

Gas monitoring in the process industry using diode laser spectroscopy

I. Linnerud, P. Kaspersen, T. Jæger

Norsk Elektro Optikk A/S, Solheimv. 62 A, P.O. Box 384, N-1471 Skårer, Norway
(Fax: +47 67 97 49 00, E-mail: ivar@neo.no; peter@neo.no; tycho@neo.no)

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Abstract. Gas monitors for industrial applications must have high reliability and require little maintenance. Monitors for in-situ measurements using tuneable diode laser absorption spectroscopy in the near infrared, can meet these requirements. A brief description of monitors using high-frequency wavelength modulation spectroscopy with second-harmonic detection is presented. Some problems related to industrial applications are discussed, in particular line broadening effects, and frequency drift of diode lasers. Typical applications for monitoring of O₂, CO, NH₃, HCl and HF are described together with measurements from several installations. The monitors show continuous measurements with fast response and good sensitivity, all of which is difficult to obtain with conventional techniques such as wet chemical analysis.

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Over the last few decades there has been increasing concern about man-made pollution of the atmosphere. The dilution of pollutants in the atmosphere makes the concentrations very low, often below 1 ppb, and therefore difficult to measure. There are numerous reported measurements of trace gases in the atmosphere (see e.g. references in [1]), and measurements of some gases such as CO and NO_x, are done routinely in many cities. In addition to measuring the gases in the atmosphere, it is important to monitor the many sources of emissions, where traffic, agriculture and industry are the most important types. Industrial processes are often large-scale point sources with gas abatement systems which can be optimised to reduce the emissions.

Traditionally gas emissions have been measured by wet chemical methods where the gas is extracted from the point of measurement and preconditioned (cleaned, dried, etc.) before it undergoes chemical reactions from which the concentration is deduced. For emissions subject to (inter)national regulation and legislation the chemical method is normally the method new techniques have to be compared with. There are several disadvantages with the chemical measurement technique. Due to low concentrations the gas has to be extracted for a long time, normally half an hour, before an amount sufficient for reliable measurement is obtained. There are many

sources of errors related to the extraction and preconditioning of the gas, and measurements are laborious. For “sticky” gases, i.e. gases which are easily adsorbed on surfaces, a large fraction can be lost in the extraction and preconditioning of the gas. Many important emission gases, such as HCl, HF and NH₃, are of this type. There are several other general measurement techniques such as gas chromatography and mass spectrometry. However, they are complicated and normally require a lot of preconditioning of the gas before measurement. They are therefore slow and can suffer from similar problems related to the preconditioning of the gas as the chemical methods do. Optical spectroscopic techniques can work well without preconditioning of the gas. They therefore have the potential of in-situ measurements with fast response and are ideally suited for industrial applications provided they can measure with sufficient sensitivity.

A number of spectroscopic techniques have been developed for trace gas measurements. The traditional technique has been non-dispersive infrared (NDIR) where the transmission has been measured at two wavelength regions, one at absorbing and the other at non-absorbing wavelengths. This technique is suited for gases with broad absorption bands. In recent years new techniques has emerged such as Fourier transform infrared (FTIR), differential optical absorption spectroscopy (DOAS), laser-induced fluorescence (LIF) and tuneable diode laser absorption spectroscopy (TDLAS). An overview of these techniques is given in [2]. There are several optical instruments commercially available for continuous emission monitoring based on these techniques. Some are extractive, where the gas has to be preconditioned before measurement in an internal cell, and others are in-situ systems. These are broad-band spectroscopic instruments working in the infrared or ultraviolet. The middle infrared (MIR, 3–15 μm) is a very rich spectral region where most of the interesting trace gases absorb on their fundamental rotational/vibrational modes. The absorption is so strong, particularly from H₂O and CO₂ molecules, that a very high spectral resolution is required to avoid interference between species. Tuneable diode lasers (TDL) have line widths of only a few MHz or less and are therefore well suited for high-resolution spectroscopy. Lead-salt-based lasers are available in the middle infrared but both the TDLs and the detectors

require cooling to around liquid nitrogen temperatures. In the near infrared (NIR, 0.8–3 μm) we have the first and second overtones of the rotational/vibrational modes of the trace gases, and there are commercial III-V semiconductor lasers available up to approximately 2 μm that operate at room temperature. The absorption typically drops by an order of magnitude for every higher overtone, however, and a higher absorption sensitivity is required to obtain sufficiently low detection limits for many of the important gases.

An easy way to increase sensitivity is to increase the optical path length. This is possible for atmospheric measurements, but for industrial applications there is usually a practical limit of a few meters. The optical path length can also be extended with multipass cells (White cell, Herriott cell). In recent paper, Ye et al. [3] discuss several high-sensitivity detection techniques, and they apply an external cavity technique with a cavity finesse of 10^5 to obtain a record absorption sensitivity of 5×10^{-13} . Although this is an impressive sensitivity, such a technique is not practical for industrial applications except in very special cases. Open multipass cells cannot usually be used because most applications have an opacity or dust load that prevents long path lengths and leads to problems with unclean optical surfaces. The use of multipass cells therefore requires filtering and preconditioning of the gas and is only practical for extractive systems.

It is tempting to try to define an “ideal” gas monitor. It should (a) measure correctly without influence from other gases or dust, (b) automatically compensate for temperature and pressure effects, (c) measure continuously with short response time. In addition, an instrument for industrial applications should (a) require little maintenance with few or no consumable parts, (b) have high reliability and availability, (c) be insensitive to vibrations and mechanical instabilities, and (d) use components operating near room temperature (i.e. no liquid nitrogen cooling).

With such requirements, open-path, in-situ near-infrared TDLAS is an attractive measurement technique. In this paper we describe a TDLAS system currently being tested by a notified body (TÜV, Germany) for assessment of conformity with regulations for continuous emission monitoring. It has been designed for continuous operation in an industrial environment where it may be exposed to corrosive or explosive atmosphere, large variations in ambient temperature, vibrations and electromagnetic disturbances. We discuss some of the special problems related to industrial applications, and show some results from actual installations.

1 Measurement principle of a TDLAS gas monitor

Many detection techniques have been developed in conjunction with TDLAS. An overview of some of these techniques can be found in [1, 3, 4]. We give a brief description of one of the techniques, which has received most attention in the literature and which we have found to be one of the best candidates for an industrial monitor. For more detailed discussions of the technique see [5–7].

All absorption spectroscopy is based on the Beer–Lambert law which states that the transmission will decay exponentially as $\exp(-Sg(f)NL)$ where S is the absorption line strength, $g(f)$ is the line shape function, N is the concentration of absorbing molecules, and L is the optical path

length. For sufficiently low pressures (less than a few bar) many gases will have distinct absorption lines of width in the order of 0.01 to 0.1 cm^{-1} depending on pressure and other line broadening effects. Line broadening effects are discussed later. By searching spectroscopic databases such as HITRAN [8], one can find absorption lines that are separated sufficiently far from those of other gases for so-called interference-free detection. The measurement might not be truly interference free, however, for reasons which are described later.

The most straightforward measurement principle is direct absorption measurement where the absorption at the line centre is compared with the absorption slightly to the side of the line. In its simplest form this technique is not used much because measuring a small difference in two large signals gives a rather low detection sensitivity. To improve on this, a modulation of the laser frequency is applied. The instantaneous laser frequency is then

$$f(t) = f_0 + m\gamma \sin(2\pi f_m t), \quad (1)$$

where f_0 is the laser centre frequency, γ is the half width at half maximum of the absorption line, f_m is the modulation frequency and m is the frequency modulation index. If $f_m \ll \gamma$ this is referred to as wavelength modulation spectroscopy (WMS), otherwise it is called frequency modulation spectroscopy (FMS). By using a lock-in amplifier, harmonic components can be selected for measurement. First- and second-harmonic detection are conventionally labelled 1f and 2f detection respectively. The amplitudes of the harmonic components generally decrease for increasing harmonics, indicating that 1f detection might be the best choice. However, since laser output power (in addition to laser frequency) is modulated with injection current, there will be a residual amplitude modulation (RAM) signal when there is no absorption line. For an ideal diode laser where the output power is linear with injection current the RAM signal is zero for 2f and higher-harmonic detection [7]. This is the main reason why 2f detection is preferred over 1f detection. In practice there is usually some RAM signal also for 2f detection, but it is much smaller than for 1f detection.

FMS usually operates with modulation frequencies of order 0.1–10 GHz. The advantage with high-frequency modulation is reduced laser excess noise, but [6, 9] have shown that high-frequency WMS (> 0.1 MHz) can give detection sensitivities comparable to FMS. The lower cost of detectors and electronics operating at high-frequency WMS makes this ideal for industrial instrumentation.

There are two major problems with the WMS and FMS techniques. One is stabilising the laser centre frequency at the absorption line centre, and the other is compensating for the RAM signal. In principle the RAM signal can be eliminated with a dual-beam subtraction technique, where the laser beam is split and one part is led outside the absorbing path to a separate detector. The extra path can also be used to frequency stabilise the laser by inserting a cell with the trace gas. However, it has been difficult to obtain good results with the dual path technique because of strong sensitivity to alignment [10].

In the gas monitors described in this paper the dual modulation (or ramp scanning) technique is applied. In addition to the high-frequency modulation at approximately 200 kHz, the laser centre frequency is scanned slowly over the absorption

line at 50–100 Hz. This is illustrated in Fig. 1a where the detector signal, S , (normalised to 1) is plotted as a function of time, t , and instantaneous laser frequency, f . The shaded surface represents the absorption line. When the laser frequency is ramped slowly with a high-frequency modulation, as shown by the curve in the t – f plane, the detector signal will be represented by the space curve embedded in the surface. The projection of the space curve onto the t – S plane is the detector signal as a function of time and is shown again in Fig. 1b. The envelope of the second-harmonic component of the signal is used for the detection of the gas. The envelope is hereafter referred to as the second-harmonic or $2f$ signal.

Because of the scanning of the laser centre frequency, the requirement for laser frequency stability can be somewhat relaxed, compared with fixing the laser centre frequency to the absorption line. We obtain adequate frequency stability by stabilising the laser temperature to within (± 5 mK from the ideal temperature). The RAM signal can be reduced by analogue and digital signal processing.

For small modulation indexes ($m \ll 1$) the $1f$ and $2f$ signals are proportional to the first and second derivatives of the absorption line shape function, and similar for higher harmonics. The technique is then called derivative spectroscopy. For higher modulation indexes the envelope will deviate from the derivative. The peak of the second-harmonic signal will

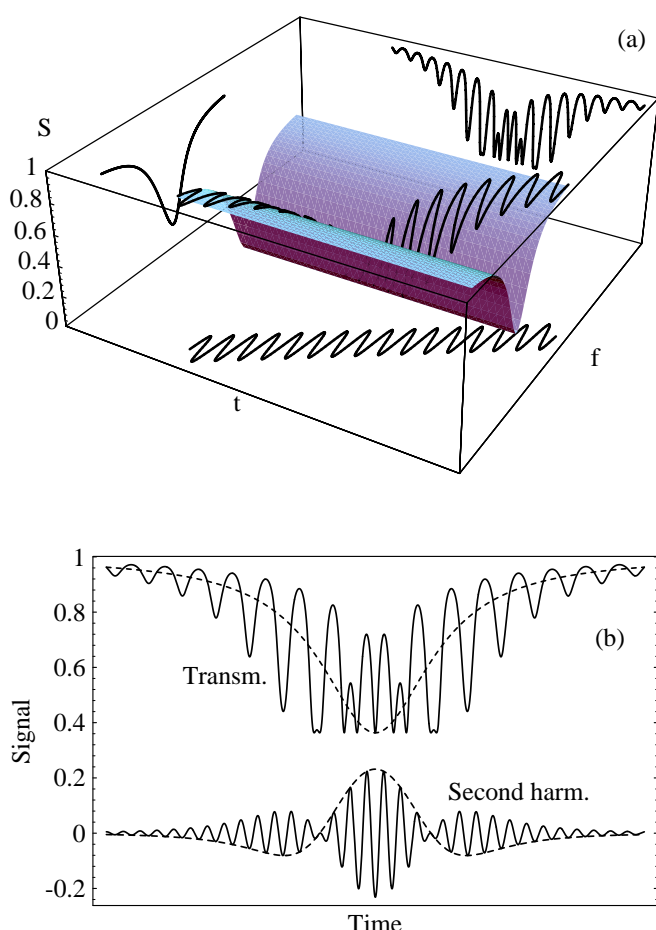


Fig. 1a,b. A schematic drawing of the dual modulation technique. **a** S is the detector signal as a function of time, t , and instantaneous laser frequency, f . **b** The envelope of the second-harmonic component of the detector signal is used for detection of the gas. See text for explanation

increase with increasing m until it reaches a maximum for $m = m_0 = 2.2$ [5, 11].

The detection sensitivity is limited by etalon and laser feedback noise to 10^{-5} – 10^{-6} relative absorption. Etalon noise is optical interference due to small reflections from optical surfaces. It will appear as oscillations superimposed on the second-harmonic signal. Small temperature variations will cause the oscillations to drift slowly relative to the second-harmonic signal and give oscillations in the measured gas concentration. In particular, optical surfaces separated by 2 to 6 cm tend to give etalon noise, which interferes in a way that is difficult to eliminate with digital signal processing. To minimise these effects the monitors have been designed with a minimum of optical components between laser and detector. We only use a collimating lens for the laser, a focusing lens for the detector and wedged protective windows for the transmitter and receiver units. No beam steering is used. The alignment (after installation) relies on a sufficiently stable mounting. Since the distance between receiver and transmitter is limited to approximately 5 m, vibrations have not given alignment problems.

The mechanical layout of a monitor installed on a stack is shown in Fig. 2. The laser and detector are located in the transmitter and receiver units, respectively. Both units are mounted on the stack by using standard flanges purged with dry air to keep the optical windows clean. The detected signal is transmitted through a cable to the electronics unit, which contains signal-processing electronics. The measured concentration is displayed on an LCD display, and for data recording and logging it is sent through an RS232 digital output and a standard 4–20 mA analogue output.

An alternative to this design would be to place the laser and possibly detector in the electronics unit and use optical fibres to the point of measurement. However, it has been difficult to obtain similar detection sensitivities without sacrificing the simplicity of the above solution.

2 Line broadening effects

It is well known that the absorption strength, S , depends only on temperature, and the integral of the line shape function is independent of line width such that the integral can be normalised to unity $\int_{-\infty}^{\infty} g(f) df = 1$. The peak amplitude of the absorption and the second-harmonic signal therefore decrease

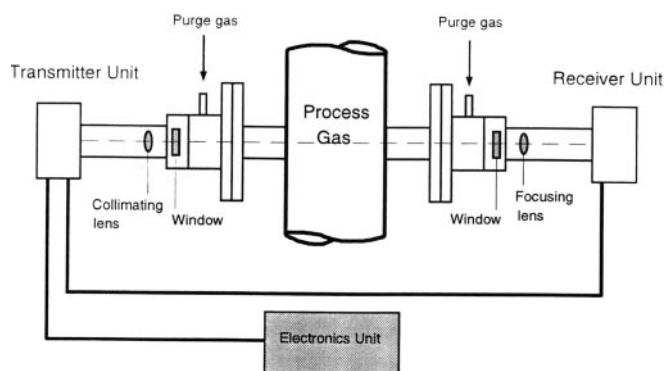


Fig. 2. Schematic drawing of the TDLAS gas monitors described in this paper

with increasing line width, γ . For a Lorentzian line shape the proportionality between the peak of the $2f$ signal and γ is between $1/\gamma^3$ (for $m \ll m_o$) and $1/\gamma$ (for $m \gg m_o$). Variations in line width are therefore of great importance for precise measurements of concentration.

There are three contributions to the line width of an absorption line: natural line broadening, Doppler broadening and collision broadening. In most industrial processes collision broadening dominates, which results in a Lorentzian line shape. For a more careful account of the line shape one has to combine the effects of Doppler and collision broadening, which gives a Voigt line shape (see e.g. [12, 13]). Pressure and temperature therefore strongly influence the line width.

In atmospheric trace gas measurements the temperature, pressure and major constituents are usually well known. This makes it relatively easy to calibrate or correct the measurement for line broadening effects. In an industrial context, however, there may be large variations in operating conditions both from one installation to another and within one and the same installation. When measuring emissions from a stack, the pressure is usually close to 1 bar, but the temperature may vary typically from 100–350 °C. For some types of gas abatement systems it is of great interest to measure at a point even closer to the process where the temperature can be greater than 700 °C. In the chemical industry it is of interest to measure at pressures ranging from a small fraction of a bar to several bars. Temperature and pressure are easy to measure and may be continuously compensated for.

Collision broadening depends not only on pressure but also on the collision cross section of the molecules. Variations in gas composition may therefore influence the line width, and hence give a strong influence on the second-harmonic signal. It is for this reason that the measurement might not be truly interference free even though there is no direct interference from absorption lines from other gases. We will refer to this type of interference as line broadening interference.

In most industrial applications, line broadening effects must be taken into account in order to achieve the required measurement accuracy. Three types of gases that occur frequently and have a large influence on the line width are H_2O , CO_2 and hydro-carbons such as CH_4 . The concentration of H_2O from waste incinerators and boilers may typically vary from 10 to 25 vol.%, but in some cases it can be as high as 40 vol.%. In Fig. 3 we show an example of the influence of H_2O concentration on the peak of the second-harmonic signal for HCl. It is clear that such a large dependence has to be compensated for. In principle, one can compensate by measuring curves similar to that in Fig. 3 for all relevant gases in the process, but since the influence will depend on pressure, temperature and instrument-specific parameters such as modulation index, it is difficult to obtain good results this way. In addition, the need to know concentrations and fluctuations of other gases makes this a very unattractive solution.

Alternatively, since the laser frequency is scanned over the absorption line, one can measure the line width. The price for this, however, is a significant increase in noise in the measured gas concentration. This can be explained by the following model. We assume that the absorption line is collision broadened (Lorentzian). A theoretical second-harmonic signal, H_{th} , can then be found [11]. H_{th} depends on gas concentration, g , line width, γ , and frequency modula-

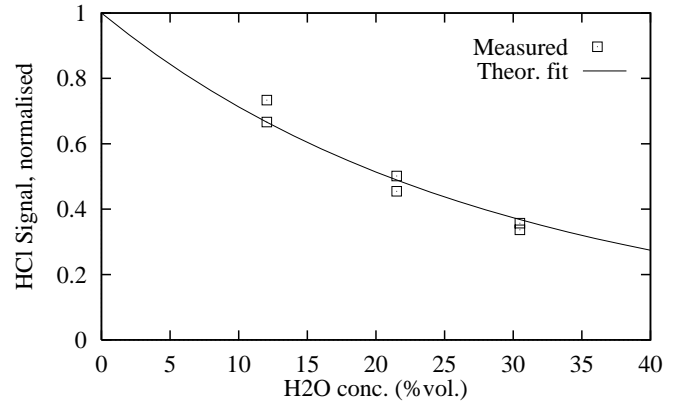


Fig. 3. Measured second-harmonic peak signal of an HCl line as function of H_2O concentration at 270 °C. The signal has been normalised to 1 for zero H_2O concentration. Note that the curve is not universal but will depend on gas temperature and pressure and on modulation index and other instrument-specific parameters

tion index, m [defined in (1)]; $H_{th}(f; g, \gamma, m) = gH(f; \gamma, m)$, where $H(f; \gamma, m)$ is the second-harmonic signal normalised to a fixed gas concentration. We further assume that the measured second-harmonic signal has some additive white noise: $H_m(f) = H_{th}(f) + n(f)$, where the noise, $n(f)$, is a stochastic variable with zero mean value and constant variance for all frequencies, f . If we know the correct line width we may find the concentration by varying g to obtain a best (least-squares) fit between $H_{th}(f)$ and $H_m(f)$ for all frequencies. Because of the noise, g is a stochastic variable with uncertainty (standard deviation) δg . If we do not know the line width we have to vary both g and γ simultaneously, which leads to an increased uncertainty, Δg , for the measured gas concentration. We have found that the two uncertainties are related as

$$\Delta g = B(m)\delta g, \quad (2)$$

where $B(m)$ is a dimensionless function depending only on the frequency modulation index, m . $B(m)$ has been found numerically and is shown in Fig. 4. For optimal modulation index, $m_o = 2.2$, we have $B(m_o) = 2.9$. Hence, the uncertainty of the measured concentration increases by nearly a factor of 3 when the line width is measured and compensated for. From the figure we see that the improvement that can be obtained by selecting a different modulation index is small. Notice, however, that $B(m)$ is independent of gas concentration and the relative uncertainty in measured concentration will therefore decrease as $\Delta g/g$ for increasing concentration.

The measurement situation is shown in Fig. 5. Without measuring the absorption line width we can have a large systematic error with a small stochastic error. Correcting the systematic error by measuring the line width will be at the expense of an increase in stochastic error.

The reduction in measurement precision can be understood from the fact that the derivative of the second-harmonic signal with respect to line width, $dH(f; \gamma, m(\gamma))/d\gamma$, has a similar shape as the second-harmonic signal itself. This has the effect that a small reduction in line width can be misinterpreted (depending on noise level) as a small increase of gas concentration, or vice versa; i.e. the two fitting parameters are correlated. Most of the information about the line width is in the tails of the second-harmonic signal, which im-

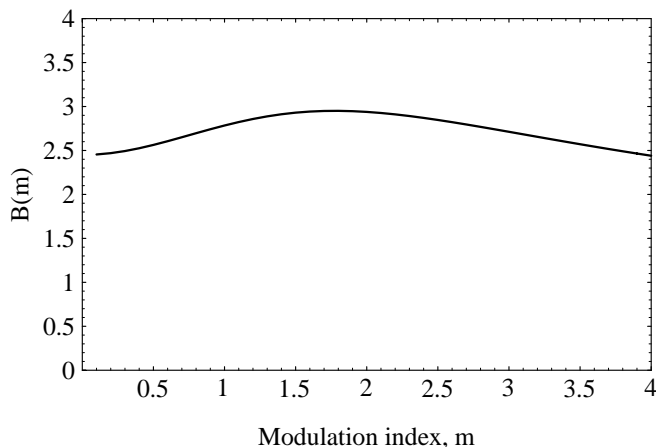


Fig. 4. The ratio between uncertainty in gas concentration with line width measurement and without, $B(m)$, plotted as a function of modulation index

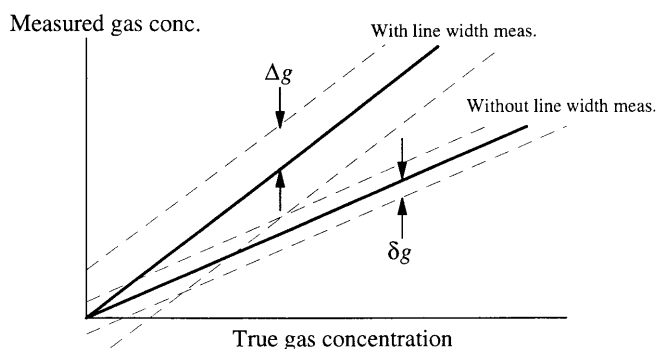


Fig. 5. Illustration of measurement errors with and without measurement of line width. The measured gas concentration without compensating for variations in line width (*lower solid line*) may have a systematic error. The correct concentration (*upper solid line*) can be obtained by measuring and compensating for variations in line width, but has a larger stochastic uncertainty

plies that measurement of line width is sensitive to the tails of nearby absorption lines. In practice there also seems to be an increased sensitivity to RAM and etalon noise compared to what is predicted in the above result. This is most likely to be because these noise sources are non-white and therefore violate the assumptions in the calculation. Such noise can give slow fluctuations in the measured gas concentration on a time scale of several minutes to hours. Noise in this frequency range is also present when the line width is not being measured. It is the worst possible frequency range because noise of higher frequencies can be averaged out and noise of lower frequencies (drift) can be compensated by recalibration, zero offset measurement and similar techniques. For this reason industrial instruments often have lower sensitivity than when the same technique is applied in a controlled lab environment.

Although the line width compensation results in a larger uncertainty of the measured concentration, the detection limit is sufficiently good for many of the most important gases and applications. Thus automatic compensation of line broadening effects should be done by measuring the line width in applications with large variations in gas composition. This is the typical situation in incinerators, whereas power plants usually use only one type of fuel and one may successfully compen-

sate for line broadening effects with fixed preset values for the parameters influencing the line width.

3 Diode lasers for spectroscopic applications

The development of semiconductor diode lasers in the near infrared has been spurred by the development of CD players ($0.78 \mu\text{m}$) and fibre optic communication ($1.3 \mu\text{m}$, $1.55 \mu\text{m}$). As technology has improved, lasers have been developed for new applications such as pumping of solid-state ($0.808 \mu\text{m}$) and fibre ($0.98 \mu\text{m}$) lasers. In addition to wavelength, other important laser parameters are mode stability, in order to obtain single-frequency operation, current tuneability, and frequency drift. The Fabry–Pérot (FP) type lasers are unreliable with respect to mode jumping, therefore other types of lasers such as distributed feedback (DFB), distributed Bragg reflector (DBR) and vertical cavity surface emitting lasers (VCSEL) have been developed. Low current tuneability has to be compensated by higher current modulation which generally increase the RAM noise. It is beyond the scope of this paper to describe lasers in detail and we refer the reader to the literature (e.g. [14, 15]).

Long-term frequency stability is one of the most important parameters for diode lasers used in industrial gas monitors. Most lasers have some frequency drift and Fig. 6 shows some long-term measurements for three lasers at 760 nm . We have observed a large spread in drift, both for lasers of the same kind, and for different types of lasers, but it is generally smaller in lasers at longer wavelengths. The drift is usually smaller after several months of operation, but a drift as shown in Fig. 6 may cause instrument failure during such a period. The drift can be overcome by adjusting the laser temperature such that the absorption line is always in the centre of the frequency scan. However, some applications normally have zero concentration and therefore no line to track (e.g. measurement of O_2 for explosion safety). In such cases one can introduce a gas cell temporarily or permanently in the measurement path, or in a split-off beam with a separate detector. However, such solutions will increase the optical noise and/or mechanical/electrical complexity. The monitors described in this paper use lasers which

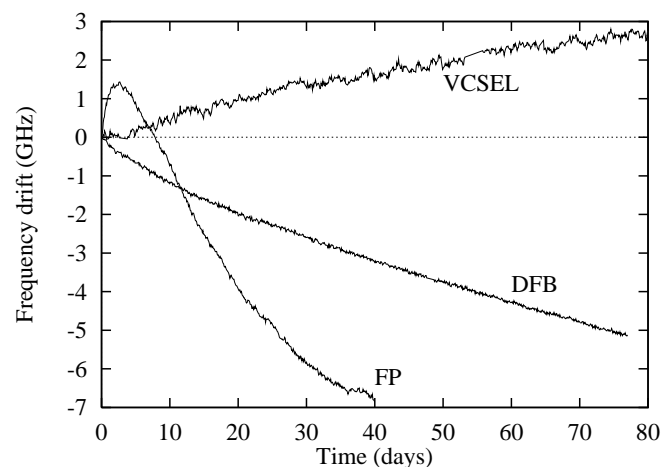


Fig. 6. Long-term frequency drift of some lasers at 760 nm . The lasers have passed “burn-in” tests prior to these measurements

Table 1. Typical wavelengths and detection limits for some gases measured with the technique described in this paper. The detection limit for O₂ is not limited by electronic or optical noise, but by uncertainty due to air in the receiver and transmitter

Gas	Laser type	Wavelength /μm	Detection limit /ppm·m
O ₂	FP, DFB, VCSEL	0.764, 0.760	1000
HF	DFB	1.28, 1.30	0.03
NH ₃	DFB, DBR	1.51	0.2
CO	DFB	1.56	20
H ₂ S	DFB	1.57	5
HCl	DFB	1.74	0.1
NO	DFB	1.81	5

have been selected for low drift, but the testing is a costly and time consuming process. It is difficult to specify a maximum acceptable drift since this is coupled to the actual mechanical/optical solution. A large, persistent frequency drift is often accompanied by drift in other parameters such as output power and to some extent current tuneability. Such effects may result in drift in the measured gas concentration and short life time of the laser.

Most of the diode lasers mentioned above are used in high-volume products. Diode lasers for gas monitors are expected to be required in low volumes only [16], and until recently only gases with strong absorption lines near the above-mentioned wavelengths have been possible to measure. However, the advances in the manufacturing of diode lasers in recent years have made it possible to make lasers at other wavelengths, and several of the lasers used in the monitors described in this paper have been specially designed for the purpose of gas monitoring.

Table 1 lists some of the types of lasers and wavelengths we have used for some gases, and the corresponding detection limits obtained. Note that the detection limit for O₂ comes not from electronic or optical noise, but from uncertainty due to air in the receiver and transmitter. More extensive lists of suggested wavelengths for several gases can be found in [4, 17].

4 Industrial applications of TDLAS

Due to the short response time, industrial TDLAS monitors are ideal as process control tools in processes requiring a fast response, and they are also well suited for continuous emission monitoring of gases such as HCl and HF where the maximum permissible emission levels are in the low ppm range. Some typical examples are presented below, followed by measurements from real installations.

4.1 Process control

O₂ measurement. The use of TDLAS offers for the first time a reliable and accurate method for measurement of oxygen by using spectroscopic techniques. While the O₂ monitor can be used in most of the traditional applications for O₂ measurements in combustion processes, the most challenging applications are found in process control and safety systems in chemical and petrochemical plants (i.e. flare gas explosion control), as well as safety systems in hazardous waste and solvents destruction plants.

The gas temperature is typically in the range 150 to 300 °C and the pressure can vary from a few millibar to 3–5 bar. For these processes the gas matrix mainly consists of hydrocarbons (25% – 80%) with the rest being H₂O, CO and CO₂ plus a low concentration of O₂ (typically from 1% to 2%).

Another process control application which has now become feasible is the use of the O₂ monitor to improve combustion control in high-temperature furnaces, such as steel and cement ovens. Performing high-temperature CO measurements at the same location will improve the combustion control even further. The temperature is typically 900–1200 °C and the gas matrix will in this case consist of O₂, CO, CO₂, N₂, NO and H₂O.

NH₃ measurement. At the moment there are no environmental emission standards for ammonia emissions from industrial processes. Ammonia is, however, widely used in power plants and incinerators to reduce NO_x emissions. Two frequently used techniques are selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) in which NH₃ is added to the flue gas. For such installations, monitoring NH₃ is valuable for optimising the consumption of the gas, as well as reducing corrosion and environmental impact from excessive use. The NH₃ slippage level should preferably be well below 5 ppm and should be measured as close as possible to the injection point. Typical conditions at this stage in the process are gas temperatures of 250–350 °C, dust levels of 10–20 g/m³ and a gas mix of 10%–20% CO₂, 10%–30% H₂O, 3%–5% O₂, with the rest being N₂ and ppm levels of SO_x, NO_x and NH₃.

CO measurement. Accurate and fast measurements of CO as close as possible to the process may be used for effective combustion control in high-temperature processes used in steel and cement ovens. The use of TDLAS offers for the first time a reliable and accurate method for this type of process control, by measuring the CO level at temperatures above 1000 °C.

H₂S measurement. H₂S is a hazardous gas normally present in refineries and other petrochemical plants, which have facilities for reduction/destruction of it. The gas mix typically includes H₂, O₂, N₂, CH₄, CO₂ and H₂O, and monitoring H₂S on a continuous basis is an efficient tool for process optimisation.

4.2 Emission monitoring

The most important emission gases believed to have an impact on the environment are related to combustion processes. In an industrial context, emissions usually come from boilers (power plants), chemical industry, waste incinerators and furnaces such as aluminium smelters and steel and glass furnaces. Other significant sources of emission are cars, buses and other motor vehicles.

Continuous monitoring of gas emissions from industrial processes has traditionally been limited to measurement of carbon monoxide (CO) nitrogen oxides (NO and NO₂) and sulphur dioxide (SO₂), and the techniques for continuous measurements are well established. Limitations in performance/detection levels of the equipment available for continuous measurements of gases such as HF, HCl and NH₃ has in practice prevented continuous monitoring for reporting of emissions. Standard practice has been sampling tests

using wet chemical analyses. Earlier in this paper we mentioned several spectroscopic methods which can be used for a large number of gases. However, for the gases that are particularly difficult to measure, TDLAS offers a new and unique method. Some examples are presented below.

HCl measurement. HCl is an emission depending mostly on the content of chlorine in the fuel. Experience from domestic waste incinerators [18] has shown that approximately 90% of the Cl in the fuel will end up as HCl in the flue gas. The maximum permissible emission level of HCl from industrial and domestic waste incinerators in Europe is now specified to not exceed 10 mg/m^3 (daily mean values). Only a few types of instrumentation can meet this requirement, the TDLAS being one of these, with a detection limit of approximately $0.1 \text{ ppm} \cdot \text{m}$ for the monitors described in this paper.

HF measurement. HF emissions come primarily from aluminium plants, glass works, tile manufacturers, incinerators and alkylation plants. For incinerators, typically 10% of the fluorine in the fuel will end up as HF in the flue gas [18]. The maximum permissible level is typically 1 to 10 mg/m^3 , depending on the process and application. Until recently HF has been a gas which has been considered impossible to measure on a continuous basis at these low levels due to the lack of suitable instrumentation. The use of TDLAS has now changed this as HF proves to be one of the most suitable gases for the TDLAS technique with a detection limit of 30 ppb for a 1-m optical path length.

4.3 Measurement of O_2 , CO and HCl from a waste incinerator

In Fig. 7 we show some simultaneous time-series measurements from the stack of a 27-MW circulating fluidized bed (CFB) combined boiler and incinerator at a paper mill. The boiler produces a maximum of 40 tons of steam per hour at 210°C and 20 bar. The steam is used in the paper mill production and may vary rapidly from 20% to 100% capacity. The boiler is designed to burn municipal waste, plastic, wood, paper, waste oil and coal. These fuels have greatly different calorific values and this puts high demands on both the process control and the abatement system.

After the combustion in the CFB reactor the flue gas passes through two cyclones and the boiler before it is cleaned in a multi-cyclone and an electro-scrubber. The flue gas is then let out through a 40-m-high stack, where the gas monitors are located.

O_2 and CO concentrations in the flue gas are the most important gases for monitoring combustion efficiency. Complete oxidation can in practice be obtained only with an excessive amount of air. Too much air, however, can cool down the combustion and increase the amount of CO in the flue gas. There exists an optimal amount of air. Figure 7a,b shows the O_2 and CO concentrations for varying efficiency of the combustion. When the O_2 concentration drops below approximately 5.5 vol. % the CO concentration peaks sharply to values as high as 4000 mg/Nm^3 , and when the O_2 concentration is approximately 6 vol. % to 7 vol. % the CO concentration is close to 50 mg/Nm^3 . The fluctuations in CO concentrations are extremely fast and large. In Fig. 7 the concentrations have been averaged over 1 min and we see changes from 50 to 2300 mg/Nm^3 from one sample to the next. The fastest response of the CO monitor is 15 s, and we have seen

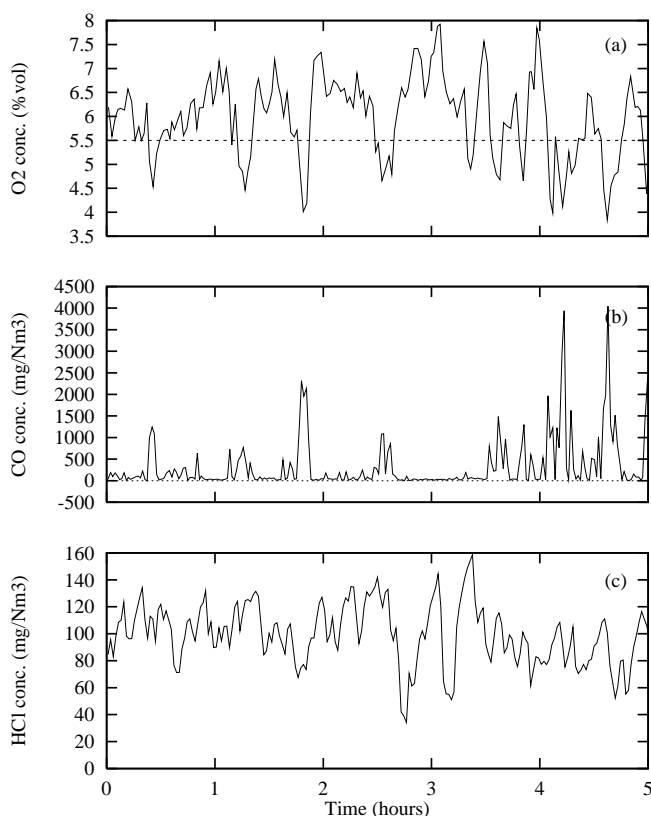


Fig. 7. Concentrations in flue gas from a waste incinerator measured over a period of 5 hours, where each sample is averaged over 60 seconds. The CO concentration peaks abruptly when the O_2 concentration drops below approximately 5.5 vol. % The HCl concentrations do not show a similar correlation

cases where the concentration has changed from 100 to 9000 mg/Nm^3 in three successive samples at this sampling rate. It is difficult to understand how conditions can change this fast in such a large furnace, but considering a gas flow of up to $20 \text{ m}^3/\text{s}$, we realise that all the gas in the furnace has been replaced in less than 15 s. Such fast response measurements can therefore give valuable information that may be used in the process control of the furnace.

HCl was also measured in the flue gas from this waste incinerator. The concentration of HCl depends mostly on the content of chlorine in the fuel and is not expected to show much correlation with process-control-related parameters. This is consistent with the measurements shown in Fig. 7 where there is no correlation between the concentration of HCl and the other two gases. The content of chlorine in municipal waste can vary greatly, which is also seen in this figure. At the time of measurement the incinerator had no abatement system for removing HCl.

HF was also measured in the stack of the waste incinerator. In the analysed period the concentrations were generally very low and rarely above the detection limit, which was approximately 0.05 mg/Nm^3 .

4.4 Measurement of HF in a primary aluminium smelter

Aluminium is produced by electrolysis of alumina (Al_2O_3) and cryolite (a blend of NaF, AlF_3 and CaF_2). The purpose

of adding cryolite is to lower the melting point of alumina. HF gas is produced as a byproduct in the electrolysis and led away with air through vent hoods at a concentration of typically 300 mg/m^3 . The flue gas is cleaned with a dry scrubber which uses alumina to remove the HF. According to emission requirements the efficiency of the dry scrubber has to be better than 99.7%. Such efficiency requires thorough control of gas flow, temperature, humidity, etc. Figure 8 shows the HF concentration measured after the dry scrubber. The fluctuations seen in the measurement are due to the process control of smelter and dry scrubber and have a period of 26 min. Such fluctuations would be invisible by traditional half-hour averaging measurements.

4.5 Measurement of NH_3 at a coal-fired power plant with SCR abatement system

The 460-MW power plant is designed to burn pulverised coal with a content of 2.5% sulphur. The plant is equipped with a conventional limestone flue gas desulphurization process for SO_2 , and ammonia-based SCR for NO_x control. NH_3 is measured at the exit of the SCR reactor where the temperature is $330\text{--}360^\circ\text{C}$. Typical flue gas concentrations are 11 vol. % to 15.5 vol. % CO_2 , 7.5 vol. % to 10 vol. % H_2O , 3.9 vol. % O_2 , 600–800 ppm SO_2 , 250 ppm NO_x and 0–5 ppm NH_3 (expected). The dust concentration is typically around 10 g/m^3 , and with an optical path length of 2.5 m this gives a transmission ranging from a few percent up to 40% at maximum. During the period of the measurements presented in Fig. 9 the plant was burning 1.5% subbituminous coal. As we can see from Fig. 9 the concentration of NH_3 was up to 10 ppm, twice that expected. Such concentrations will contaminate the desulphurization byproduct material (gypsum) and reduce the SCR catalyser lifetime. We further see a large correlation with power production. This is a clear indication that the injection of NH_3 is not optimised for the varying load of the power plant.

5 Summary and Conclusions

Instruments for industrial applications have to be easy to use, require little maintenance and be reliable. For these reasons, cryogenically cooled TDLAS instrumentation operating

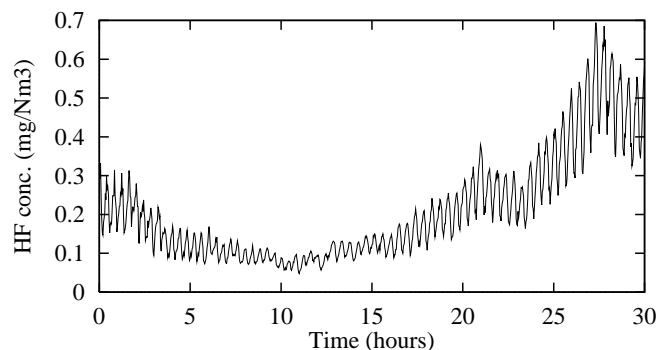


Fig. 8. HF concentration in flue gas from an aluminium smelter measured after the dry scrubber. The detection limit is 0.015 mg/m^3 with a measurement length of 2 m

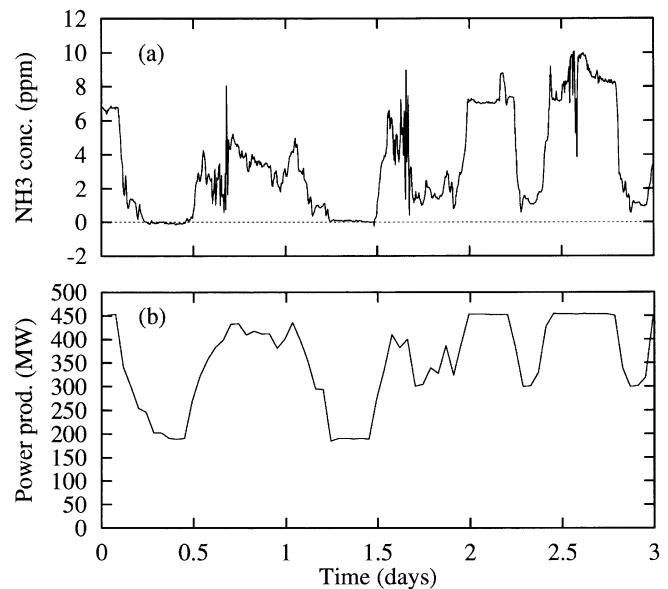


Fig. 9a,b. Measurements of NH_3 in flue gas from a coal fired power plant with SCR abatement system. The NH_3 concentration **a** shows a clear correlation with the power production **b** of the plant

in the middle infrared with lead-salt lasers have not found widespread use in industry. Although the absorption lines are weaker in the near infrared than in the middle infrared, the simplicity that follows from operating laser and detectors at room temperature makes such instruments more attractive for industrial applications. Gas monitors based on TDLAS with high-frequency WMS and second-harmonic detection have been used in several applications with large variations in operating conditions and requirements to detection sensitivity. The monitors have to be flexible with respect to gas temperature, pressure, gas composition and optical transmission. For several applications, in particular flue gas measurements, the monitors have to work in a high-dust atmosphere giving an optical transmission down to 1% or lower. High temperature applications ($\sim 700\text{--}1200^\circ\text{C}$) are also of great interest for many gases, such as O_2 , CO and NH_3 .

The large variations in operating conditions impel the monitors to be flexible and versatile. One important factor in this respect is to compensate for line broadening interference in applications with large variations in the concentration of some gases such as H_2O , CO_2 and hydrocarbons. We have found that measuring the line width by fitting a theoretical second-harmonic signal will increase the stochastic noise in the measured concentration by a factor of 3 or more. In spite of this, a sufficiently high measurement precision has been obtained for many of the most important gases and applications. Detection sensitivities can be further improved with multipass cells, but this requires an extractive system, which has a slower response and potential problems related to filtering and preconditioning of the gas.

To keep high reliability with low production costs it is essential to use highly reliable laser diodes with low drift in frequency. Lasers with high current tuneability generally have lower RAM-induced noise than lasers with low tuneability. As production technology for diode lasers improves, problems related to such matters are expected to be reduced, and development of lasers for new wave-

lengths will make it possible to measure new gases in new applications.

The great variety in the needs for gas monitoring, and acceptance of the TDLAS measurement technique in the process industry, is generating an increasing demand for TDLAS-based gas monitors. In this article we have demonstrated that in-situ, open path measurements in the near infrared using TDLAS can be done with the accuracy and reliability required for industry in a number of different applications.

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