Zirconia sensors vs. compact TDLAS systems

Scope

This document compares current-limiting zirconia oxygen sensors and low-cost diode-laser oxygen measurement systems (TDLAS).

1 General Considerations

High end TDLAS systems from established brands cost 10k€+ and are known to be reliable and accurate in their respective applications. Still, physical limits like line broadening, temperature dependence, overlap of absorption lines and interference of other gases, fouling of optical surfaces and the fact, that they do not directly measure oxygen remain. High end TDLAS systems use high grade optical components, a stable mechanical design to ensure alignment, make use of sophisticated data analysis and error management algorithms.

High-quality current-limiting zirconia sensor systems are typically significantly less expensive than high-end TDLAS analyzers. They address a different application space and use a fundamentally different measurement principle. Current-limiting zirconia sensors are selective oxygen sensors and are well established in many industrial and OEM applications. Their performance is mainly determined by ceramic materials, electrode stability, heater control, diffusion geometry, pressure effects and sample-gas compatibility, while the signal processing is comparatively straightforward.

2 Optical Absorption Spectroscopy Principles and TDLAS

UV-Vis and IR spectroscopy are well-established techniques in science and industry. Let us consider the basic measurement principles, some technical and physical limitations as well as data analysis.

2.1 A Very Short Outline of UV-Vis & IR Spectroscopy

2.1.1 Setup and Measurement

In a lab absorption spectrometer white light source passes through the medium of interest and the spectrum of the transmitter light changes as some energies match the electronic state of the medium’s molecules and get absorbed. We then measure the light intensity while a monochromator sweeps through all available wavelengths.

A reference measurement is required, to compare the spectrum of our medium of interest to the baseline of the setup – optical components, sample holders, system components, sensor and light source characteristics all contribute to this baseline spectrum.

2.1.2 Physical and Technical Considerations and Limiting Factors

The resolution of the spectrum depends on many factors, which include fundamental physical effects like:

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- **Detector sensitivity** – thermal noise is a limiting factor, especially in the IR range and detectors may need to be cooled to detect weak absorbance peaks
- **Optical alignment and mechanical stability** – lab spectrometers are precise instruments: shocks and vibration can lead to misalignments and ruin the measurement
- **Optical path length** – size matters - the correct choice of optical path length through the sample is vital. Weak absorbing lines require a long optical path while strong absorbing lines favour a shorter path.
- **Line overlap** – absorption lines are "just" intensity dips around a given wavelength. If several substances are present in the medium of interest (background matrix), absorption lines often overlap and the shape of the background signal can change the spectrum
- **Environmental factors** – high quality spectra rely on controlled environmental conditions. Changes in temperature, humidity, condensation or background matrix of the sample can make it difficult to get reliable results. In industrial applications, degradation and fouling of optical surfaces can present a serious issue, depending on the application.
- **Matrix and broadening** – the local environment of a target substance changes the shape of a specific absorption line. At elevated pressure line broadening may also have to be considered

2.1.3 Reference Baseline and Line Shape

The reference measurement in a lab environment is taken by measuring an absorption spectrum of just the carrier matrix, that holds the sample – this may be a solvent, gas or any other sample carrier.

The sample carrier is chosen carefully and with intent such that it does not have any peaks or background features that interfere with the spectral region of interest.

This measurement is conducted each time a new sample or sample batch is measured to reconfirm the baseline and make sure that there were no changes due to contaminations, matrix related alterations, and variations in alignment/setup related factors. There are additional methods one can employ as a "reality check", like the use of broad band light power meters to assure the total intensity of the light source is unchanged and algorithmic tools like comparing the peak fit parameters, background intensity and shape

A good reference for baseline absorption is absolutely vital for all absorption measurements and any interference that changes the baseline and peak line shape can lead to significant errors. This is where most commonly issues arise, especially when one employs automatic evaluation of numerous spectra.

2.1.4 Data Analysis

Once the two spectra (sample & reference) are acquired, we can use the attenuation law to calculate absorbance:

As peaks tend to have different shapes and/or consist of several peaks, one often needs to fit their shapes in order to find their area and thus the total absorbance of the target peak.

Peak fitting in spectroscopy can be difficult and is often the subject of debate as there are several approaches and it is not always clear which one is appropriate for a given combination of sample and matrix.

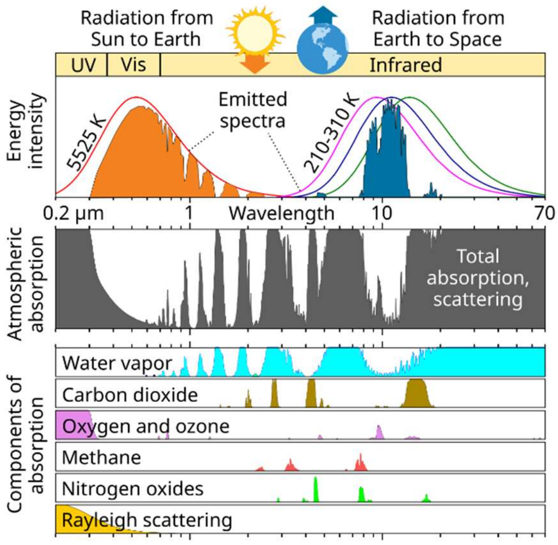
To find the concentration of a substance, we need to evaluate the Beer-Lambert law:

$$A = \varepsilon c l$$

A ... Absorbance
ε ... Absorption coefficient
c ... concentration of the absorbing substance
l ... path length

2.1.5 Example: Atmospheric Absorption of Sunlight Analysis

The optical absorption spectrum of the atmosphere is quite complex. As far as an absorption measurement of oxygen is concerned, the ~760nm absorption peak is mostly used.



At O_2 wavelengths near 760 nm, humidity is often a key practical concern. Depending on line selection, pressure and path length, water vapor can affect nearby spectral features and baseline fitting; condensation or film formation on optical surfaces can be even more severe.

3 How Compact TDLAS Analyzer Work

Compact TDLAS systems use a tuneable diode laser to scan across a selected O_2 absorption line, commonly near the O_2 A-band around 760 nm. The detector measures the wavelength-dependent transmission through the sample gas. The O_2 concentration is calculated from the absorption feature using Beer–Lambert behaviour and a line-shape model.

In practice, the system does not directly measure oxygen. It estimates concentration from an absorption signal. The result depends on baseline estimation, pressure, temperature, optical path length, line broadening, interference from nearby spectral features, optical fouling and algorithm quality.

3.1 Advantages and Disadvantages of compact TDLAS systems

For these systems, the choice of high-grade materials and components, geometry and sophisticated algorithms are essential.

3.1.1 Advantages

- Safe for use in applications with flammable materials
- Fast response (<1s)
- Long lifetime (assuming high grade optical components, application dependant)
- Little/no interference in dry environments
- Wide measurement range
- Wide temperature range
- High quality systems offer good accuracy (but are costly)

3.1.2 Disadvantages

- Indirect O2 measurement – absorption of light is correlated with O2 concentration
- Temperature dependant diode laser characteristic
- Long term drift due to aging and degradation of laser diode
- Contamination and fouling of optical surfaces (application dependant)
    - Requires high grade optical surfaces (costly)
- True zero/span checks require known reference gas; normal operation typically relies on baseline fitting, modulation/normalization and internal diagnostics
    - Only a narrow part of the spectrum can be measured and evaluated
- Humidity/condensation and particles can cause diffuse scattering, severely impacting the measurement
- Automatic data analysis unreliable in some applications
- Complex algorithms can result in “black box” errors and implausible measurement results
- At high pressures: matrix interaction, line broadening

4 How Current Limiting Zirconia Sensors Work

Here, we will only briefly touch on the measurement principle of this type of sensor, as it has already been described in **AN002e.**

At elevated operating temperature, yttria-stabilized zirconia is, for all practical purposes, exclusively an oxide-ion conductor. Oxygen transport occurs by vacancy-mediated O^{2-} motion through the ceramic electrolyte. Here, the zirconia acts as an oxygen pump, while the diffusion opening limits the inflow of oxygen, making diffusion the dominant transport process. Hence, the sensor current is proportional to the diffusion flux.

This provides a defined, sensor-specific relationship between limiting current and oxygen concentration:

$$I_s([O_2]) = -k \cdot \ln\left(1 - \frac{[O_2]}{100}\right)$$

$I_s([O_2])$	Sensor current in the measuring medium
$[O_2]$	Oxygen concentration in the measuring medium in %
k	Sensor-specific constant

4.1 Advantages and Disadvantages of Zirconia Sensors

4.1.1 Advantages

- Proven, mature sensing principle
- Selective oxygen measurement
- Wide temperature range
- Long lifetime (3-10 years in the field)
- Very reliable and simple data analysis algorithm
- Cost effective solution
    - Especially in the sub 1000ppm range
- Very small pressure dependence above 0.7 bar
- Sensor characteristics very stable – no re-calibration is required over sensor lifetime

4.1.2 Disadvantages

- High cell operating temperature
- Not compatible with flammable gas mixtures and Ex applications
- Condensation can damage sensor when cold
- At low O2 ranges, oxygen releasing and/or consuming gases and a reductive atmosphere can lead to measurement errors
- Pressure dependence should be compensated below 0.7 bar

- Elevated hydrocarbon concentrations may shorten sensor lifetime
- Limited use for exhaust gas applications
- Electrode poisons (sulphur compounds, silanes) can degrade performance rapidly

5 Summary

Compact TDLAS systems are attractive where fast response, no hot sensing element and long optical-component lifetime are important. Their limitations are mainly optical and algorithmic: baseline estimation, line broadening, pressure/temperature compensation, fouling and condensation.

Current-limiting zirconia sensors are attractive where compact size, low cost, mature OEM integration and selective oxygen measurement are required. Their limitations are mainly material and process related: heater operation, pressure dependence, condensation, reducing gases and electrode/diffusion-path contamination.

Neither technology is universally superior. Selection should be based on gas matrix, O_2 range, pressure, humidity, contamination risk, response-time requirement, safety classification and total system cost.

5.1 Executive Summary Table

	Current-limiting zirconia	**Compact TDLAS**
Main strength	Simple, selective, cost-effective	Fast, no hot ceramic element
Main weakness	High cell temperature, poisoning	Optics/laser degradation, contaminations, baseline/model errors
Failure mode	Contaminations/poisoning	Fouling/contamination/algorithmic
Use when	Cost, simplicity, robust OEM fit, long lifetime matter	Speed, no hot element, long lifetime matter

5.2 Detailed Comparison Table

	Current-Limiting Zirconia Sensors	Compact TDLAS Oxygen Systems
Measurement principle	Selective O_2 measurement via oxygen-ion transport and diffusion-limited current	Optical absorption; O_2 concentration inferred from absorption feature
Selectivity	More direct O_2-specific sensing mechanism	Indirect; light absorption is correlated with O_2 concentration
Signal processing	Comparatively simple and transparent	Complex algorithms for baseline fitting, line shape, compensation and diagnostics
Response time	Moderate, 2-10s	Fast, often <1 s
Operating temperature	High, ~580°C	Around ambient
Ex applications	Hot element limits use in flammable gas mixtures	Possible
Lifetime	Long lifetime in suitable gas matrices (2-10 years)	Long lifetime, if optics remain clean/without fouling
Degradation	Application specific contamination	Laser aging, detector aging, degradation of optical surfaces
Calibration / reference	Stable characteristics; recalibration often not required	True reference measurements require reference gas; normal operation relies on baseline estimation
Pressure effects	Pressure dependence at low pressures	Pressure affects line shape and broadening; compensation required at elevated pressures
Temperature effects	Active temperature control recommended	Laser output and line shape are temperature dependent
Humidity / condensation	Condensation on sensor can lead to damage	Humidity affects spectral/baseline; condensation or films on optics can affect measurement
Particles / fouling	Diffusion opening or electrodes can be contaminated/blocked	Optical surfaces can foul; scattering can interfere with line fitting model and signal quality
Gas interferences	At low O_2 concentrations: reducing gases or oxygen-consuming/releasing species	Nearby spectral features, baseline distortion and matrix effects can cause model errors
Hydrocarbons	Elevated hydrocarbons levels shorten lifetime	Usually weak direct O_2-line interference, but condensable vapors/oil mist can foul/contaminate optics
Poisoning / contamination	Sensitive to electrode poisons such as sulfur compounds and silanes	Sensitive to contamination/degradation of optical surfaces
Mechanical	Standard variants susceptible to vibrations	Optical alignment/path stability matters
Cost / complexity	Cost-effective, compact, mature OEM solution	More complex and typically more costly due to high grade optical components/coatings and algorithms
Main advantage	Simple, selective, mature and cost-effective O_2 sensing, max. gas temperature ~350°C	Fast, optical measurement without hot zirconia element
Main disadvantage	Heated element, contamination/poisoning risks	Indirect measurement, optical fouling, baseline estimation/model complexity