

A Compact Ruggedized Tunable Diode Laser Spectrometer for Oxygen Sensing

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ABSTRACT

Key results from the development work towards a compact ruggedized Tunable Diode Laser Absorption Spectrometer (TDLAS) and sensor for industrial gas analysis are presented. The optomechanical design of the sensor minimizes the unwanted interference and etalon effects as well as optical feedback to the diode laser light source. All sensor parts are of a compact design that makes it possible to fit the optical path inside an insertion probe of a reasonable size.

Main principles, advantages and limitations of the TDLAS technique will be briefly reviewed. Results from optical modelling and simulations of the sensor structure will be presented. Highlights and main results from the development work towards a measurement algorithm and electronics appropriate for a compact field instrument will be described. In the experimental part, the basic performance characteristics of the instrument will be shown with oxygen as the test gas. Furthermore the performance of the sensor and instrument for oxygen measurements in widely varying environmental conditions will be presented. Finally, the potential application areas for the instrument will be discussed.

INTRODUCTION

The use of optical absorption spectroscopy for gas detection has a long history. The use of tunable diode lasers as light sources has long been considered promising in optical absorption spectroscopy because of the many attractive properties of these lasers, such as small size and low power consumption. The emission wavelength of such a laser can be tuned by either direct heating or cooling of the laser chip via a heatsink or by varying the injection current used to drive the laser. The use of narrow-linewidth tunable semiconductor lasers provides many benefits over other (optical) measurement techniques: a freedom from spectroscopic interferences from other molecular species, high sensitivity, a wide dynamic range of over four orders of magnitude, fast

sub-second response times and immunity to poisoning. However, the strict requirements set for the operation wavelength and single-mode operation across the tuning range have limited the availability of suitable lasers for spectroscopic applications.

While the strong absorption bands of most atomic and molecular species are found in the mid-infrared (2.5-50 μm) range, semiconductor laser diodes in this region are not commercially available. However, it is often possible to find a weaker molecular transition in the visible or near infrared, where semiconductor lasers do exist. The availability of III-V based diode lasers at near-infrared wavelengths has accelerated the adoption of lasers for optical gas sensing. In particular, single-mode tunable edge-emitting distributed feedback (DFB) laser diodes developed for telecommunications applications in the 1.3 and 1.55 μm wavelength ranges have been used for sensing of various molecular species, such as CO_2 , NH_3 and CH_4 [1-3]. A DFB laser that emits near 760 nm has been demonstrated also for the detection of O_2 [4]. However, to achieve single-mode operation across the whole tuning range the preparation of DFB laser chips requires complicated and hence expensive production steps. Furthermore, due to their edge-emitting nature, the packaging of the DFB lasers is relatively complex and expensive.

Vertical-cavity III-V surface-emitting lasers (VCSELs) combine many attractive spectral and other properties. Unlike edge-emitting lasers, since the effective cavity length of VCSEL is typically only the order of one wavelength, the longitudinal mode spacing is so large that single-longitudinal-mode operation is ensured intrinsically. Other favourable properties of VCSELs over DFBs are low divergence, a circularly symmetric output, and fast wavelength tunability due to rapid thermal response. Additionally, simple and low-cost manufacturing and packaging methods make the commercial exploitation of VCSELs feasible in industrial spectroscopic instruments.

The basic tunable diode laser spectroscopy setup for gas sensing is straightforward. The laser light passes through the measured gas onto a photodetector. Due to the very narrow spectral line width of the laser (FWHM ≈ 0.05 pm) compared to the width of a single absorption line (FWHM ≈ 5 pm), the tuning of laser wavelength across the absorption spectrum (Figure 1) or one peak creates the fingerprint of the selected gas, which can be used to either identify a molecule or determine its concentration. For molecules having weaker absorption features, modulation of the wavelength during step-like tuning is a commonly used method for improving the detection sensitivity of optical spectroscopy measurements. In this technique, the sensitivity of measurement is increased by modulating the laser wavelength across the absorption line. When the gas absorbs the light, it converts the wavelength modulation into a synchronous amplitude modulation. When the laser wavelength is modulated at a relatively low frequency (<50 MHz), this method is usually referred to as wavelength modulation spectroscopy (WMS) [5].

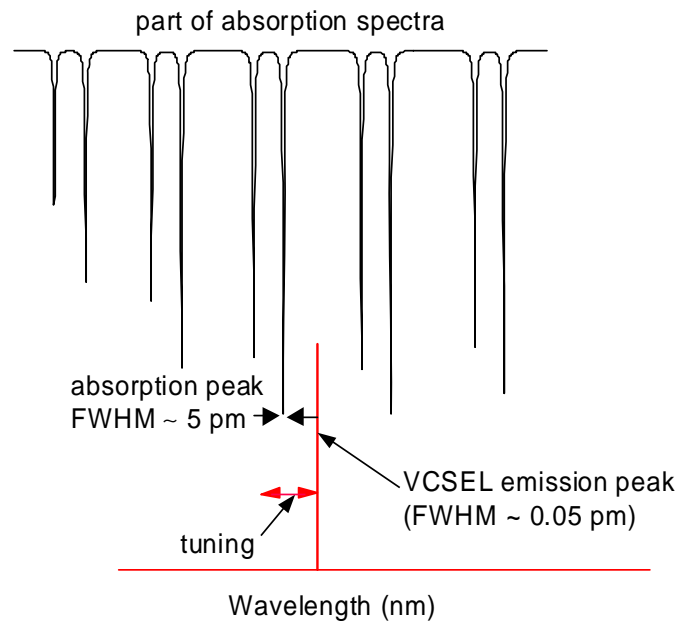


FIG. 1 - An illustration of a TDLAS measurement.

Figure 2 illustrates the effectiveness of the modulation technique. In Figure 2a the intensity and the wavelength of laser light increases linearly beyond the laser threshold current. Due to relatively weak absorption peaks, only shallow dips in the linear portion of the light intensity curve can be seen. However, these almost negligible dips can be recovered by using the WMS technique. In this method, the signal is multiplied in-phase by a sine wave signal of twice the modulating frequency resulting in the second derivative of the output signal ($2f$) (Figure 2b). Similarly, a third derivative ($3f$) can be calculated. The $3f$ signal can be utilized, e.g. for peak locking purposes, in order to avoid the need for a continuous high-resolution sweep across a wide current range.

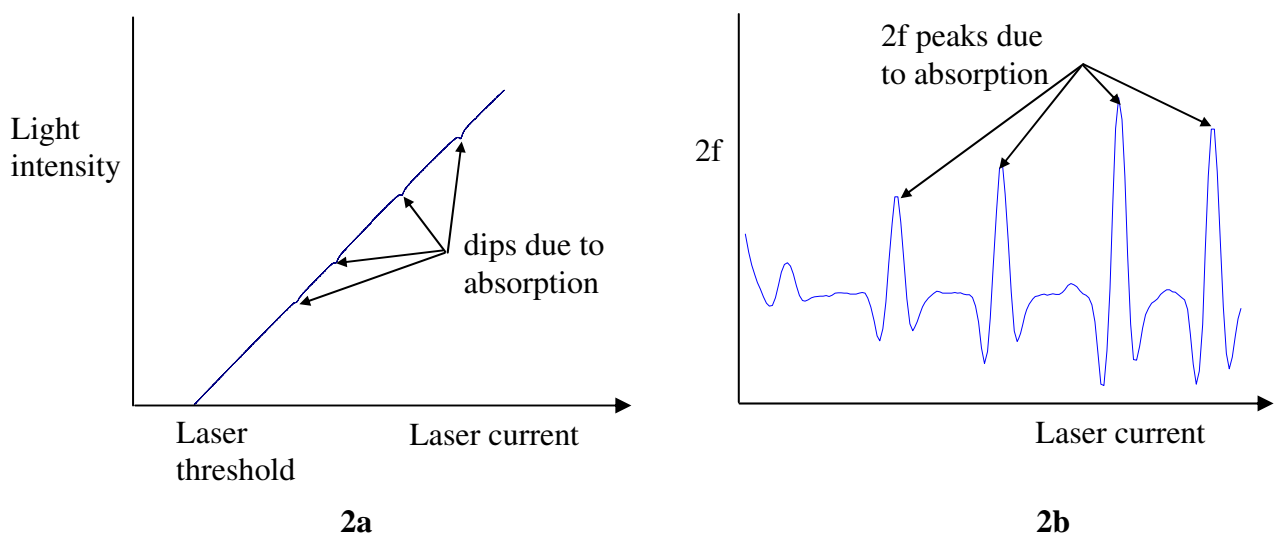


FIG. 2 - Recovery of shallow absorption peaks by applying the method of wavelength modulation spectroscopy (WMS). 2a - Modulation caused by absorption in the transmitted intensity. 2b - The corresponding $2f$ signals.

An alternative method for WMS is frequency modulation spectroscopy (FMS), where laser is modulated at a radio frequency [5]. FMS is more complicated than WMS, but is usually also more sensitive, because laser and system noises are lower. Yet another method is a variation of FMS known as two-tone frequency-modulation spectroscopy (TTFMS) [6]. It consists of laser modulation at two separate radio frequencies and detection of the generated signal difference between these two frequencies. TTFMS is an attractive technique when monitoring broadened absorption peaks at high pressures.

DESCRIPTION OF THE SPECTROMETER

The absorption spectrum of oxygen is shown in Figure 3. It consists of about 40 distinguishable lines in the wavelength range of 759 nm to 767 nm. The normal ambient oxygen concentration of 21 % O₂ together with an optical path length of 1m results in an absorption of 2.5% for the strongest lines, as shown in Figure 3. On the other hand, an absorption level on the order of 1 10⁻⁵ is roughly the detection limit for a TDL based system utilizing the WMS signal extraction method.

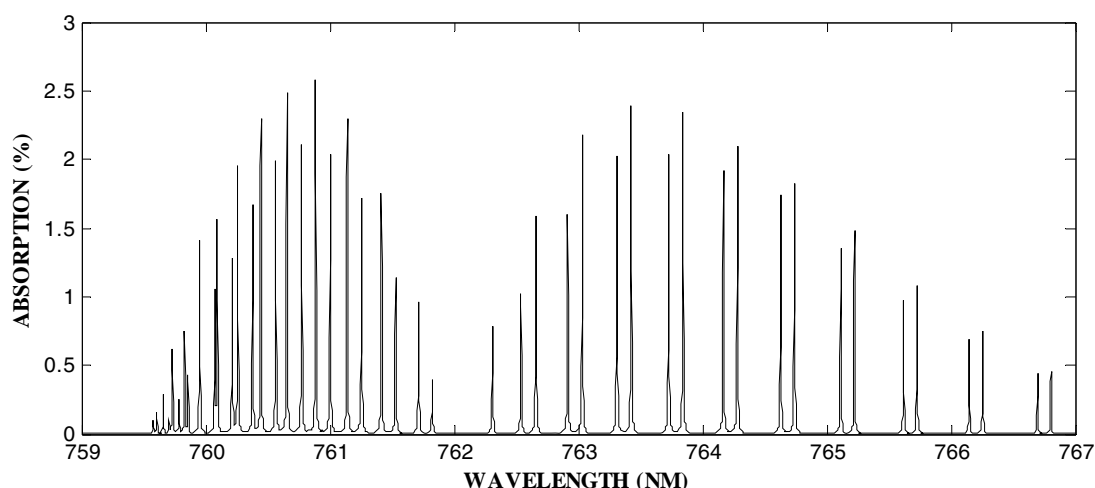


FIG. 3 - Absorption spectrum for O₂, calculated with 21 % O₂ and 1 m optical path length.

The optical path length of a TDL spectrometer is chosen based on the strength of the absorption lines to be measured together with targeted accuracy and detection limit values. In this paper, an oxygen spectrometer with a 30 cm optical path length and having an accuracy on the order of 0.2 %O₂, is presented.

Optical design of the spectrometer is one of the key issues in developing a rugged device for demanding environmental conditions. In the design presented here, special attention was paid to eliminate interferences and optical feedback to the laser. Interference effects are caused, for example, by reflections between parallel optical surfaces or by scattered stray light finding its way to the photodetector. Both interference effects and feedback to the laser cause intensity variations in the detected signal, which can significantly decrease the stability and accuracy of the measurement. In practice, interferences caused by reflections from a distance of a few centimetres will be most problematic, because their period is comparable to the modulated O₂ signal.

Interference and feedback problems can be greatly reduced by careful design of tilt angles, reflected light analysis, stray light control and apertures. A modern optical design program facilitates the design task significantly.

The spectrometer was developed in a probe-like design. It consists of collimating optics, a window and a top mirror for a single reflection back to the detector. With such a design, the wetted parts of the sensor can be made of stainless steel and optical glass, a fact that ensures good tolerance against a variety of process environments. A picture of the spectrometer mechanics together with ray tracing is shown in Figure 4a, and Figure 4b shows a detail of a ray reflection from the top mirror. A picture of the complete spectrometer is shown in Figure 5.

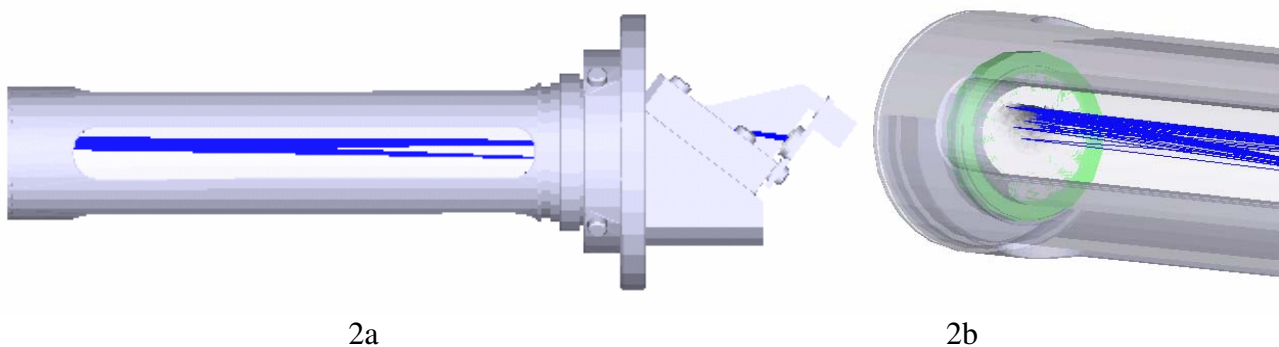


FIG. 4 - A picture of the spectrometer mechanics and optical path (2a), and detail from the top mirror ray distribution (2b).

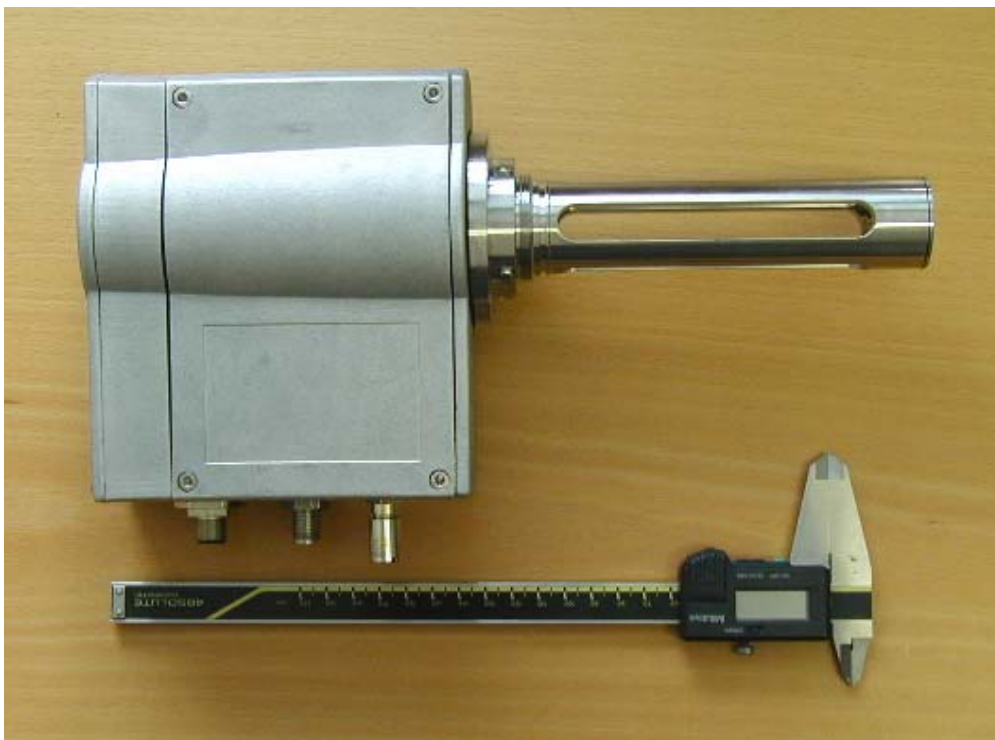


FIG. 5 - A picture of the oxygen transmitter, consisting of the spectrometer probe and associated electronics.

LABORATORY TEST RESULTS

In this chapter, some laboratory test results are shown to describe the typical performance of the spectrometer.

Figure 6 shows oxygen concentration and linearity measurements for nitrogen and two precise bottled concentrations of 4.95 % O₂ and 21.1 % O₂. By plotting the measured values as a function of known gas concentration, it can be seen that the measurement is relatively linear (Figure 6b). This is mainly due to the weak (and hence linear) absorption of O₂. A small, typically polynomial, linearity correction could be used to ensure good linearity up to 100 %O₂ and is easily implemented in the software of a functional instrument.

Looking at Figure 6a, it can be seen that the hysteresis behaviour of the device is very good. This is a general advantage of optical gas measurements, where hysteresis is mainly determined by how the mechanical structure of the device allows gas to diffuse in the measurement geometry.

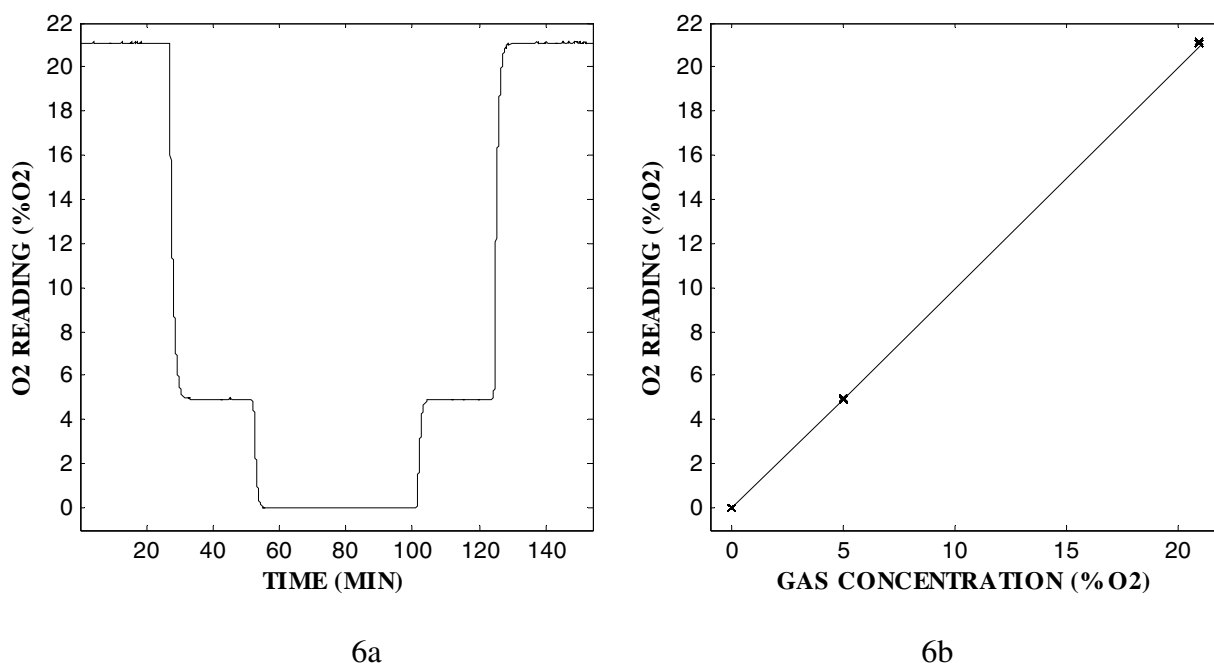


FIG. 6 - Oxygen response (6a) and linearity (6b) measurements.

An example of the temperature dependence of a non-compensated O₂ measurement is shown in Figure 7. The result is only indicative, since the change in absorption over temperature is different from one oxygen absorption line to another, and the net temperature dependence as depicted in Figure 7a is the combined effect from the ideal gas behaviour and the temperature dependence of the absorption strength of the line being used. Temperature dependence is relatively high and requires a temperature compensation, which can be done, for example, with a temperature sensor, or with more advanced algorithms involving measurements at more than one absorption line. The graph in Figure 7b shows that the temperature dependence is linear, suggesting an easy compensation in software once the gas temperature is known.

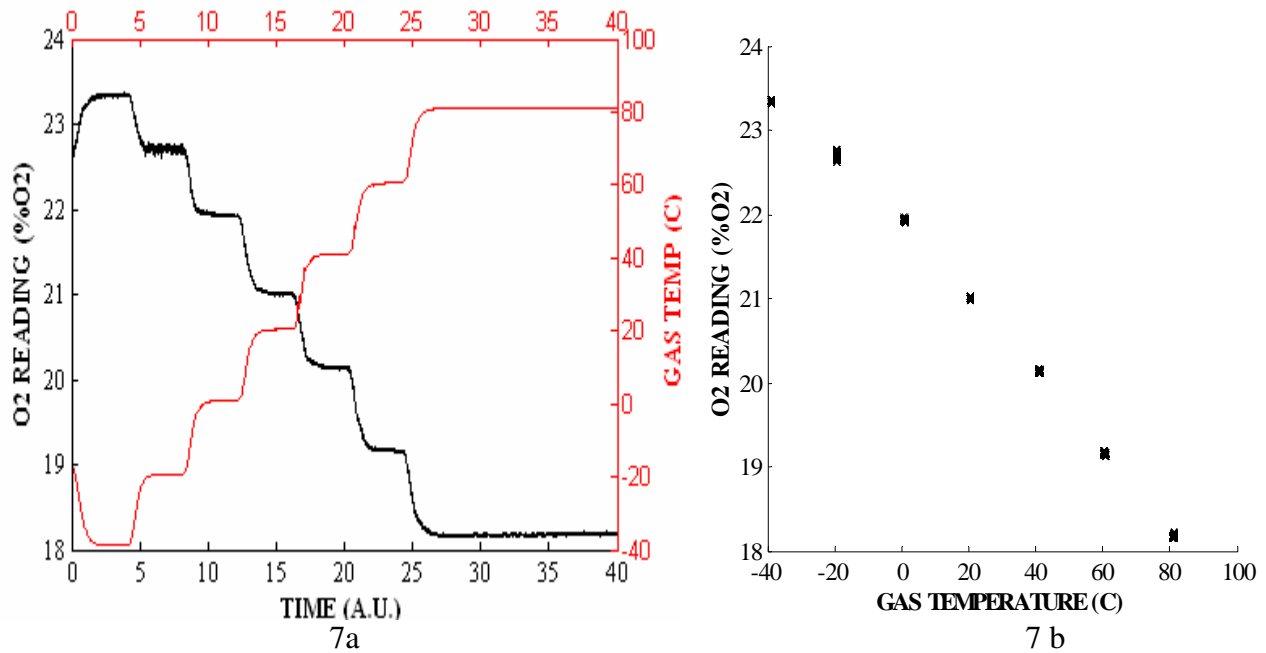


FIG. 7 - Temperature dependence of a non-compensated O₂ measurement.

Pressure dependence is shown in Figure 8 for a measurement of 20 % oxygen concentration. The end result is a combination of the ideal gas law and the pressure broadening effect of the absorption line as it effects the WMS signal extraction algorithm. For true concentration measurements in varying barometric pressure these effects can be tuned to compensate each other so that in a limited pressure range of, say, 0.8 to 1.2 bar, the change in measured signal is within 2 % of the reading.

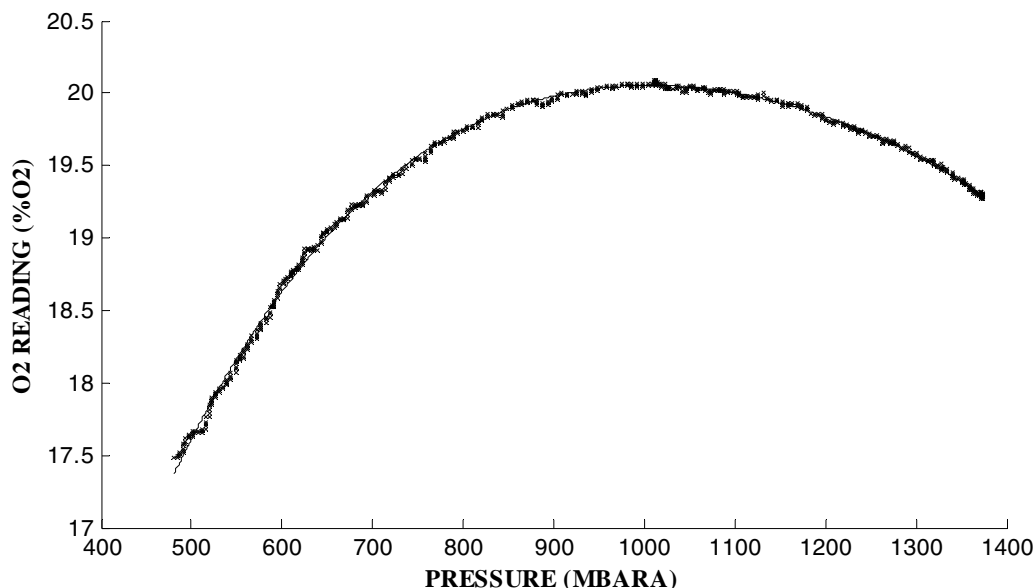


FIG. 8 - Pressure dependence when measuring a concentration of 20 % O₂.

Figure 9 shows the measurement result for a flow speed dependence test, indicating no dependence on flow speed over a relatively large flow range of 0 to 50 m/s.

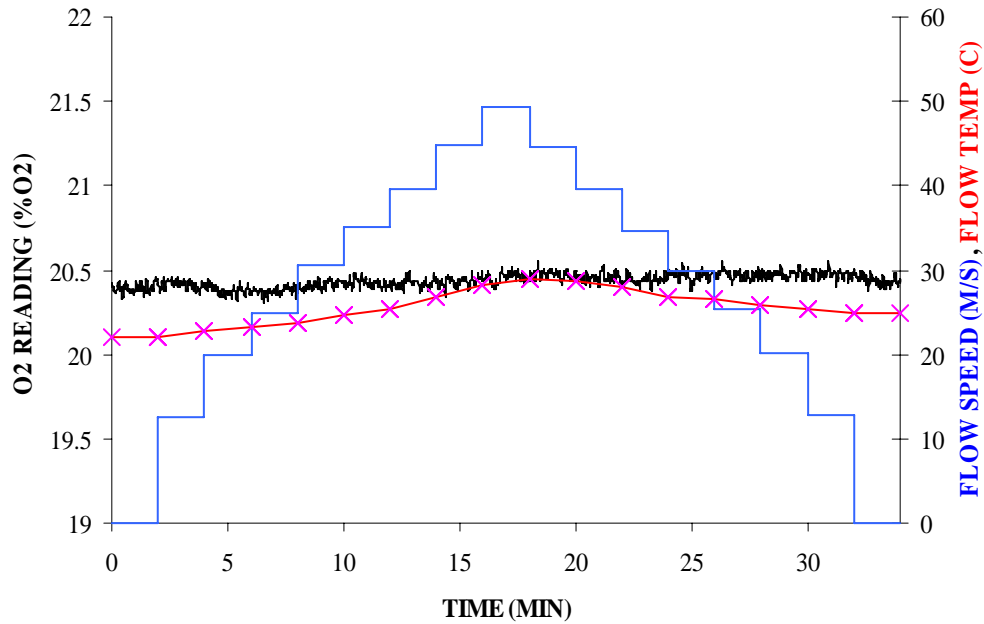


FIG. 9 - Flow speed dependence test for gas flows of 0 to 50 m/s.

Figure 10 shows an extraction of two weeks of data at 20.9 % O₂, demonstrating medium-term stability, or repeatability of the device. No net drift is observed and the level of fluctuations is well within the design limit of 0.2 % O₂. Medium term stability is mainly determined by optical performance of the design (possible interferences etc), whereas long term stability for periods of years is dependent on laser aging characteristics. Calculations based on laser aging characteristics during accelerated aging tests indicate a long term stability of 0.1 % O₂ / year @ 21 % O₂.

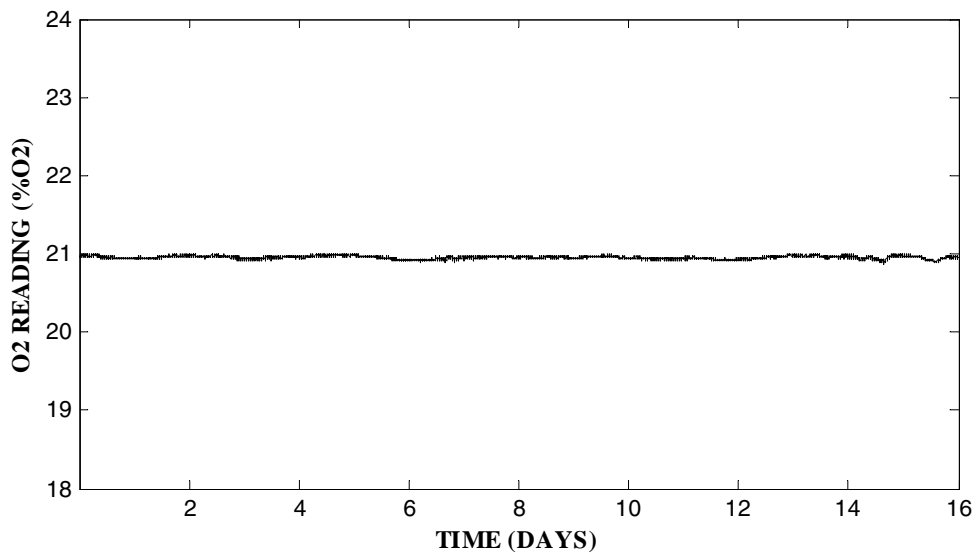


FIG 10 - Stability run for two weeks.

FIELD TEST RESULTS

To verify the operation of the spectrometer in real life conditions, a number of field tests were conducted in different types of processes. Experiences of two of these field tests are described here.

The first field test took place in a pharmaceutical factory where pharmaceutical end products in the form of powders are separated from a typical solvent based liquid solution in a large industrial centrifuge. In order to reduce the explosion hazard of the process with large amounts of solvent vapours present, the centrifuge and associated pipes and tanks are blanketed with nitrogen to reduce the oxygen concentration below the LOC (limiting oxygen concentration) value, suppressing combustion. The prototype oxygen spectrometer was installed in the headspace of a buffer solvent tank where the solvent from the centrifuge was pumped when the centrifuge was in operation. The tank and the surroundings are classified as a hazardous areas, so special measures were taken to make the installation, albeit a temporary one, safe.

The prototype spectrometer probe was mounted horizontally through the tank wall with a flange mount so that the probe protruded inside the tank headspace. A stainless steel mesh filter was used to protect the probe from particulates, and a simple splash guard was used to protect the probe from excessive solvent splashes. During the test, the probe was exposed to a variety of different solvents used in the process, and to fast temperature ramps caused by rapid introduction of solvents with temperatures up to 60 °C in the tank.

The oxygen concentration inside the tank was logged throughout the 6 month period that the probe was mounted in the tank. Figure 11. shows an extraction of 10 days of data. Instances when the centrifuge is in operation and the nitrogen blanketing flow is switched on are clearly visible. After 6 months of operation in the solvent tank the instrument did not show significant drifting of reading, or fouling of the parts exposed to the process.

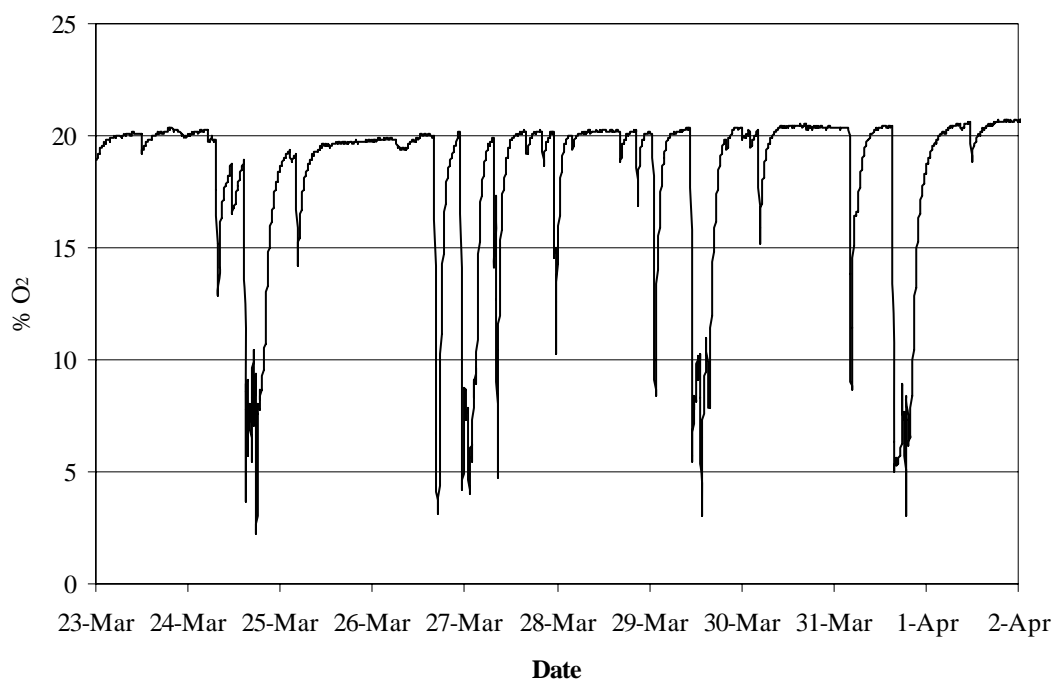


FIG. 11 - O₂ concentration during a 10 day period in the solvent tank. Low O₂ values indicate when the nitrogen blanketing has been in use.

A second field test took place in a chemical manufacturing facility where oxygen concentration from a mixture of fresh air and oxygen poor recirculation gas after an oxidation reactor is measured to control the oxygen concentration in the gas that is injected back to the oxidation reactor. The spectrometer probe was installed directly in-line after a recirculation pump, and the readings were compared with a paramagnetic analyser installed in an extractive configuration with a sample treatment system ensuring that the sample gas conditions are suitable for the analyser.

Figure 12 shows oxygen readings during a 5 month period in the recirculation gas, as measured with the paramagnetic reference analyser and the spectrometer probe. The readings follow each other with good correlation and a more thorough analysis indicates that in roughly 50 % of the measurement points the readings are within 0.2 % O₂ of each other, and 95% of the points are within 0.5 % O₂ of each other. Keeping in mind that both instruments have their associated errors, and that barometric pressure fluctuations have an effect on the reading of the paramagnetic analyser, this is a relatively good result.

Even though permanent fouling was not observed in this test, some level of dirt accumulation on the optical surfaces of the spectrometer probe was observed. During the total 6 month period, the DC light intensity measured by the photodetector was observed to drop by 35 %, but since the measurement algorithm compensates for variations in the DC light level this had no effect on the oxygen reading. In this test only a coarse (100 μ m) stainless steel mesh filter was used to protect the spectrometer from dirt, and significantly better protection has been observed in later tests by, for example, using microporous PTFE filters.

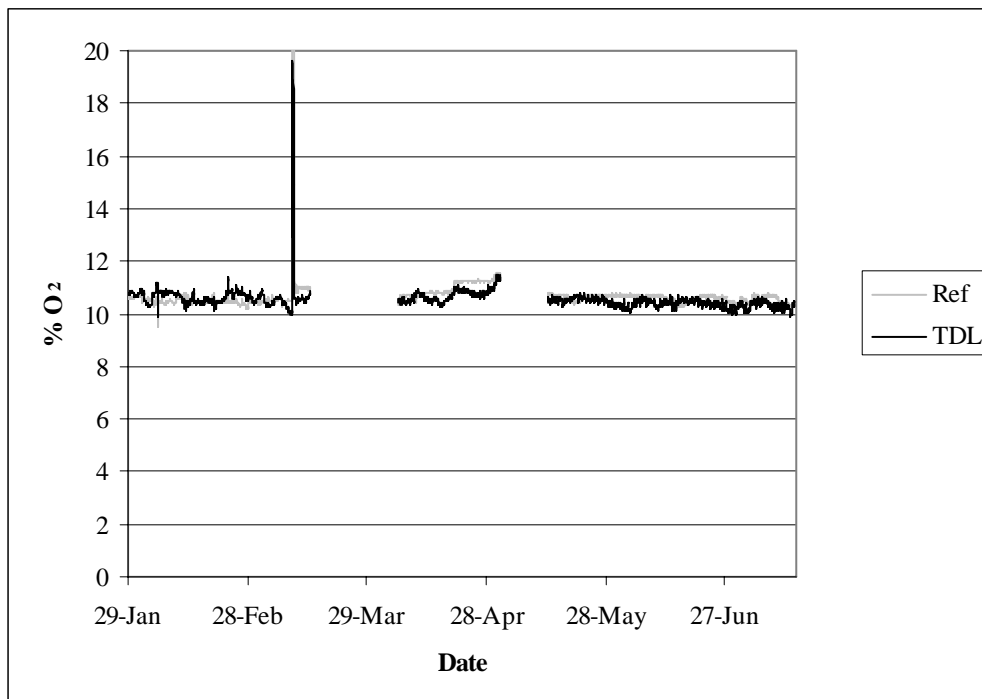


FIGURE 12 - Oxygen readings in a chemical process recirculation gas during a five month period. Readings from a reference paramagnetic analyser and the spectrometer probe are shown.

SUMMARY AND CONCLUSIONS

The feasibility for the use of a compact TDL spectrometer for oxygen sensing has been demonstrated both with laboratory testing and in field tests in industrial processes. With careful optical design and using an optimized implementation of a WMS measurement algorithm the oxygen concentration can be measured with an accuracy of 0.2 % O₂ in real life conditions with a compact instrument. Chemical and environmental tolerance, as determined by the materials used in the spectrometer construction, has been found to be sufficient for in-situ measurements in a wide variety of industrial processes. Electrical and mechanical parts of the prototype spectrometer have been designed for industrial manufacturing, which suggests that the design can be transferred to mass production.

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REFERENCES

- [1] V. Weldon, J. O'Gorman, P. Phelan, J. Hegarty, and T. Tanbun-Ek, "H₂S and CO₂ gas sensing using DFB laser diodes emitting at $\lambda = 1.57 \mu\text{m}$ ", Sens. Actuators, B29, 1995, 101.
- [2] A. P. Larson, L. G. Sandström, S. Höjer, H. Ahlberg, and B. Broberg, "Evaluation of distributed Bragg reflector lasers for high-sensitivity near-infrared gas analysis", Opt. Eng., 36, 1997, 117.
- [3] V. Nagali, S. I. Chou, D. S. Baer, R. K. Hanson, and J. Segall, "Tunable diode-laser absorption measurements of methane at elevated temperatures", Appl. Opt., 35, 1996, 4026.
- [4] C. Corsi, M. Gabrysch, and M. Inguscio, "Detection of molecular oxygen at high temperature using a DFB-diode-laser at 761 nm", Opt. Commun., 128, 1996, 35.
- [5] D. S. Bomse, A. C. Stanton, and J. A. Silver, "Frequency modulation and wavelength modulation spectroscopies: comparison of experimental methods using a lead-salt diode laser", Appl. Opt., Vol. 31, 6, February, 1992, 718.
- [6] D. E. Cooper, and R. U. Martinelli, "Near-infrared diode lasers monitor molecular species", Laser Focus World, November, 1992, 133.

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