Tunable Diode Lasers find their way to the factory floor

AIR MONITORING

Dr. Mikko Laakso, Samuli Laukkanen, M.S.c. (Eng.), Dr. Hannu Talvitie
Vaisala Oyj, PO Box 26, FI - 00421 Helsinki, FINLAND Tel: +358 9 8949 2604 Email:mikko.laakso@vaisala.com

In modern process analytics optical methods and technologies are used to measure a wide variety of parameters that describe the state of an industrial process. Practically all the ways in which light interacts with matter are utilized in the wide spectrum of instruments available today for optical analysis. Non-dispersive infrared (NDIR) and gas filter correlation (GFC) analysers operating in the near and mid-IR wavelengths have for decades been the workhorses for demanding industrial gas analysis. More refined spectroscopic methods such as FTIR (Fourier Transform InfraRed) and Raman spectroscopy provide analysis of multiple components with single measurement. A relatively recent addition to the family of optical IR gas analysers are analysers utilizing the unique properties of tunable diode lasers for gas analysis. This technique is often referred to as Tunable Diode Laser Absorption Spectroscopy (TDLAS), and the analysers are known as TDL gas analysers.

Optical methods are also used for the analysis solids and liquids. For liquid samples spectrophotometers measuring light absorption are used for quantitative chemical analysis, whereas diffraction and scattering of light are used for particle size and density measurements. Light refraction is in turn utilized in process refractometers measuring the composition of process liquids and slurries, to name a few examples.

Tunable diode lasers

Characteristic for tunable diode lasers as light sources is their extremely narrow spectral line width (FWHM ~ 0.05 pm) and wavelength tunability by laser temperature or operation current. A typical wavelength tuning range for a diode laser used for gas sensing is around 1 nm, which means that, as a rule of thumb, a few absorption lines of a single gas species can be scanned using the full tuning range of the diode laser. Furthermore, it should be noted that the linewidth of the diode laser is several tens of times narrower than that of a typical absorption line, which means that the lasers can be used for meaningful determination of absorption line shapes and intensities. Figure 1. illustrates the spectral characteristics of a tunable diode laser in comparison with a sample gas absorption line.

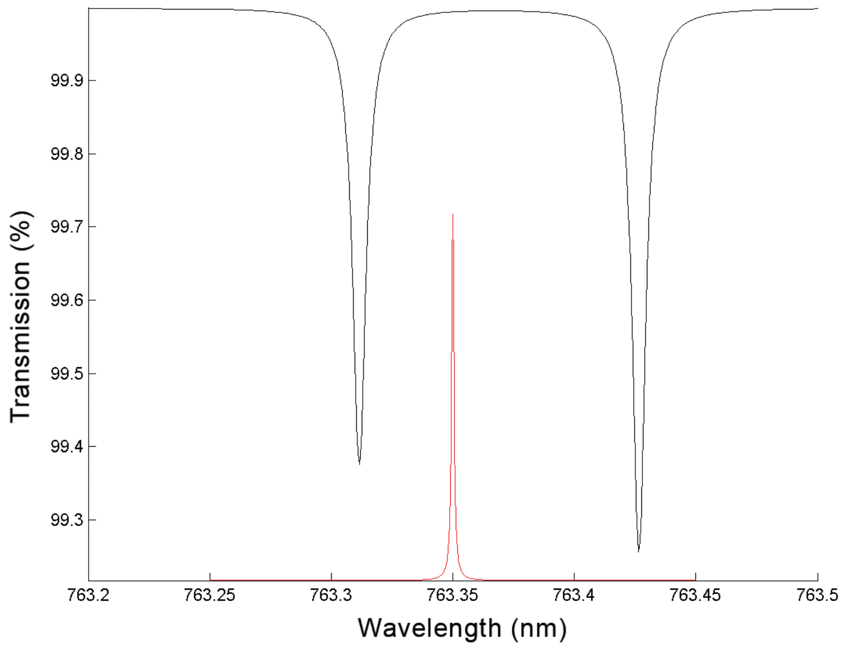

Figure 1. Typical emission line spectrum from a tunable diode laser and some oxygen absorption lines in the near infrared.

From a historical standpoint the use and applicability of TDLAS for analytics has evolved hand in hand with semiconductor diode laser component development. Already some 10 years after the invention of the semiconductor diode laser in the early 1960's the first gas spectra were recorded in the laboratory using a diode laser as light source, but it wasn't until the advent of the first tunable room temperature single mode lasers known as distributed feedback (DFB) lasers in the early 1980's that field applications could be envisaged. After some 5-10 years of technology maturing the first bulky commercial analyzers appeared in the marketplace. At the same time, in the late 1980's and early 1990's, already a new laser technology was emerging. Thanks to their vertically layered structure the new Vertical Cavity Surface Emitting Lasers (VCSELs) are better compatible with planar processing techniques used in IC manufacturing and hence better suited for mass production.

Today the single mode VCSEL technology development is strongly driven by the use of VCSEL lasers in telecom and datacom applications and optical mice, and the TDLAS gas sensing applications have proved to be a fruitful niche blooming under the auspices of telecom component development. Thanks to the high volume manufacturing practices that have been taken into use for communications lasers the cost structure and reliability of sensing VCSELs are at a level that makes their use possible in a whole new range of products: compact industrial transmitters whose performance equals that of costly analysers.

Measurement principle

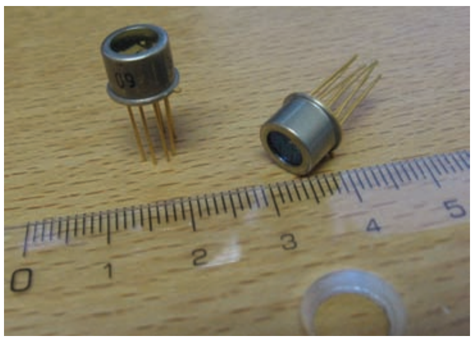

Figure 2. VCSEL component packages for gas measurements.

In comparison, NDIR gas analysers and TDL gas analysers have both remarkable similarities and important differences. In both types of devices light from a radiation source is directed through a sample of gas being measured, and the intensity of light traversing the sample at a wavelength characteristic for the analyte gas is measured and analysed to obtain the concentration of a certain molecular species in the sample.

Another common feature in dual wavelength NDIR analyzers and TDL devices is the continuous reference measurement at a wavelength adjacent to the absorption wavelength of the measured gas. With intelligent use of the reference measurement the effects of obscuration of the optics by e.g. dust or dirt can be eliminated, and variations in the light source intensity compensated for.

A major difference between conventional NDIR analysers and TDL analysers is the bandwidth of the light used for the measurement. In an NDIR analyser this band is typically extracted from a wideband source such as a hot filament using an optical interference filter with bandwidth optimized to match the full absorption band of the analyte gas at the desired wavelength region. This bandwidth may be anywhere between 0.1 and 0.5 μm, depending on the gas being measured and on the chosen absorption band. In a TDL analyser, however, the measurement wavelength is defined by the extremely narrow linewidth of the tunable diode light source, and the measurement typically utilizes only one out of the multitude of peaks within an IR absorption band of a gas species. Figure 3. illustrates the spectral bandwidth differences of NDIR and TDL techniques.

Another significant difference in the NDIR and TDL techniques lies in the modulation frequency or speed of the wavelength modulation. Modulation techniques are often used to extract the weak absorption signal from a noisy background. Mechanical filter wheels that are mostly used in NDIR analysers rarely reach modulation speeds exceeding 1 kHz, whereas tunable diode laser wavelength modulation may be done up to a speed of 100 kHz. The tuning frequency has a direct effect on the noise of the measurement which is critical when small levels of absorption are being detected - the larger the signal frequency, the smaller the relative measurement noise can be made.

Thanks to the easy modulation and tuning of diode lasers a number of advanced methods can be used in a TDL device for spectroscopic detection of absorption peak intensity. In wavelength modulation spectroscopy (WMS) the wavelength is sinusoidally modulated via laser current with a frequency f across the absorption peak, and different harmonics (1f, 2f, etc.) of the measured intensity signal are recovered. In a further analysis it can be shown that the second harmonic signal is proportional to the concentration of the molecules being measured. Higher harmonic signals can be used for important auxiliary functions such as locking the laser wavelength to the desired absorption peak. Using this scheme a detection sensitivity of 10^{-5} in relative absorption can successfully be achieved.

A sensitive detection method is necessary for good resolution and low detection limit for the measured concentration. However, even more important factors in process control are accuracy, repeatability and reliability of the measurement instrument. These properties are affected by optical effects such as etalon interferences and laser feedback, and by the algorithm used for signal extraction. With a careful design of the optical gas sampling cell and detection algorithm the WMS technique can provide accurate results and robust operation for gas concentration measurements.

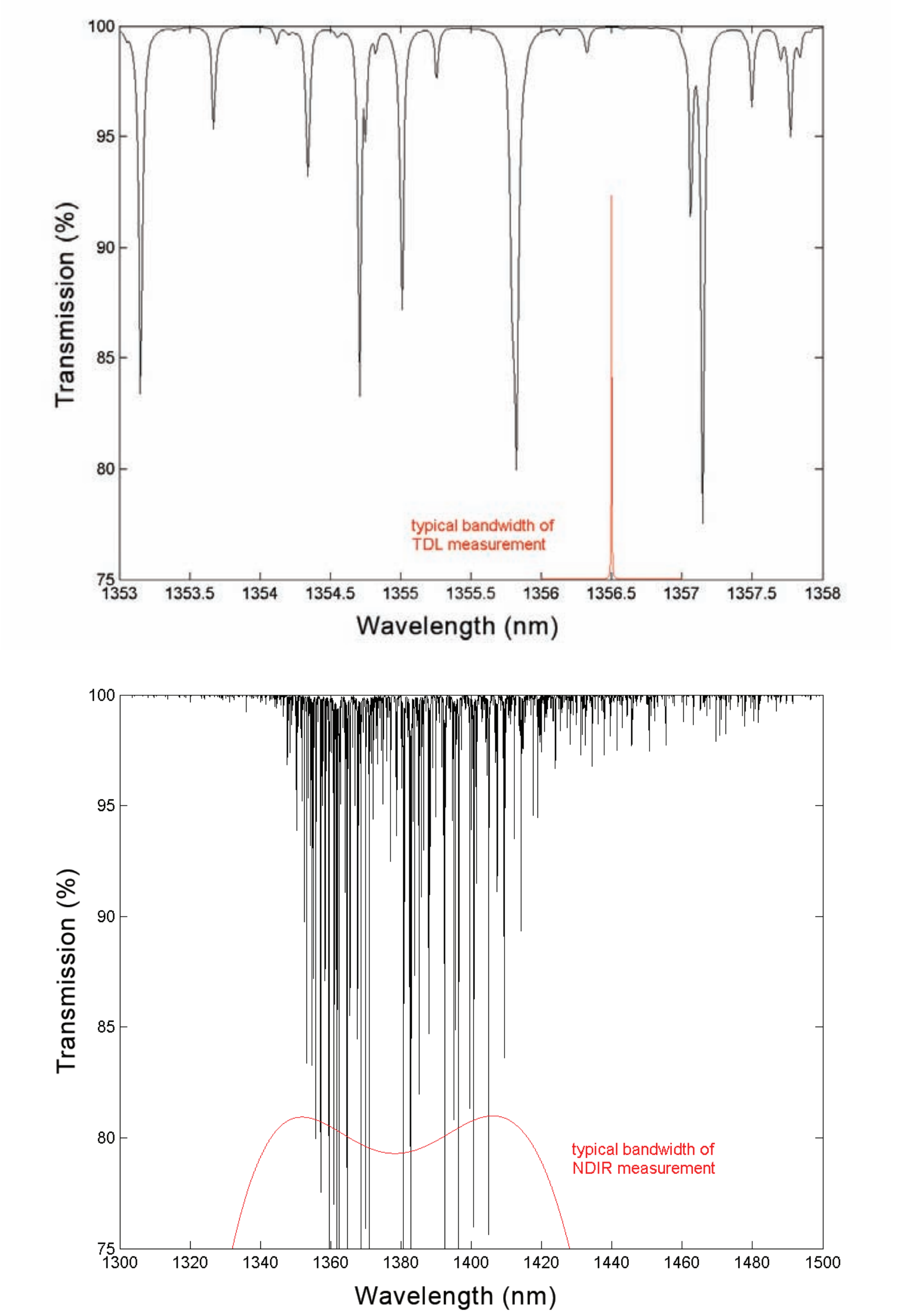

Fig 3a and Fig 3b: Spectral bandwidth differences of NDIR and TDL techniques, with the absorption spectrum of water as an example. Note the difference in wavelength axis scales.

Advantages and limitations of the TDL technique

Characteristic of a TDL gas analyser is that it contains no sample wetted sensitive chemical materials or moving parts, which means that the analyser can tolerate relatively severe process conditions even when the optical cell is inserted directly in-line for making an ideally representative gas measurement. Taking extra precautions to safeguard the optical path from obstructions and e.g. using optical fibers to transmit light to and from the process a TDL system can be used to make meaningful measurements even from the harshest industrial environments such as those encountered in industrial furnaces used in power generation and heavy metal industries.

The extremely narrow spectral bandwidth used for the measurement is the source of another significant advantage of TDL spectroscopy in gas sensing, which is its very good selectivity. For another gas to interfere with the measurement through unwanted absorption it would require that one of its absorption lines falls precisely in the narrow wavelength region where the TDL device operates. Due to the wide separation of the peaks this is improbable even if the interfering gas would happen to have an overlapping absorption band. In the exemplary case of oxygen , which is one of the most widely studied TDL analyte, its absorption band is practically free of any interfering absorptions which renders the measurement essentially free of interferences.

For anyone applying the TDL technology for gas composition measurements Mother Nature has also prepared some challenges to cope with. The line widths and shapes of the molecules are to a certain extent affected by collision interactions with the neighbouring molecules through an effect commonly referred to as collision broadening. This broadening of the absorption lines of a certain molecule is affected both by the absolute pressure of the gas and the properties of the neighbouring molecules. The effect of these two sources of broadening on the gas TDL concentration signal is theoretically quite difficult to resolve but can in practice often be done using a properly chosen measurement algorithm and experience from the process where the measurement is made.

Molecules that can be detected

As indicated earlier, the biggest development efforts and advances for reliable and tunable semiconductor diode light sources operating in room temperature have occurred in the near infrared (NIR) spectral region of 0.8 - 2.0 μm. From the gas species absorption viewpoint this is a regime where the absorption generally occurs through so called vibrational overtone or combination modes of molecules, as opposed to the fundamental band absorptions which take place in the mid-infrared (MIR) range of 2 - 20 μm. A further consequence of this is that the NIR absorption strengths are 2 to 3 orders of magnitude weaker than those occurring in the MIR range. Despite this there are NIR absorption bands and lines well suited for a wealth of applications for most of the gases of interest. Table 1. lists examples of gases, the location of their absorption bands in the NIR region and the minimum detectable concentration assuming a 1 m optical path and a state of the art electronics operating with 1 Hz integration time.

Table 1. Some gases with absorption bands in the NIR region, and their detection limits with a 1 m optical path length.

Molecule	Symbol	$\lambda(\mu m)$	ppm
ammonia	NH_3	1.5	0.8
carbon dioxide	CO_2	1.96	3.0
carbon monoxide	CO	1.57	30
		2.33	0.5
methane	CH_4	1.65	0.6
nitric oxide	NO	1.8	60
		2.65	1.0
nitrogen dioxide	NO_2	0.68	0.3
nitrous oxide	N_2O	2.26	1.0
oxygen	O_2	0.76	80
water	H_2O	1.39	0.06

When looking at the data in Table 1. a few notions should be borne in mind. Firstly, in a practical instrument the minimum detectable concentration cannot as such be interpreted to represent the noise in the actual output reading of the instrument. As a rule of thumb one might say that the noise of the whole instrument is some 5 times larger than the minimum detectable concentration indicated in the table. Secondly, in addition to the absorption strength of, say, the strongest absorption line in an absorption band of a said gas a number of other factors affect the applicability of the said line in a practical instrument. Among these factors are for example the line spacing of neighbouring major lines, presence or absence of small absorption features in the immediate vicinity of the line in question, width of the whole absorption band etc. All of these need to be taken into account in the instrument design.

A new generation TDL gas transmitter

An example of a new generation diode laser gas transmitter is the Vaisala SPECTRACAP® Oxygen Transmitter OMT355 for oxygen measurements in industrial processes. It introduces a novel optical path arrangement for a diode laser gas analyzer by having the optical measurement cell integrated inside an insertion probe that can be mounted directly inside a process vessel or pipe with a flange. The diode laser light source, associated optical components and the light detector are all mounted within the same rigid sensor structure, which completely removes the need for optical beam alignment. In the structure the light source and detector are positioned behind a protective window through which the light is introduced to the measurement cell, and reflected back through the same window onto a photodetector. This way it has been possible to construct a sensor where the wetted parts are made of chemically resistant materials such as stainless steel, optical glass and antireflective optical coatings. Using a sample cell the in-situ transmitter can be turned into a sampling analyzer of a more conventional type.

The new form factor for a tunable diode laser analyser makes it possible to utilize the stability and robustness of optical oxygen sensing in many applications where paramagnetic, zirconium oxide or electrochemical sensor technologies have traditionally been used.

Figure 4. Advanced optical gas measurements are particularly needed in the petrochemical and process industries.

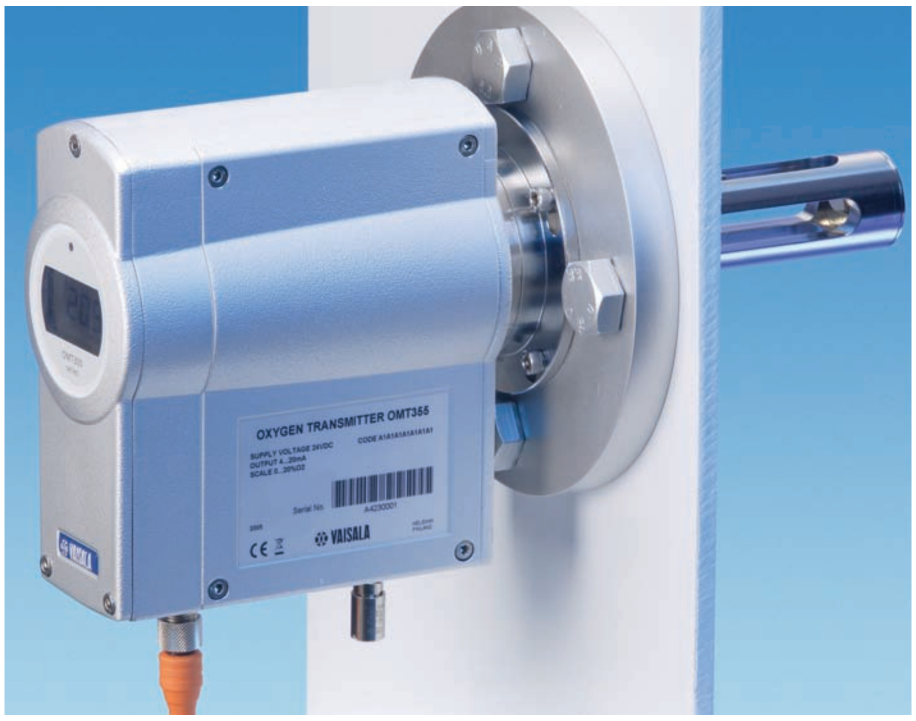

Figure 5. Example of a new generation diode laser based gas measurement instrument: The Vaisala SPECTRACAP® Oxygen Transmitter OMT355.