The Evolution and Application of Trace Gas Analyzers based on Tunable Diode Laser Absorption Spectroscopy


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Outline

- TDLAS Description
- 10 Years of TDLAS Evolution
- Single-Board TDLAS Control Platform
  - Standoff Gas Detector/RMLD
  - Miniature Stand-Alone TDLAS Package
Tunable Diode Laser Absorption Spectroscopy (TDLAS) is an optical method for detecting trace concentrations of one or more selected gases mixed with other gases.

- It is highly-selective; generally insensitive to cross-species interference.
- It is highly-sensitive, offering sub-ppm detection of many gas species.
- It is fast, offering sub-second response time.
- It is non-contact; the probe beam need not make contact with the gas stream.
- It is configurable as a point, open-path, or standoff sensor.
Absorption Spectroscopy Fundamentals

- Gas molecules absorb light at specific colors ("absorption lines")

**Beer-Lambert law**

\[ I_\nu = I_{\nu_0} \exp \left[ S(T) \, g(\nu - \nu_0) \, Nl \right] \]

Where:
- \( \nu \) = optical frequency
- \( \nu_0 \) = line center frequency
- \( g(\nu) \) = lineshape function
- \( l \) = path length
- \( N \) = absorbing species number density
- \( S(T) \) = temperature dependent linesstrength
- \( I_{\nu_0} \) = unattenuated laser intensity
- \( I_\nu \) = laser intensity with absorption

\[
\text{Absorbance} = -\ln \left( \frac{I_\nu}{I_{\nu_0}} \right)
\]
A frequency agile (i.e. tunable) laser beam transits a gas sample.

The laser frequency (inverse of wavelength) scans repeatedly across an absorption line that uniquely identifies the target gas.

Absorption of the laser beam by the target gas creates a signal at the detector, which is processed to provide an output indicating concentration in target gas:

- Senses absorbances < $10^{-5}$
**Practical Detection Limits for Some Gases Measured with Near-IR TDLAS**

(ppm-m at 1 atm)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Limit (ppm-m)</th>
<th>Gas</th>
<th>Limit (ppm-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.2</td>
<td>HCN</td>
<td>1.0</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>20.0</td>
<td>CO</td>
<td>40.0</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>5.0</td>
<td>CO$_2$</td>
<td>40.0</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.0</td>
<td>NO</td>
<td>30.0</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1.0</td>
<td>NO$_2$</td>
<td>0.2</td>
</tr>
<tr>
<td>HCl</td>
<td>0.15</td>
<td>O$_2$</td>
<td>50.0</td>
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<tr>
<td>CH$_3$CN</td>
<td>10.0</td>
<td>CH$_3$CHOHCH$_3$</td>
<td>20.0</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>10.0</td>
<td>CH$_3$CH$_2$OH</td>
<td>20.0</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>20.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**TDLAS System Components**

- TDLAS systems typically utilize near-infrared diode lasers that operate at room temperature
  - these are the same type of solid state lasers that are utilized for long-distance, high-speed telecommunications
Wavelength Modulation Spectroscopy (WMS)

- Laser is tuned, via temperature, to the center of the absorption line ($\nu_0$)
- Laser wavelength is repeatedly scanned, via its injection current, across a portion of an absorption line
  - Produces an amplitude modulation of the laser power received at the detector
  - AM frequency is twice the $\omega_m$ frequency
- Phase sensitive (lock-in) detection of the small AM signal yields the molecular concentration in the laser path

\[
\nu(t) = \nu_0 + \delta \sin(\omega_m t)
\]

\[
A(t) \sim A_0 [1 - a \cos^2 \omega_m t]
\]
Example TDLAS Waveforms

Absorbance = $\ell \ln(\text{evacuated/signal})$
- common-mode signals suppressed
- waveform is called the 2f signal

Demodulating 2f signal provides low-noise signal proportional to absorbance
Low-Noise Demodulation

- Demodulation converts a high frequency oscillation into a low frequency signal with amplitude proportional to the oscillation amplitude
  - example: rectification

- Phase-sensitive demodulation employs a “reference” signal to demodulate only input components matching the reference frequency and phase
  - example: lock-in amplifier, or mixer (multiplier), and low pass filter
  - Provides a very-narrowband filter that rejects out-of-band noise
PSI TDLAS Evolution

SpectraScan®
(1995)
- WMS (analog)
- Four Measurement Paths
- Industrial I/O Ports

WaterScan™
(1998)
- BRD
- Self-Contained Sampling Cell
- Dedicated Industrial Computer

SolventScan™
(2003)
- WMS (digital)
- Pharmaceutical Manufacturing
- Laptop Computer

GasScan™
(2004)
- Stand-alone detector/alarm
- 7” x 6” x 1.5” package
- Configurable as point, open path, or standoff sensor

RMLD™
(2003)
- Lightweight, handheld, battery-powered
- Stand-off detection
- Embedded microprocessor

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**Measurement Example**

| Analyte gas   | H₂O
|---------------|----------------|
| Sample gas mix | NH₃, BCl, DCS, SiH₄, PH₃, AsH₃, B₂H₆, N₂, Ar, H₂, He, O₂, Kr, Ne, Xe, CH₄, C₂H₆, C₂H₄, C₃H₈, C₃H₆
| Measurement ranges | 0 to 0.1; 0 to 1; 0 to 10 ppm
| Detection limit | 50 ppb (S/N=1)
| Repeatability | ±5% of full scale or 50 ppb
| Cell pressure range | 0.1 mm Hg to 1.5 atm
| Wetted materials | 316L stainless steel, MgF, Viton
| Response time (t₉₀) | 1 Hz, time between zero and 90% of final concentration
| Dynamic range | 50 ppb to >10 ppm

- Comparison with Capacitance Manometer
  - 85m optical pathlength extractive multi-pass cell

![Graph showing Neat H₂O Vapor concentration vs. [H₂O] cm⁻³ (Baratron Measurement) with 374 ppb at STP and 37 ppm at STP points.

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**Graph Details:**

- X-axis: [H₂O] cm⁻³ (Baratron Measurement)
- Y-axis: [H₂O] cm⁻³ (BRD)
- Data points: 374 ppb at STP, 37 ppm at STP

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In-Situ Optical Measurement Cell

- Multi-pass optics improve sensitivity by providing a 10 m optical path in 25 cm physical length
- Measurement section may be heated to 250 C with no performance loss
Multipass Cell in Close-Coupled Heated Flue Gas Extraction Probe

Ammonia (NH₃) Monitor for NOx reducing SCR/SNCR systems

Probe Installed in Ceramic Manufacturing Kiln Exhaust Duct
**Example Data using Extractive Sampling**

- Extractive flow through compact non-incendive multipass cell
- Extractive heated close-coupled cell in highly-reactive process
Multipass Cells in CO₂ Eddy Covariance Flux Measurement System
Installation Example:
Control of Oxygen-Enriched Furnaces

- In-situ cross-duct configuration
- Pulsed-fuel operation mode
  - 0.5 Hz oscillation
Open Path Alarm Installation Example

One day’s data

[Diagram showing the installation of an open path alarm system, including components such as electronics console, passive retroreflector, laser beam, processing area, and optical fiber and interface cable. The diagram also includes a graph showing received laser power over time.]
**PSI Single-Board WMS Platform**

- Incorporates laser control and data processing on battery-operated board
- Digital signal processor for high-speed data acquisition and processing
- Embedded microcontroller for laser operation, data reduction, communication
- Serial (RS-232) data output stream and setup interface
- SPI communication available for interface with other microcontrollers
Portable Standoff Hazardous Gas Detector

- Senses target gas along path between transceiver and a surface up to 30 m (100 ft) distant
- No cross-species interferences
- Shoulder-mounted control unit; handheld transceiver
- Total weight < 6 lb
- Eye safe
- Battery-operated, > 8 hours between charges

TDLAS vs Position at Municipal Gas Leak
Miniature Ambient Gas Sensor

- Instant (< 1 s) response
- No cross-species interferences
- Audible alarm
- Serial data port
- AC or Rechargeable Battery Power
- Internal or Remote Sensor Head
- Configurable as Point, Open Path, or Standoff Sensor

Applications
- Industrial/Commercial Toxic Gas Alarms
- On-line trace gas process monitoring and control
- Environmental monitoring
- Combustible Gas Alarms
- Combustion Gas (Fire) Sensors
Summary

- TDLAS has evolved over the past decade from a laboratory specialty to rugged, reliable commercial industrial instrumentation.
- Current applications for permanently-installed systems abound in industries that include: petrochemical and chemical processing, aluminum smelting, energy production, pharmaceutical and ceramics manufacturing, agriculture, and medicine.
- Novel, battery-operated, hand-portable TDLAS systems will soon be used widely for natural gas pipeline leak surveying and other standoff detection applications.
- Compact packages with low power consumption are expected to find application for distributed fast alarms and oxygen sensing in highly-combustible environments.