leading to frequent replacement. Solid-state sensors sometimes experience drift, hence giving a low confidence level.

Optical methods operate *in-situ* and in non-contact mode; They have the inherent advantage of measuring right at the spot[1]; In contrast to techniques that rely on sampling, the measurements can be done in a timely fashion and are not so prone to errors. Several species cannot be sampled at all because they are too reactive (radicals), short-lived or not volatile enough [171].

In the literature [172], the discrepancy in the concentration values for sampled and directly determined CO in a flame has been found to reach one order of magnitude for different designs and conditions. It was suggested that the conversion of CO to CO_2 inside the suction probe according to $CO + OH \rightarrow CO_2 + H$ accounts for the non-representativeness of conventional methods. The difference in CO gas concentration measured inside and outside a laboratory fluidized bed combustor (FBC) unit is described in [44].

TDLAS is suited to measure multiple flow field parameters. Species concentrations can be detected in a large dynamic range (e.g. 500 ppm to 10% CO_2 as reported in [20]) with high sensitivity and high selectivity at fast time response. The method is non-intrusive;

Semiconductor diode lasers are compact, rugged, cost-effective, and easy-to-operate devices with compatibility with optical fibres. TDLAS enables real-time measurements, also at elevated temperatures and pressures in multi-phase environments [173-174]. Intermediate species can be detected.

The advantages of TDLAS over conventional gas analytical techniques like wet chemical analysis can be listed as follows (modified and extended from [57], [175-176]):

- *In-situ*, continuous, real-time (1s integration time)
- Possible in harsh environments (high pressure, temperature, humidity, flow speed, dust load, corrosive gases)
- Minimum interference from other gases
- Linear response over wide concentration range
- Very sensitive – ppm to ppb levels
- Robust and reliable
- No consumables (non-depleting)
- Low-replacement-cost optics and detectors for data sampling in hostile environments

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[1] Note that in some industrial TDLAS applications, the sample is analysed in a long-path cell outside the process area for improved sensitivity.

- Reduction of intangible costs related to an unreliable sensor
- No frequent field calibration necessary

Costly shutdown times can be shortened, e.g. if a purging process is monitored by a fast TDLAS sensor instead of a slower sensor, see the following Fig. 14 for illustration.

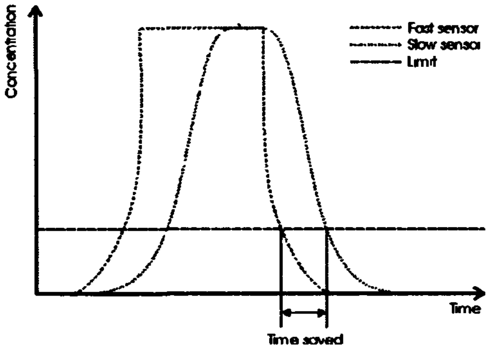

Fig. 14: The purging time of a reactor vessel can be reduced by using a fast sensor. This allows for a faster start-up, which translates into cost savings (Modified from [177]).

Also, TDLAS is a robust technique. Changes in optical window transmissivity, mirror reflectivity, laser light intensity fluctuations or slight changes in alignment will cause a different signal at the detector, however, the instruments' concentration reading will not be affected as TDLAS is a relative measurement between I_0 and I.

3 TDLAS IN THE PROCESS INDUSTRIES

3.1 General

In order to control an industrial production plant, process parameters must be measured without interfering with the process. The spatial distribution of a fluid concentration or temperature has an impact on product quality and process efficiency (yield). Probes at different locations give time-averaged information that can lead to misinterpretations particularly in non-stationary flows [72].

Tunable diode laser absorption spectroscopy is used to measure gas dynamic properties along the laser path in the reactor. Starting out as a laboratory technique, TDLAS has become a well-established technology for the field.

15 years ago, an *in-situ* ammonia sensor for DENOX optimization in a power plant was tested; It was based on a large CO_2 laser [178-179] and therefore not practical for widespread application. Tunable diode lasers are much more versatile tools; The early lead salt lasers, due to the required cryogenic cooling, did not experience a widespread use in industry, either; Room-temperature operated diode lasers in the near infrared, though probing the weaker overtone and combination bands, have been more attractive and have shown an impressive breakthrough in industrial applications.

Commercial solutions can be obtained from a range of specialized companies, one of which has announced its 1000th field installation as early as 2004 [180-181]. Continuous operation of TDLAS systems without any unscheduled interruptions for over 4 years has been reported in [57]. High sensor reliability is vital in the process industries to prevent costly unscheduled downtimes.

The following Fig. 15 shows a schematic drawing of a TDLAS installation on a stack.

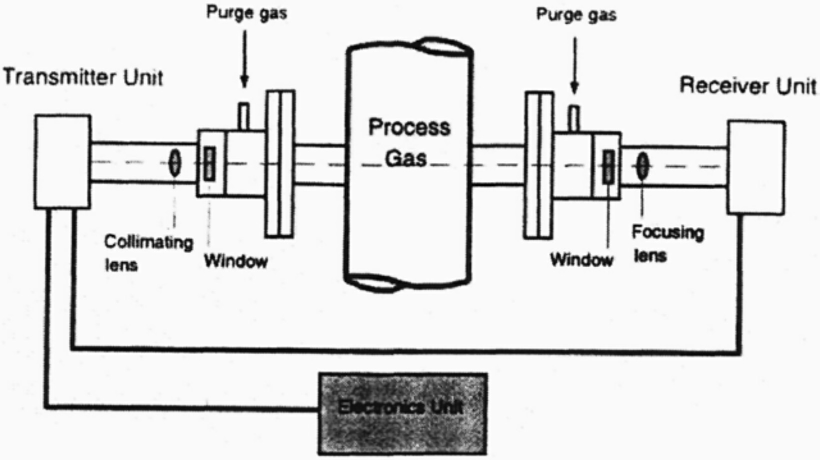

Fig. 15: TDLAS installation on a stack. Reprinted from [51] with permission from Springer.

On the way to develop expensive and complicated laboratory spectrometers into robust, state-of-the-art field instruments, cost and complexity reduction has been a major concern [6], [182].

The harsh conditions that are encountered by industrial TDLAS-based sensors in the field are discussed in [55], [183]. In a typical commercial embodiment, the laser is housed in a central unit (e.g. 19" rack mounted). The light is transported to the measurement spot by optical fibres, which can be several 100 m away [184]. The process interface can be purged, if necessary, and is available in IP 67 protection [184], with sensor temperature conditions ranging from 243-343 K.

Starting out as a laboratory speciality, TDLAS has evolved to an accepted technology for process monitoring and comes in lightweight, battery-operated devices that cost a few thousand dollars [6] and meets industries' requirements with regard to sensitivity, selectivity and compactness [144].

An overview of TDLAS in industrial gas monitoring is given in [35], [51], [114], [160], [184-188].

How this chapter of the paper is organized: First, the measurement of special molecules by TDLAS in industrial applications is discussed. Then, specific industries are addressed. Note that due to the vast array of industries and applications, this review cannot be fully comprehensive. The aim is to highlight several widespread and interesting applications of TDLAS in industry.

3.2 O_2 measurements

In many industrial processes where gases are generated or consumed the oxygen concentration is an important parameter, especially in combustion applications where optimum oxygen supply is necessary for high efficiency and minimum pollutant formation. In other applications, the absence of oxygen needs to be monitored. One conventional technique for oxygen sensing is by using zirconia (ZrO_2) sensors [189]. ZrO_2 transports oxygen ions at elevated temperatures; If there is a difference in O_2 concentration on the two sides of a heated ZrO_2 disk, an electrical potential proportional to the O_2 concentration gradient can be measured. ZrO_2 sensors are insensitive towards thermal, chemical and mechanical stresses. They are widely used. A prominent example is the λ probe in passenger cars running on gasoline. Alternatively, the paramagnetic properties of O_2 can be exploited for its measurement. An inhomogeneous magnetic field is applied to a gas sample in a special cuvette; The field attracts the O_2, the resulting torque can be measured. Since this technique is sensitive to vibrations, it is not as properly suited for harsh process environments as the ZrO_2 sensor.

Laser-based sensors offer the advantage of faster time response, non-intrusive nature and path-averaged measurements. Oxygen can be probed by TDLAS at around 760 nm. Since the absorption signal is weak, extended path-lengths and/or a sensitive detection technique have to be used. Laser-spectroscopic O_2 measurements were reported with several different laser sources, see [190] and references therein plus [128], [191-192].

Frequently, O_2 is measured for safety-related reasons (oxygen presence or deficiency monitoring) and combustion control [184].

In [190], O_2 concentration measurements at up to 10.9 bar were carried out using a VCSEL at 760 nm (50 and 500 Hz). The detection limit at a minimum detectable absorbance of 10^{-4} (limited by etalon noise) was 800 ppm*m. WMS was used in that study where the suggested use was for aero propulsion gas-turbines.

Another application describes the *in-situ* monitoring of oxygen concentration and gas temperature (see later) in a furnace [193].

In [194], the measurement of molecular oxygen in a dense water mist environment to study the effectiveness of fire suppressing measures is described.

As fuel is withdrawn from the fuel tank aboard aircraft, the empty space is replaced by nitrogen-enriched air in order to minimize the risk for fires and explosions. In [6] and [195], a VCSEL-based sensor was developed and tested to measure oxygen in the ullage of such aircraft tanks.

Typical commercial TDLAS-instruments for O_2 sensing are available with a resolution of 100 ppm from 0-10% and a resolution of 0.1% from 0-100%. Such a sensor is discussed in [196]. The TDLAS-based oxygen monitoring of nitrogen blanketing (corrosion protection of a vessel) and to prevent dust explosions is described in [197]. Commercial O_2 sensors have also been installed in paper mills and refineries [197].

A potential field of use for a TDLAS-based O_2 sensor are applications where the ZrO_2 sensor cannot be used, e.g. processes at very high temperatures as encountered in furnaces or steel mills. Another possible application is in explosive environments or in processes where a fast time-response or path-averaged results are desired.

3.3 HCl measurements

Hydrogen chloride is an important chemical in many industrial processes and also encountered as a toxic combustion by-product.

In [198], the application of TDLAS to the HCl measurement in a plasma etching process in described. In [56], HCl measured by TDLAS is used as an early indicator for fire, which might stem e.g. from smouldering PVC cables. The advantages of measuring several early combustion products instead of using a conventional smoke detector are fast time response and less risk for false alarms. It was found out that approx. 90% of the Cl in the fuel will end up as HCl [51], hence a TDLAS-sensor monitoring HCl is less likely to cause a false alarm than an instrument working on more general parameters like infrared (heat) radiation or smoke. The HCl measurement in an incineration plant is suggested in [51], [199]. In [200], a spectrometer for the simultaneous detection of HCl and HF in the flue-gas of a waste incineration plant is described with lower detection limits of 8 ppb for HCl and 18 ppb for HF, both measured at reduced pressure (133 mbar).

3.4 CH_4 measurements

Methane, its major source being natural gas, is used as a fuel and feedstock in many chemical processes such as the production of hydrogen, methanol, ammonia or acetic acid. CH_4 has a significant green-house warming potential [201]. It is widely transported via pipelines and has an explosive range of 5-15% in air, so leak detection in natural gas drilling, production and processing operations and at consumers is a primary concern. Another source of methane, which is increasing in importance, is biogas. The CH_4 content of natural gas and biogas is a critical value. Natural gas was investigated by TDLAS in [202-203]. Biogas was probed for the CH_4 content in [204]. The TDLAS-derived CH_4 concentration was compared to a NDIR-gas analyser. The reported accuracy was +/-0.1%. The monitoring of CH_4 in landfills for the detection of dangerous so-called "hot-spots" is described in [57].

Remote helicopter-borne sensing of CH_4 leaks from pipelines was reported in [205]. The tests in the air lasted 20 hours, a natural gas leak down to 50 l/s could be detected. The measurement sensitivity was dependent on the weather conditions, the flight height of the helicopter and the albedo of the ground. An improved version of the instrument allowed flight heights as high as 600 m [206]. High temperature TDLAS measurements of CH_4 are described in [207].

3.5 H_2O measurements

Gaseous water can be measured using electrochemical cells, however, the confidence level for trace concentration measurements is low because of instrument drift and the fact that the sensor is desensitized over time, giving rise to frequent recalibration in the field. Water can be detected by TDLAS, too. In [208], an overview on the trace water vapour determination in N_2 and corrosive gases is given.

Trace moisture contamination in high purity gases poses a problem in several industries and is often hard to detect (water is a "sticky" molecule, meaning that it has a pronounced tendency to being adsorbed on surfaces, yielding too low concentration readings). By switching from FTIR to TDLAS, the detection limit for H_2O in NH_3 [209] [210] could be improved from 2 ppm to 50 ppb [211]. The detection limit of H_2O in Cl_2 is given with 0.3 ppm [184]. A limit of detection (LOD) of 65 ppt for H_2O was achieved with a laboratory TDLAS hygrometer [107]. The detection of trace water is also detailed in [212].

Water is measured in a natural gas pipeline to prevent icing [59].

The concentration of water is a good indicator for the overall combustion efficiency [18] (typically 5-30% of the flue gas are H_2O), so combustion is another area where TDLAS-based H_2O measurements might be beneficial.

3.6 NH_3 measurements

Ammonia is one of the chemicals with the highest yearly production. It is converted into urea, ammonium nitrate, ammonium phosphates, nitric acid, and ammonium sulphate, with the highest consumption in the fertilizer industries. Operations producing or consuming large amounts of NH_3 have the potential for significant fugitive emissions. The atmospheric ammonia concentration can be measured for air quality monitoring and for emissions monitoring purposes. Ammonia trace concentration measurements are demanding because NH_3 is a "sticky" gas.

NH_3 is also used for NO_x removal in post-combustion gases [213]. The latter is known as selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR) or Thermal DeNOx process, where NH_3 is injected into the flue gas downstream of the combustor to reduce NO_x [214]. The emission of unconverted, excess NH_3 (the so-called NH_3 slip) has to be measured to optimize the process. This is needed to reduce corrosion, to minimize consumables and to reduce the environmental impact. The NH_3 slip should not exceed 5 ppm [51]. Typical conditions at the measurement point are 520-620K, dust levels of 10-20 g/m³ and 10-30% H_2O in the gas [51].

Conventional technologies to measure NH_3 are the dew point technique and several technologies that involve wet chemical analysis (sampling and subsequent quantification by ion chromatography, or ion mobility spectroscopy).

In-situ TDLAS directly in the exhaust stack is attractive because NH_3 sampling from the hot flue gas is prone to errors as discussed in [215-216], including long response time, clogging of the extractive sampling probe and NH_3 adsorption inside the probe. Ultra-sensitive NH_3 measurements with a detection limit of 1 ppb in a 5-minute-measurement time using a commercial CRDS instrument are described in [163] (see section on the semiconductor industry below). NH_3 emissions in agricultural operations have also been measured by TDLAS in an open-path arrangement [57]. NH_3 is further used in refrigeration systems. The air in storage rooms of perishable materials like high-cost biopharmaceuticals needs to be controlled for NH_3 in order to safeguard the material [163]. NH_3 lines around 1.5 μm are tabulated in [217].

3.7 Alkali atoms

Alkali compounds pose a problem in the combustion of coal and renewable fuels because they lead to high-temperature corrosion in the combustion chamber and flue gas ducts. Due to their natural abundance, Na and K are deposited on the walls as sulphates. They form low-melting eutectica, making the surface more susceptible to corrosives such as chloride and SO_2 [171].

Alkali atoms were the first species to be probed by laser spectroscopy [218], however, their determination in trace concentrations is no trivial task.

In [219], potassium atoms were measured in two pulverized coal combustors at pressures of 1 and 12 bar. Conventionally, the determination of alkali atoms involves the sampling from the flue gas with a water scrubber and the subsequent analysis by atomic absorption spectroscopy (AAS). In

[220], a more advanced online method is suggested. A major advantage of the TDLAS technique is that elementary K can be discerned from other K-containing species (speciation).

By seeding the air flow to a combustor with alkali atoms, the residence time distribution can be measured [221]. The residence time is a key parameter in the design of a process plant; In combustors, authorities often specify a minimum residence time at a given temperature for complete conversion of certain pollutants. [171] also describes the *in-situ* TDLAS measurement of Li and Cs ions. A review on diode laser atomic spectroscopy can be found in [222]. Atomic spectroscopy is reviewed in [223].

3.8 HF and aluminium industry

Hydrogen fluoride is a highly toxic gas. Emissions stem primarily from aluminium plants, glass works, incinerators, alkylation plants and tile manufacturers. HF emissions need to be controlled stringently, so most of the gas is collected and treated.

Aluminium is produced from the electrolysis of alumina (Al_2O_3). Cryolite (Na_3AlF_6) is used to reduce the melting point of the alumina, at the expense that HF emissions are caused.

In [224], HF monitoring in aluminium smelters using TDLAS is described. Alternative techniques to measure HF are wet chemistry preceded by sampling, FTIR spectroscopy or the use of a fluoride-ion selective electrode (ISE).

An intercomparison of 3 methods to detect HF in a stack of an aluminium smelter is presented in [225]. In [200], HF is measured by two tone frequency modulation spectroscopy (TTFM). Using a 30 m long path Herriot-cell, the minimum detectable concentration of HF was determined to be 1.0 +/- 0.06 ppb at 127 mbar and 70 +/- 4 ppb at 1013 mbar.

HF can be detected in aluminium smelters to assess the scrubber efficiency or to control emissions from stacks or fugitive HF on the roofline [57]. The TDLAS-based detection of HF is seen as an accepted method for industrial applications [226].

In [227], CF_4 (tetrafluoromethane) and C_2F_6 (hexafluoroethane) are measured by TDLAS. CF_4 and C_2F_6 are two perfluorinated compounds (PFC) that are generated as byproducts in aluminium plants.

In [175], the concentration of HF during the testing of Halon alternatives for fire suppressing was measured.

In [59], the TDLAS-based measurement of HF in an alkylation plant is mentioned; In an open path arrangement, a length of 100 m close to the unit and a length of 200 m in a fence line monitoring [59] are controlled for HF emissions.

3.9 Steel making industry

Steel and cement furnaces operate at particularly high temperatures where O_2 monitoring for process control can be done by TDLAS [51]. By measuring CO simultaneously, combustion control can be further improved [51]. The analysis of stack emissions by TDLAS in a steel reheating furnace is discussed in [228]. An overview about absorption and emission spectroscopies in the steel making process is given in [229]. A sensor for gaseous H_2O was installed at a steel maker in a stream of mostly hydrocarbons and nitrogen [177]. In [230], the *in-situ* monitoring of oxygen concentration and gas temperature in a metallurgical process is described. In [231], the TDLAS-based monitoring of CO and CO_2 fumes of an EAF (electric arc furnace) for the dynamic control of oxygen injection (response time < 1s) is discussed. The fumes from the EAF process have a very high temperature of approx. 1850K and are highly dust-laden (150 g/Nm^3). Previously, the measurement was done by sampling gas through a water cooled probe, to filter and dry it, and to analyse it with traditional gas analysers, which gave a response time of 30s [231]. For an overview of where TDLAS can be applied in the steel industry, see [176]. Examples include iron making plants (O_2, CO, CO_2, CH_4), steelmaking plants (O_2, CO, CO_2), coke-oven plants (O_2, CO, CO_2) and gas plants (O_2) [176].

3.10 Power plants and combustion

In order to minimize emissions of CO_2 and pollutants and to increase the efficiency of thermal power plants, species concentration and temperature measurements are important [47].

As the fuel composition varies, especially in batch-fired processes like rotary kilns or in the burning of municipal solid waste, the control of air/fuel ratio is not a trivial task. This could be tackled by measuring CO downstream of the combustor.

CO reduction is achieved by using excess air. However, too much air can lead to increases in CO again.

CO_2 could also be measured in the stack of a boiler to measure the total carbon, e.g. for compliance monitoring with regard to CO_2 emissions [19]. CO_2 measurements at elevated temperature using a diode laser are described in [232].

In-situ species concentration measurements in a stack are typically carried out at 370-620K at pressures around 1 bar [51]. In some applications, a measurement even closer to the process is needed where temperatures and pressures are much higher.

A slow combustion control, maximizing CO_2 and minimizing CO, was demonstrated in [233] with a rate of 2 Hz. In [73], a CO sensor based on non-dispersive IR spectroscopy for combustion feedback control is described.

In-situ TDLAS allows rapid measurements at kHz rates and more [234] and can be used to probe combustion environments. Due to the high pressures and temperatures, the spectroscopic parameters of the absorption spectra have to be known in detail [19]. Combustion off-gases are a demanding matrix for gas concentration measurements because of the high water content, temperature and presence of solid particles.

Tunable diode laser absorption spectroscopy applied to combustion control in industrial plants and furnaces is described in [235-236]. Waste incineration monitored and optimized by TDLAS is covered in [237-239]. TDLAS was tested in a coal-fired plant [240], a gas-fired plant [241] and a lignite-fired power plant [242]. The following Fig. 16 is an example of a TDLAS measurement in a lignite-fired, 600 MW (thermal) power plant.

The product gas from the gasification of biomass was also investigated by TDLAS [243], and so was biogas [244].

In [234], it was possible to actively control a combustor within 100 ms using TDLAS.

Laser-based sensors for pollutant measurements in flue gas stacks are becoming established [245], see also the NH_3 measurement in the SCR/SNCR process described above. Since many pollution abatement technologies such as staged combustion, flue gas recirculation, pulsed combustion, electrostatic precipitation or thermal DENOX are not affordable for small combustors [73], combustion control by a cost-effective infrared sensor might be a viable solution. The active adjustment of air/fuel ratio is the most straightforward technique and could be achieved by minimizing the

CO in the flue gas. By monitoring CO, NO_x can be controlled indirectly [73]. In [160], CO and O_2 concentrations were measured in a 300 t/day incinerator furnace. The TDLAS based-sensor showed a 2-3 min faster response than the existing sensor. By controlling the secondary air allocation of the furnace with the laser measurement, combustion efficiency could be increased and CO emissions lowered from 11.9 to 8.0 ppm.

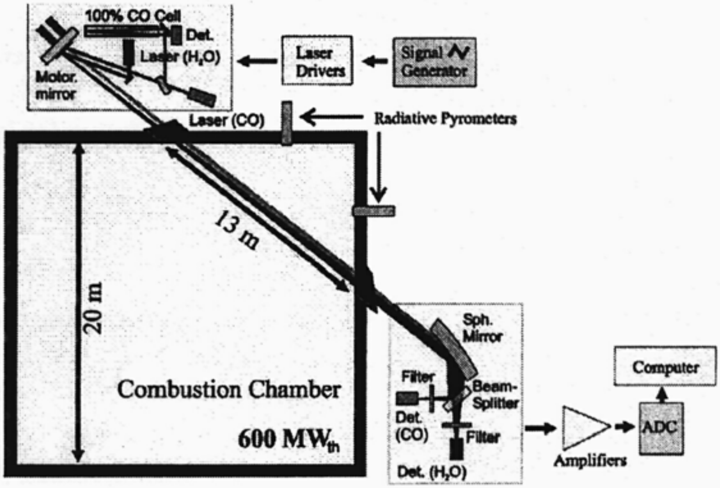

Fig 16: Scheme of TDLAS-based H_2O measurement in a 600 MW (thermal) power plant. Reprinted from [57] with permission from the Optical Society of America.

Control of combustion instabilities in swirl-stabilized combustors is detailed in [246]. The closed-loop control of a forced-vortex combustor is described in [247].

A review on combustion control and sensors is given in [248]. A review on laser-based combustion diagnostics can be found in [249-250].

3.11 Petrochemical industry

In order to optimize the yield of the final product, rapid sensors for hydrocarbons are needed by the petrochemical industry [144].

Ethylene (C_2H_4) [251] and propylene (C_3H_6) [252] can be probed by TDLAS, see also [144]. The determination of CO in hydrocarbons was demonstrated in [253].

The fence line monitoring of fugitive emissions of H_2S and NH_3 from refineries was reported in [4] and [254], respectively. The detection of explosive plumes by handheld devices and open path measurements (see below) is also used in petrochemical operations worldwide.

The trace water determination in olefins product streams is described in [177]. Moisture in the feed stream can cause discoloration of the product and poison the catalyst [177] and hence needs to be controlled.

In [94], TDLAS of acetylene (C_2H_2) and C_2H_6 (ethane) is described. TDLAS of 1,3-butadiene (C_4H_6) can be found in [252]. The TDLAS-based determination of H_2S up to 100% concentration is mentioned in [187] and detailed in [127].

VCSEL-based O_2 monitoring is also used in refineries, where oxygen is important in many processes such as fluid catalytic cracking or flow enhancement in oil and gas wells [191].

Flare gas explosion control by measuring the O_2 gas content is mentioned in [51].

The detection of trace water in the hydrogen recycle stream of a catalytic reforming unit is described in [177].

For an overview of where TDLAS can be applied in the petrochemical industry, see [255]. Examples include catalytic cracking (O_2, CO_2, CO), synthetic ammonia (O_2, CO_2, CO, H_2S, SO_2, CH_4, NH_3), urea synthesis (O_2, CO_2, NH_3), the Claus sulphur recovery process (O_2, H_2S, SO_2), phenol (O_2) and methanol production (H_2O) [255].

3.12 Chemical vapour deposition (CVD)

Chemical vapour deposition (CVD) is a process used for the deposition of thin films. To this end, the substrate is exposed to volatile precursors that, by reaction or decomposition, form the intended layer on the substrate. Purity is extremely important, since the layers often need to be flaw-less epitaxial or crystalline films.

The process is typically of the open-loop type, and optimization of process parameters is carried out based on lab characterization of the finished material [68]. Fig. 17 illustrates how the CVD process can be monitored by optical techniques (FTIR and TDLAS).

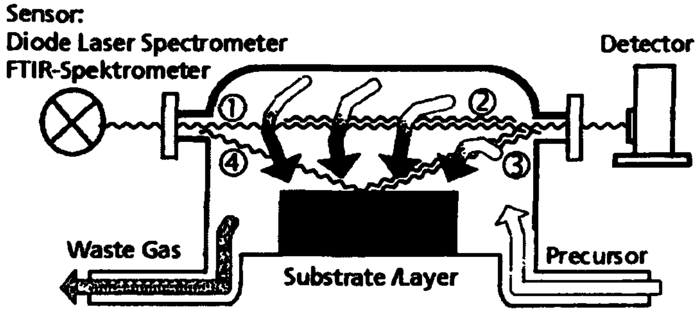

Fig. 17: Principle of optical monitoring in an industrial CVD process; (a) transmission; (b) emission of hot gases; (c) surface emission; (d) reflection. Reprinted from [68] with permission from Elsevier.

It is suggested to measure a reaction product where there is a strong correlation between its concentration and the process performance. In the CVD process, relatively small changes in yield can have a significant impact on economics [68]. In [256], TDLAS is used to characterize a CVD process for diamond growth.

More information on the use of TDLAS in CVD can be found in [257]. The semiconductor industry (see below) makes extensive use of CVD.

3.13 Semiconductor industry

Semiconductor component manufacturing involves delicate processes like CVD, photolithography and etching [258]. The purity of the process bulk gases used in those processes is of utmost importance. Typical bulk gases are N_2, Ar and He. For process control, a continuous measurement of the ultra high purity (UHP) feed gases is vital as discussed in [259]. The maximum contamination of the bulk gases with impurities such as O_2 and H_2O typically must not exceed 10 ppb, but requirements for purity can be as low as 1 ppb [260]. The impurities lead to undesirable defects on the wafers.

In [261], a low ppb-level for moisture and a low ppm-level for oxygen in inert gases at atmospheric pressure is given as instrument detection limit. In [260], a lower detection limit of 200 ppt for H_2O in UHP gases is claimed. Measurements were also done in pressurized gas lines at up to 5 bar. Progress in the *in-situ* contamination control by TDLAS in reported in [261]. Not only can the production process itself in terms of quality be improved, also the overall equipment effectiveness (OEE) can be optimized by TDLAS by cutting down the time for purging before production line start-up to the required minimum [262] (compare also Fig. 14). Moisture is a good tracer for atmospheric contamination and amongst the most difficult atmospheric impurities to remove. By measuring true contamination levels of water, rather than simply relying on pre-set timing, significant operability improvements in semiconductor operations can be achieved. Also, the percentage of non-product wafers can be reduced and trouble-shooting is facilitated [211].

A major advantage of TDLAS is that it is compatible with aggressive gases such as HCl, NH_3 and Cl_2 and also with strongly depositing atmospheres as in Si_3N_4 low pressure CVD [258].

In [163], the measurement of NH_3 by CRD is described to control the air in a wafer fabrication plant. NH_3 interferes in a disadvantageous way in the lithography process, so the CRDS-based sensor is used to monitor the performance of the NH_3 air filter.

The measurement of HBr in a plasma etch reactor is described in [263]. The measurement of HCl is detailed in [199]. For an overview about *in-situ* contamination control in the semiconductor industry, see [264].

3.14 Bioreactors

Process monitoring of bioreactors by TDLAS is described in [265]. The emissions from a bioreactor for water recovery in spacecraft, notably NH_3 and CO_2, were measured with a DFB laser in [20]. The detection limits were 0.25 ppm for NH_3 and 40 ppm for CO_2. A 45-h window of reactor performance under varying conditions is shown in that paper.

Less sophisticated, but more important in terms of number and emission flux are the numerous agricultural operations all over the world. Odorous emissions are seen increasingly critical by local communities, so emissions monitoring becomes more and more important. TDLAS can be used for this purpose. In [266] the measurement of emissions of N_2O and CH_4 during the composting of liquid swine manure was reported. In [267], NH_3 emissions from Canadian hog farms were measured using TDLAS in an open-path arrangement to find emission rates of 4.8-38.2 g $NH_3/(m^2{*}h)$ from the manure storage area.

3.15 Pharmaceutical industry

The pharmaceutical industry poses high demands on process and product quality. Process Analytical Technology (PAT) [268] has been defined by the United States Food and Drug Administration (FDA) as a "mechanism to design, analyze, and control pharmaceutical manufacturing processes through the measurement of critical process parameters and quality attributes". The aim of PAT is to continuously improve the production process. There are several examples of how TDLAS can be used in the pharmaceutical industry; Measuring trapped moisture or oxygen in sealed, transparent vials that could degrade the drug inside is discussed in [269]. In [270], the non-invasive determination of porosity in pharmaceutical tablets using tunable diode laser spectroscopy is described. The latter application is based on a derivative technology of TDLAS known as Gas in Scattering Media Absorption Spectroscopy (GASMAS) [271]. In this work, the porosity of solid pharmaceutical tablets is determined by using the fact that oxygen is dispersed in the material; a comparison with mercury based porosity measurements was performed. [272] and describes the identification of pharmaceutical agents by infrared spectroscopy.

A water sensor for the control of a lyophilization process (freeze drying) in the pharmaceutical industries is described in [5]. By measuring the water vapour concentration and the gas velocity, the mass flux of H_2O is determined.

3.16 Safety

Clandestine carriage of explosives has recently become a major concern to the transportation industries. Most explosives such as trinitrotoluene, hexogen, octogen and tetranitropentaerithrite are subject to slow decomposition also at room temperature, the most prominent decomposition products being NO and NO_2. The required sensitivity in order to be able to detect hidden explosives is approx. 10 ppb [273]. This sensitivity can be reached by using diode lasers at 635-670 nm in conjunction with a long multi-pass cell as discussed in [273-274]. Early fire sensing by tracing CO, CO_2, HCN and C_2H_2 [56], the investigation of novel fire extinguishing techniques by tracking O_2, CO and H_2O concentrations [194] and the detection of O_2 in potentially explosive atmospheres [195] are other safety-related applications of TDLAS (see also the CH_4 leak detection discussed in this review).

3.17 Automotive industry and engines

Interesting applications of TDLAS in the automotive industry include sensors for O_2 for test beds [275] and CO for remote sensing [276].

In [277-279] a remote cross-road sensor for vehicle emissions of nitrous oxides is described.

In [280], it was possible to determine the oil consumption at steady-state engine operating conditions from the oil-derived SO_2 emissions in the automotive exhaust gases. In [281], it is described how ethanol in the air of passenger cars can be detected by remote sensing on the highway for better driving law enforcement.

In [282-284] in-cylinder gas temperatures are measured using TDLAS.

Gas turbine combustors are operated at high pressure (up to 50 bar) for high efficiency and in ultra-lean combustion mode for low NO_x emissions. Those operating conditions can move the gas turbine into unfavourable stability regimes, resulting in engine damage or flame blow-off [136]. A sensor to measure critical engine performance parameters for a closed-loop control system is needed for advanced device control. Such a sensor, despite its need [285], is not yet available. In [286], a sensor to measure exhaust gas temperatures in a gas turbine is described. Another piece of work characterizing gas turbine exhaust gas using a QCL is discussed in [287]. Gas turbine efficiency increase and blow-out prevention is described in [57].

An HCCI engine was probed by TDLAS in [288-289], a scramjet combustor in [290-291].

TDLAS sensing and adaptive control of a pulse detonation engine is described in [292-295].

The air flow entering into a jet engine is measured by sensing the velocity and density of the oxygen in the incoming air in [296]. TDLAS has further been used for the investigation and control of aero engines [297].

3.18 Other industries and species

The use of TDLAS in safety systems in hazardous waste and solvents destruction plants is mentioned in [51]. In the food industries, oxygen has to be kept away from perishable products. This is frequently done by filling the food container with nitrogen and using plastic enclosures or films. This is normally done for meat packaging, for example. It is possible to control the quality of oxygen seal-off from food packages and drinking bottles by

TDLAS [298]. Oxygen exchange of fruits for storage and packaging optimization is discussed in [299]. TDLAS-based temperature and water concentration measurements in a glass furnace are described in [300]. The ppm-level concentration measurement of CO at 1573 K in a glass furnace is mentioned in [187].

In another application, TDLAS is used to characterize the heat insulating properties of windows with noble gases between the two glass layers in order to reduce heat conductance of windows [301]. Also, cigarette smoke has been analysed puff by puff using TDLAS to measure acrolein and 1,3-butadiene [302]. TDLAS-based analysis of cigarette smoke is also detailed in [303]. Based on GASMAS [271], the wood drying process was investigated in [304]. The literature also contains several examples of how TDLAS has been used in human healthcare, e.g. for breath analysis [305].

Acrolein was measured by TDLAS in [306], SO_2 in [307], PH_3 in [308], NO_2 in [309-311], NO in [312], CH_3Cl in [313], O_3 in [314], formaldehyde (CH_2O) in [315], hydrazine (N_2H_4) in [316], nitric acid (HNO_3) in [63], and oxirane (C_2H_4O) in [317]. The mapping of tracer gas concentrations in a large indoor space is described in [318]. In that work, TDLAS is combined with computer tomography and CH_4 is used as tracer. The temporal resolution was 7s, the spatial resolution 0.5m in the 7x9x11 m^3 large room. Air flux is measured by TDLAS in [319].

3.19 Handheld devices for TDLAS measurements

Leaks of methane from natural gas pipelines constitute a safety risk and must therefore be spotted early. Currently used leak survey tools comprise flame ionisation detectors (FID) and combustible gas indicators (CGI). They all have in common that the detector must be located within the gas leak plume in order to detect the leakage [320], requiring the operator to travel directly above the pipeline. A portable sensor for toxic and explosive gas sensing is described in [321-326].

These devices typically have an eye-safe laser (power <10 mW) illuminating a passive surface such as a wall or the ground behind the gas pipeline. From the reflected light, the presence or absence of the target species, most often methane, along the laser path can be determined. The technique is particularly advantageous if confined spaces or hard-to-reach areas have to be probed, resulting in time savings of typically 25-40%

compared to conventional gas leakage detection [320], which is substantial keeping in mind that large gas production fields and gas processing plants have several kilometres of piping and several hundred valves that can become a leak.

The device reported in [321-322] is battery-operated and has a standoff range of ~ 30 m. It can work continuously for an 8-h-day. It is based on differential absorption LIDAR using wavelength modulation spectroscopy. A similar instrument is described in [151]. A 1.65 μm DFB laser is used. Detection of the diffusely backscattered light, which is collected on a photo detector by a 120 mm diameter Fresnel lens to capture laser powers > 10 nW, is done using frequency modulation spectroscopy. The detection limit was determined as a 10 cm³/min gas leakage within a range of approx. 10 m. The receiver optics efficiency can be improved by a special cone concentrator [327]. In [328], a handheld unit for the simultaneous detection of methane and ethane is described.

3.20 Open path TDLAS measurements

In industrial processes, gases are often released as controlled emissions (stack emissions) or escape as fugitive emissions. Fugitive emissions tend to come from more than one source, so line-of-sight measurements are advantageous to point samples. By sending the collimated laser beam to a retro reflector and back, open path measurements can be carried out. In [57], an instrument with up to 8 measurement paths for 1 or 2 species (e.g. CH_4, CO_2, NH_3, HF) is reported. A basic scheme is depicted below in Fig. 18.

The instrument consists of a transmitter/receiver unit and a remote, passive retro reflector array. Alignment is facilitated by a parallel, visible aiming laser. Path lengths of 1 up to 1000 m were demonstrated for open path and across stack and duct measurements, with 100 m being typical [57].

Applications of installed open path TDLAS monitoring instruments include the fence line monitoring of NH_3 and H_2S emissions in a refinery [57], CH_4 leak detection [329] in gas processing plants and fugitive HF emissions from aluminium smelters [330].

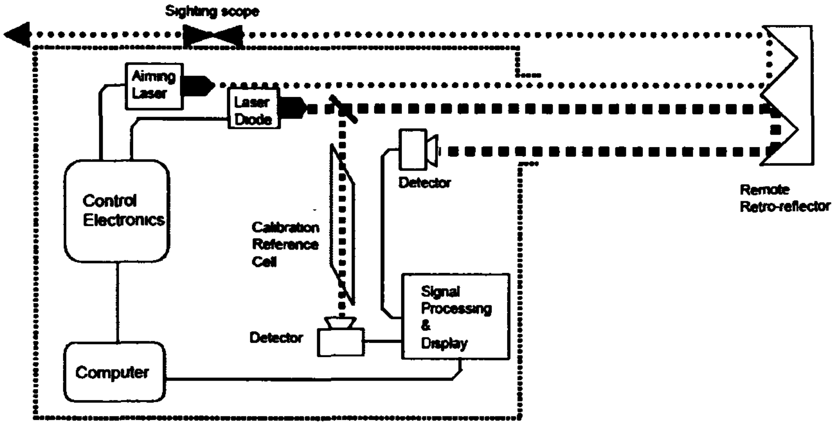

Fig 18: Scheme of open path gas monitoring with a retro reflector. Path lengths between 1 and 1000 m are possible. Reprinted from [57] with permission from Boreal Laser Inc.

3.21 Temperature and temperature distribution measurements

The line strength of any given absorption line is temperature dependent, so by measuring two absorption lines of a certain target molecule simultaneously, both its column density and the gas temperature can be determined, assuming a homogeneous temperature profile. This technique is referred to as two-line absorption temperature sensing as deployed in [35], [331].

In [18], the two-line absorption temperature sensing based on two H_2O lines with a single laser near 1.8 μm is described. By calculating the ratio of the two line intensities (of known temperature dependence), the temperature can be inferred. Another work describes the gas temperature determination using two distinct diode lasers at 1.343 and 1.392 μm, respectively [332]. The obvious advantage of using only a single laser is reduced system cost and complexity. Temperature determines the overall thermal efficiency of a combustion process and can therefore be used as input for a control circuit. Another temperature measurement by the two line technique is described in [333].

In [18], the laser is wavelength-scanned at 500 Hz to yield gas temperatures in the burnt-gas region of a C_2H_4/air flame of a laboratory burner for every scan (2 ms time resolution), which were compared to the readings from a type S thermocouple. The thermocouple had to be corrected for radiative heat loss, typically 50 K, as described in [334]. The temperature was measured as 1620 ± 30 K along the path. This was found to be 170 K (7%) below the true temperature. The reason for this deviation was the assumption of homogeneous conditions along the path (TDLAS delivers path-average results). As a trapezoidal-shaped temperature distribution was assumed, the TDLAS-derived temperature was 1760 K, only 20 K (1.2%) from the true temperature [18]. This example illustrates the limitations of the two-line absorption temperature technique in the case of non-uniform conditions along the beam path. In such a case, the use of multiple absorption lines is proposed. Oxygen lends itself for the determination of gas temperature distributions because it shows several closely spaced absorption lines that can be accessed using a single diode laser. This was demonstrated in [335] using a VCSEL. The measurement error scales with temperature and is given as 1.8 K at 400 K and 100 K at 1350 K in [35].

Low temperature determinations (333-353 K) and water partial pressures measurements in a proton exchange membrane (PEM) fuel cell using a 1.47 μm VCSEL are described in [336]. Rotational and vibrational temperature are distinguished and measured by TDLAS in [337].

3.22 TDLAS measurements at high pressure

To increase the detection sensitivity by reducing line overlap, extractive-sampling TDLAS instruments often operate at reduced pressure, especially when probing trace concentrations of the target molecule, see e.g. [97]. As discussed in the front section of this review, absorption lines are subject to pressure broadening. Many industrial processes operate well above atmospheric pressure, e.g. internal combustion engines or many power generation plants.

In [190], the *in-situ* determination of O_2 at pressures up to 10.9 bar was demonstrated along with a technique of data evaluation. The determination of water vapour at high pressure using TDLAS is discussed in [338-339]. Species concentration measurements at high pressure are of interest for gas turbine combustors [136] and engines [289], see also above. The following Fig. 19 shows the shape of an absorption peak of CH_4 at 2 bar and 20 bar, respectively, measured inside an optical engine.

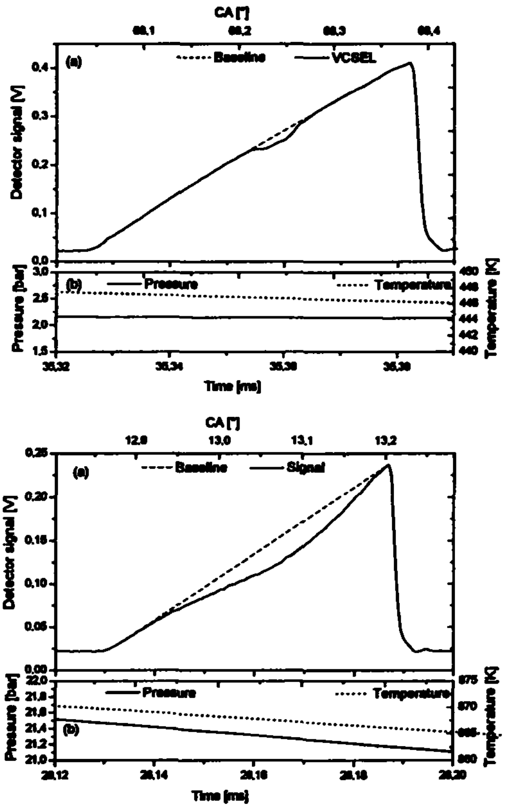

Fig. 19: Illustration of high-pressure CH_4 detection in an optical engine; Top: Peak of CH_4 at 2 bar and 445 K (engine running at 1000 rpm, 10% CH_4) Bottom: Absorption peak of CH_4 at 21.4 bar (engine running at 1000 rpm, 10% CH_4). Reprinted from [289] with permission from Haus der Technik e.V.

4 CONCLUSIONS

This article has reviewed the exciting and rapidly expanding field of tunable diode laser absorption spectroscopy (TDLAS) with focus on applications in the process industries. In TDLAS, the specific light attenuation of a probing laser beam is used to derive various flow properties of gases such as species concentrations, temperatures, pressure or velocity. By tuning the laser wavelength, non-specific effects can be compensated for so that *in-situ* measurements are feasible. In the NIR, compact, room-temperature operated diode lasers between 0.76 and 2.5 µm are frequently used to probe gases for e.g. O_2, CH_4, H_2O, CO, CO_2, NH_3, HCl and HF. In the MIR, where the more strongly absorbing fundamental bands are located, fewer suitable laser sources are available. For instance, detection limits for H_2O are 2 ppb in the MIR (5940 nm) and 60 ppb in the NIR (1390 nm), both at an absorbance of 10^{-5} over 1 m path length at 1 Hz band width. The availability of compact, reliable and cost-effective diode lasers has catalyzed the development of sensors for species concentration measurements, gas temperature, velocity and pressure for broad field use. With more than 1,000 units installed worldwide in plants, TDLAS has become an established technology for demanding measurement tasks. Although the technique has been used in research over the last 25 years, it has only been in the last years that TDLAS has found widespread use in industrial installations. It is assumed that 5-10% of all infrared-based gas sensors that are sold every year are already based on TDLAS, which is considered the best available technology for several demanding, industrial measurement tasks. For instance, the minimum detection limit of H_2O in NH_3 could be improved from 2 ppm to 50 ppb by using TDLAS instead of an FTIR instrument. This article presents a brief introduction to the method, detailing detection limits, laser sources, advanced detection techniques, related technologies and a comparison of TDLAS to conventional techniques. In the main section of this paper, several interesting applications in numerous industries are highlighted. First, after a few general remarks, the measurement of O_2, HCl, CH_4, H_2O, NH_3, HF, alkali atoms and temperature is discussed and reviewed besides a section on handheld and open path applications. Then, the use of TDLAS in several industries is described, ranging from steel and aluminium production to the semiconductor, pharmaceutical, automotive, petrochemical and other industries.

5 OUTLOOK

Tunable diode laser absorption spectroscopy can be considered a mature technology. In recent years, the proliferation of TDLAS-based instruments in the field has increased considerably. It is expected that the use of the technology in industrial applications will increase even more in the forthcoming years, due to improvements in economical and systems performance.

TDLAS applications need highly reliable laser diodes with high power with a wide continuous single mode tuning range and low frequency drift. In this area, laser development has made a tremendous development, and it can be assumed that novel lasers with even higher wavelength tuning range such as MEMS-tunable VCSELs [142], and more laser sources in the MIR like room-temperature operated, cw QCLs will appear on the market, accompanied by improvements in reliability, lifetime and costs. A recent piece of work on tunable MIR laser-based sensors can be found in [340]. MIR lasers allow more sensitive detection, whereas lasers with a broader tuning range make possible multiple species detection with a single laser. This means that a future instrument might be able to selectively detect several gases using a single laser, or to work as universal, cost-effective spectrometers. Improved performance will open up new fields of applications, whereas reduced costs will allow the replacement of conventional sensors by TDLAS-based ones.

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