From fundamentals to field: Understanding TDLAS

Colin Robertson

2025 | CGA Energy Nexus | Annual Technical Conference

Fuelling the Future

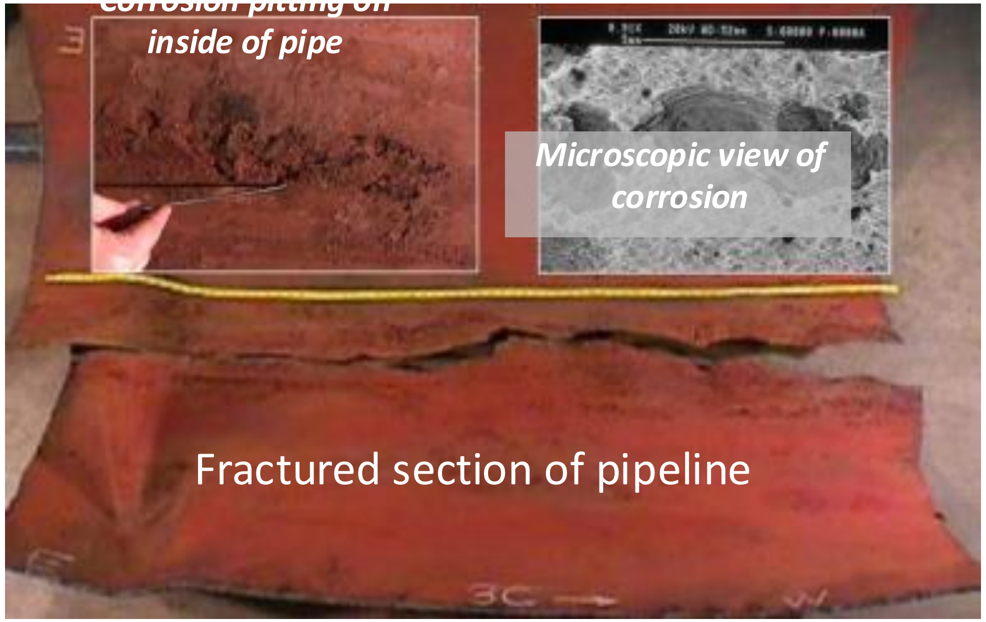
Why Measure H_20 and H_2S

Common Technologies

What is TDLAS

TDLAS Benefits

Why measure H_2O and H_2S in natural gas?



Root cause: Unreliable techniques for H_2O measurements in natural gas, i.e., aluminum oxide (Al_2O_3), phosphorus pentoxide (P_2O_5), and quartz crystal. Most techniques are affected by aggressive gases such as H_2S, & CO_2. The presence of water makes these gases more aggressive, accelerating loss of sensitivity, making it difficult to maintain accuracy.

Solution: use TDLAS because it is unaffected by contaminants

CGA Energy Nexus & Annual Technical Conference 2025

Hydrate formation - Ice-like crystalline solid (forms with natural gas and water at high pressure)

- Deeper wells, high pressure: risk of hydrate formation
- May require de-pressurization or pigging
- Lost production / revenue millions of $$
- Methanol injected to combat hydrates
- Electrochemical sensors are cross-sensitive to methanol

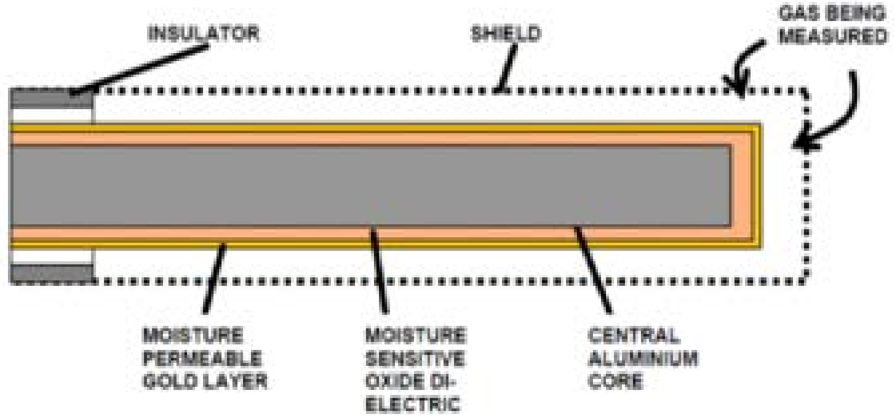
Solution: use TDLAS moisture analyzer which is insensitive to methanol

Measurement Techniques for Trace-level H_2O in Natural Gas

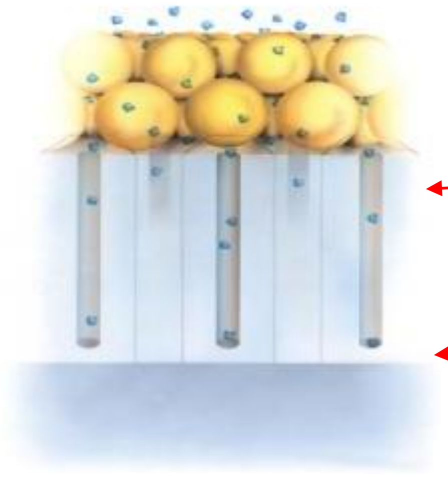
- **Aluminum Oxide (Al_2O_3) Electrochemical Sensor**
- **Quartz Crystal Microbalance (QCM)**
- **Tunable Diode Laser Absorption Spectroscopy (TDLAS)**

Al_2O_3 Moisture Probes

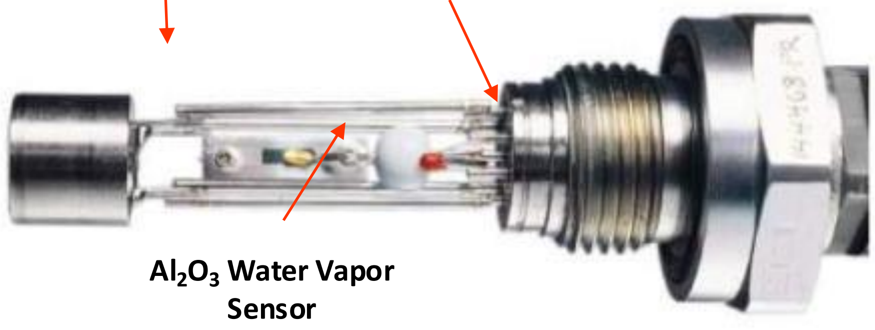
Probes shown with stainless steel shield to minimize sensor contact with condensable liquids and particulate matter



Rate of H_2O vapor diffusion into and out of probe determines wet-up and dry-down times and analyzer response time to H_2O concentration changes

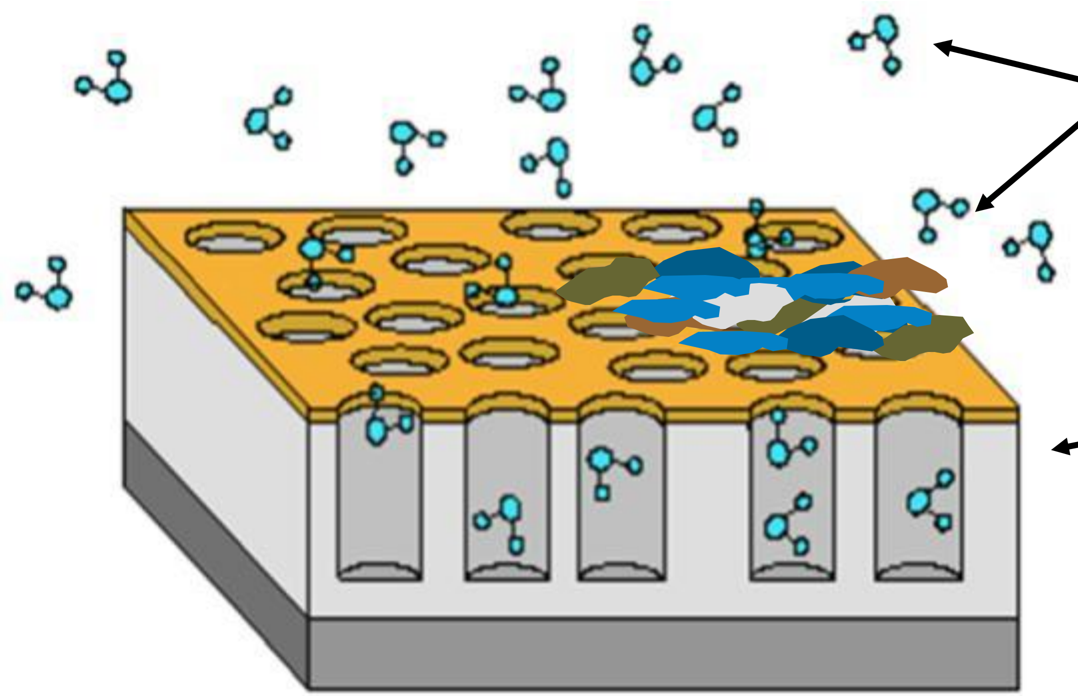


Al_2O_3 Electrochemical Sensor Construction



- The oxide layer is porous and under dry conditions the pores are filled with air which has a dielectric constant ≈ 1
- Water has a dielectric constant of ≈ 80
- When exposed to water, micro-condensation occurs in the pores increasing capacitance between the substrate and upper electrode
- The sensor's impedance is calibrated against a dew point reference standard

Al_2O_3 Electrochemical Sensor



Liquid or solid contamination on surface:
Portion of surface no longer effective

Water trapped outside
causes low readings

Water trapped inside
causes high readings

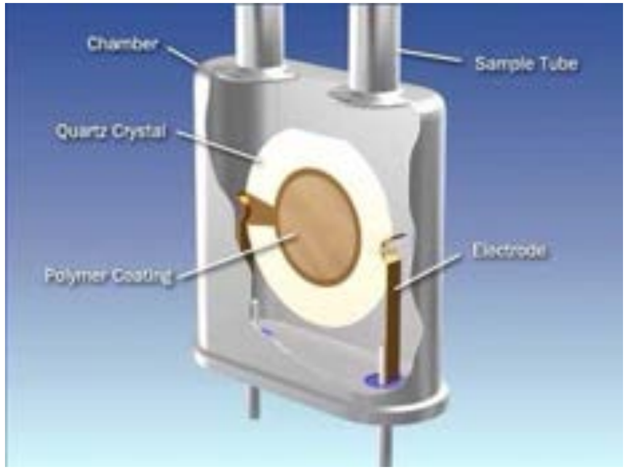
Methanol and Glycol
detected as water

Al_2O_3 Electrochemical Sensors

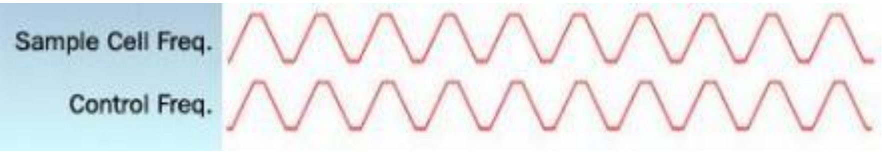
Design / Performance Characteristic	Associated Problem
Sensor is in direct contact with gas	Prolonged exposure to dry gas desensitizes the sensor element causing it to “go to sleep” and report false low H_2O values
Measurement Principle: Capacitance (indirect measurement of H_2O)	Sensor response is not specific to H_2O Other molecules in gas can cause a change in capacitance and an erroneous measurement
Response Time to H_2O Changes	Several minutes time which may miss the onset of a breakthrough in a molecular sieve bed
Measurement Repeatability ($\pm$ 2%)	While Al_2O_3 sensors are simple and inexpensive - they are not precision instruments for critical measurements

QCM (Quartz Crystal Microbalance) H_2O Analyzer

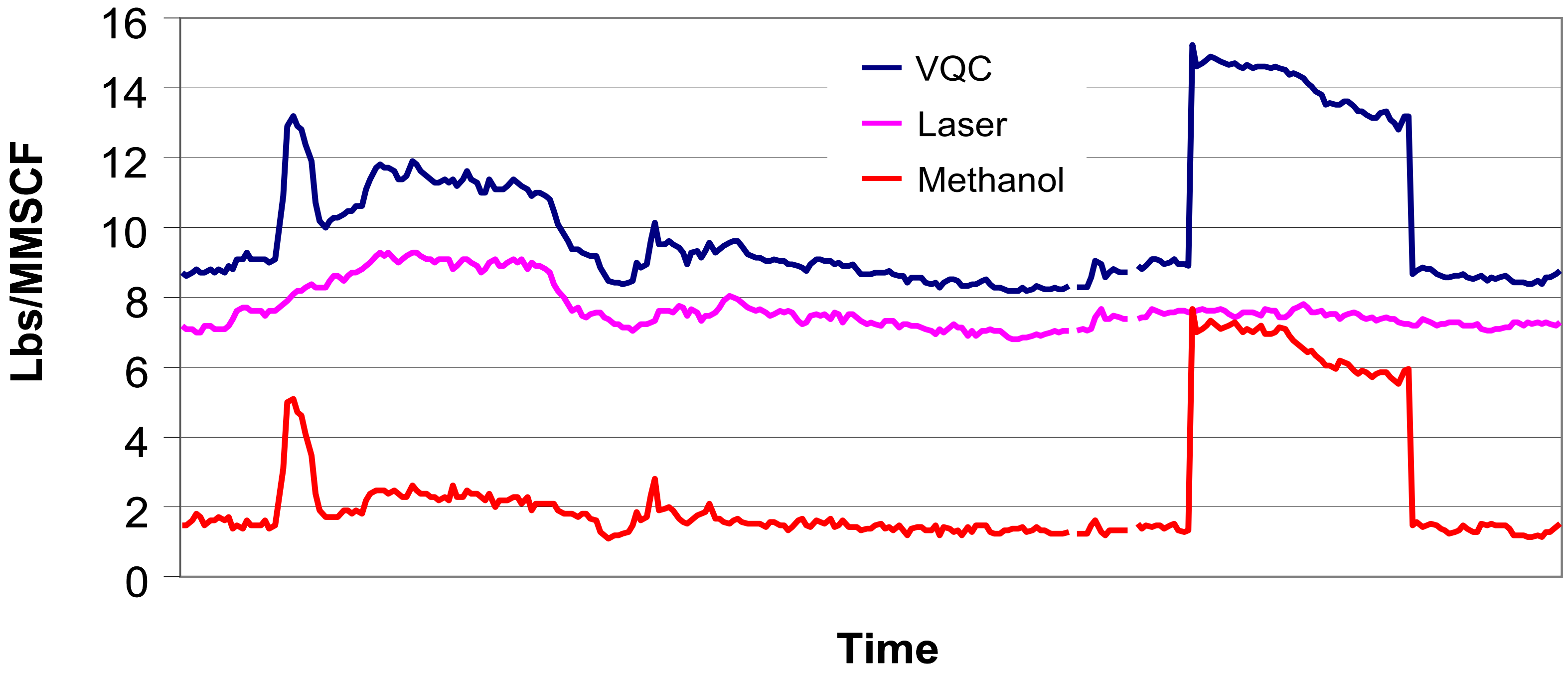
CGA Energy Nexus & Annual Technical Conference 2025



- A pair of electrodes support the QCM sensor
- Voltage is applied to produce oscillation
- Surface of oscillator is coated with a hygroscopic polymer
- Moisture sorbs on to polymer
- As mass of the QCM sensor changes it changes the frequency of oscillation which is measured



Response of TDLAS and QCM Analyzers to Water and Methanol in Natural Gas



- **Trace H_2O monitored by two analyzers analyzing the same natural gas stream**
- **Injection of methanol does not affect H_2O measurement of the TDLAS analyzer**
- **The QCM analyzer does not discriminate between H_2O and methanol giving a false reading of H_2O concentration**

Design / Performance Characteristic	Associated Problem
Sensing element is in direct contact with gas	Surface of sensing element must be in contact with H_2O molecules to perform measurement and must then dry down to detect a change in concentration
Measurement Principle: Oscillation Frequency Change due to change in mass of a gas sample (indirect measurement of H_2O)	Response is not specific to H_2O Contaminant molecules in gas and/or change of stream composition can cause a change in frequency and an erroneous / biased measurement
Response Time to H_2O Changes	Several minutes or longer due to dry down time of the sensing element, which may miss the onset of a breakthrough in a molecular sieve bed

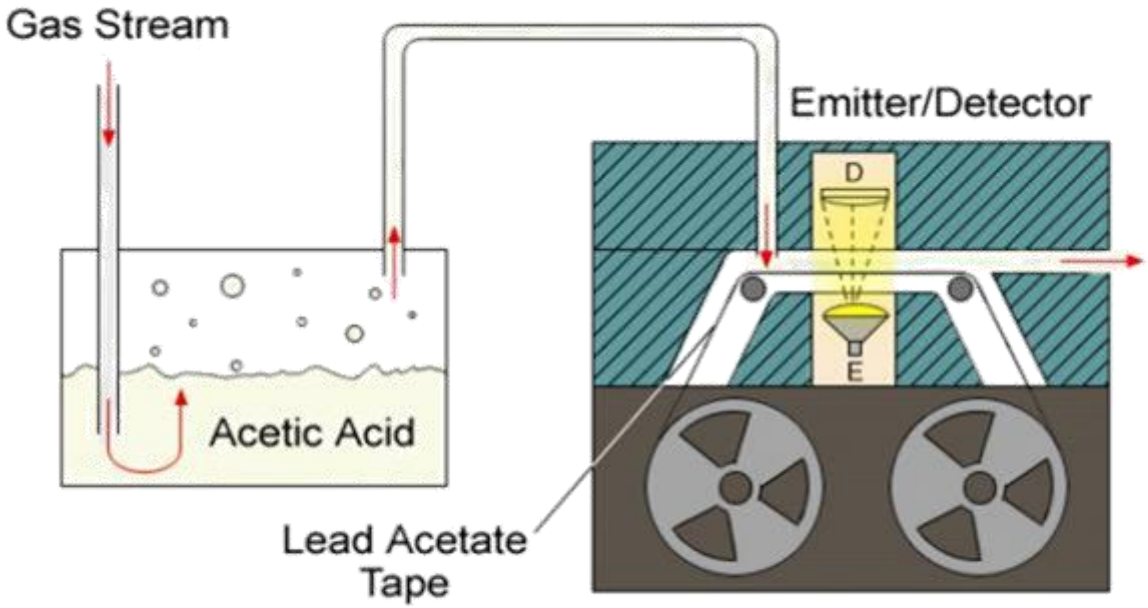
Measurement Techniques for Trace-level H_2S in Natural Gas

- **Lead Acetate Tape**
- **UV Photometer**
- **Tunable Diode Laser Absorption Spectroscopy (TDLAS)**

Lead Acetate Tape Analyzers for H_2S Measurement

Lead Acetate Tape Analyzer – Principle of Operation

$H_2S + Pb \rightarrow PbS + H_2O$



- Photometric measurement of H_2S reaction with lead acetate impregnated paper tape
- PbS is brown and causes the paper tape to darken – the degree of darkening is proportional to the concentration of H_2S
- Tape advances every 3 – 5 minutes to expose fresh tape

Lead Acetate Tape Analyzer – Pros & Cons

Pros of Lead Acetate Tape Analyzer

- Analyzer is relatively inexpensive
- Supports measurement of H_2S and Total Sulfur

Cons of Lead Acetate Tape Analyzer

- High maintenance requirements for tape replacement (4 to 8 weeks)
- An H_2S spike can fully expose the entire tape (requiring immediate replacement)
- Tape breaks often (must be repaired immediately)
- Tape reels wear out
- Refilling acetic acid
- Technicians handle lead tape and may be exposed to H_2S when checking analyzer
- Lead acetate paper tape (CAS 6080-56-4) is classified as a hazardous waste (RCRA Code D002/D003 , EU 16 05 06) requiring hazardous waste disposal

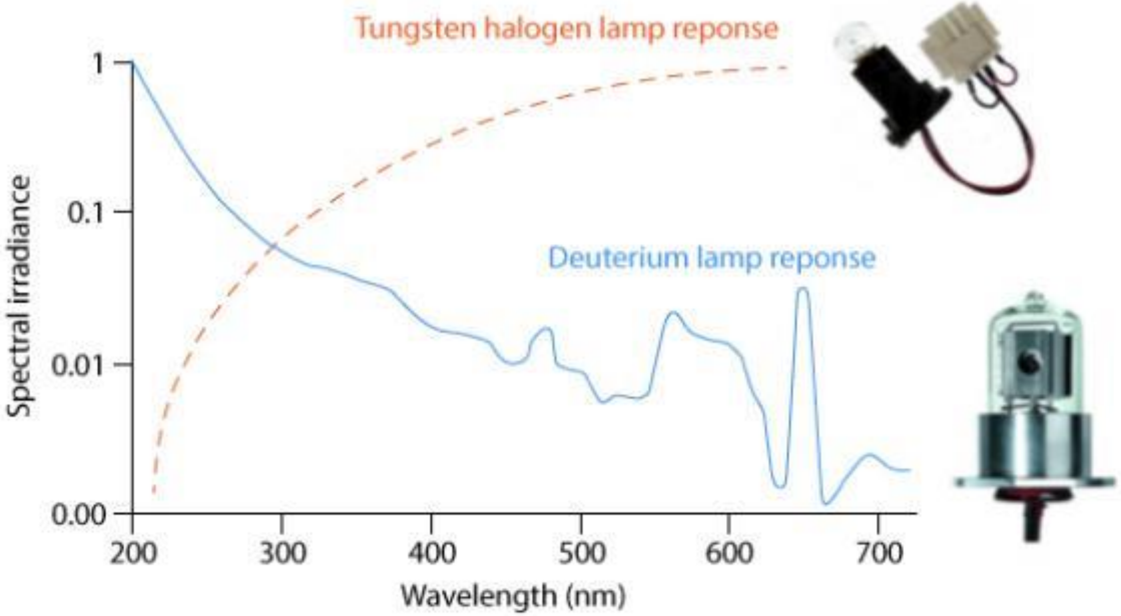
UV Photometer for H_2S Measurement

(UV lamp)

(Filter Wheel)

PMT
(Photomultiplier Tube)

UV Photometer – Filter Wheel Mechanism



- Broad wavelength output of UV lamp requires narrow band width spectral filter to minimize interferences by filtering out UV wavelengths that would be absorbed by other components in the gas stream

UV Photometer – Pros & Cons for H_2S Measurement

Pros of UV Photometer Technology

- Measures H_2S with option for carbonyl sulfide (COS) & methyl mercaptan (MeSH)

Cons of UV Photometer Technology

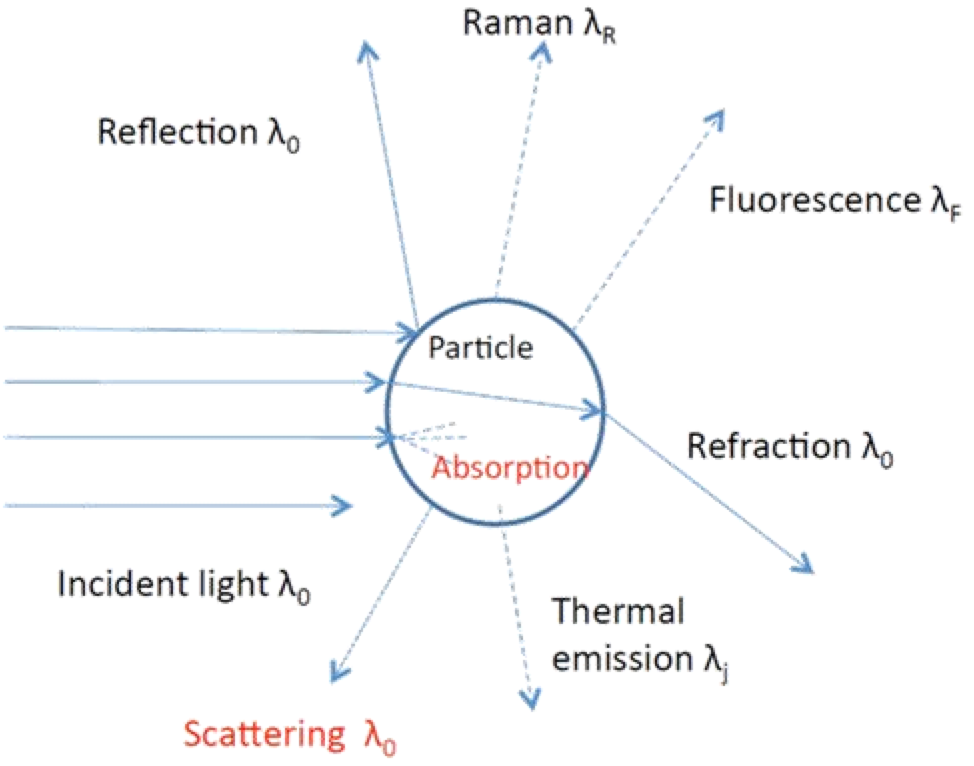
- Interferences from sulfur & aromatic compounds
- UV light output from lamp diminishes over time resulting in drift and requiring a zero calibration every 24 hours
- Filter wheel used for UV wavelength selection / transmission has lower resolution
- Expense of replacement UV lamps

TDLAS Analyzer

Definition of spectroscopy – (I)

- **Spectroscopy** is the use of the absorption, emission, or scattering of **electromagnetic radiation** by atoms or molecules to qualitatively or quantitatively study the atoms or molecules, or physical processes

- **Tunable diode laser absorption spectroscopy (TDLAS) analyzers** use **absorption** to perform measurements of a target molecule (analyte)



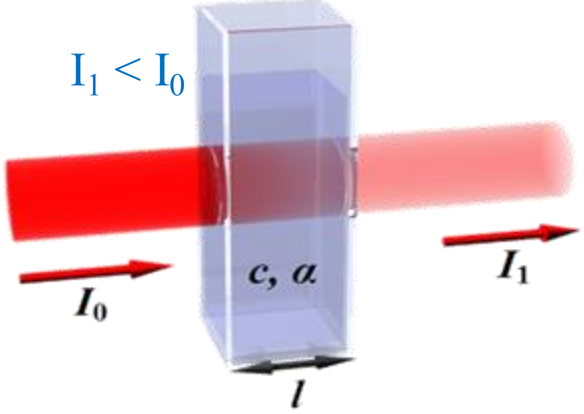
Absorption spectroscopy

Sample

- Absorbance is a function of (concentration, path length, and absorptivity)
- Concentration (c) increases → absorption increases
- Path length (l) increases → absorption increase

Light source

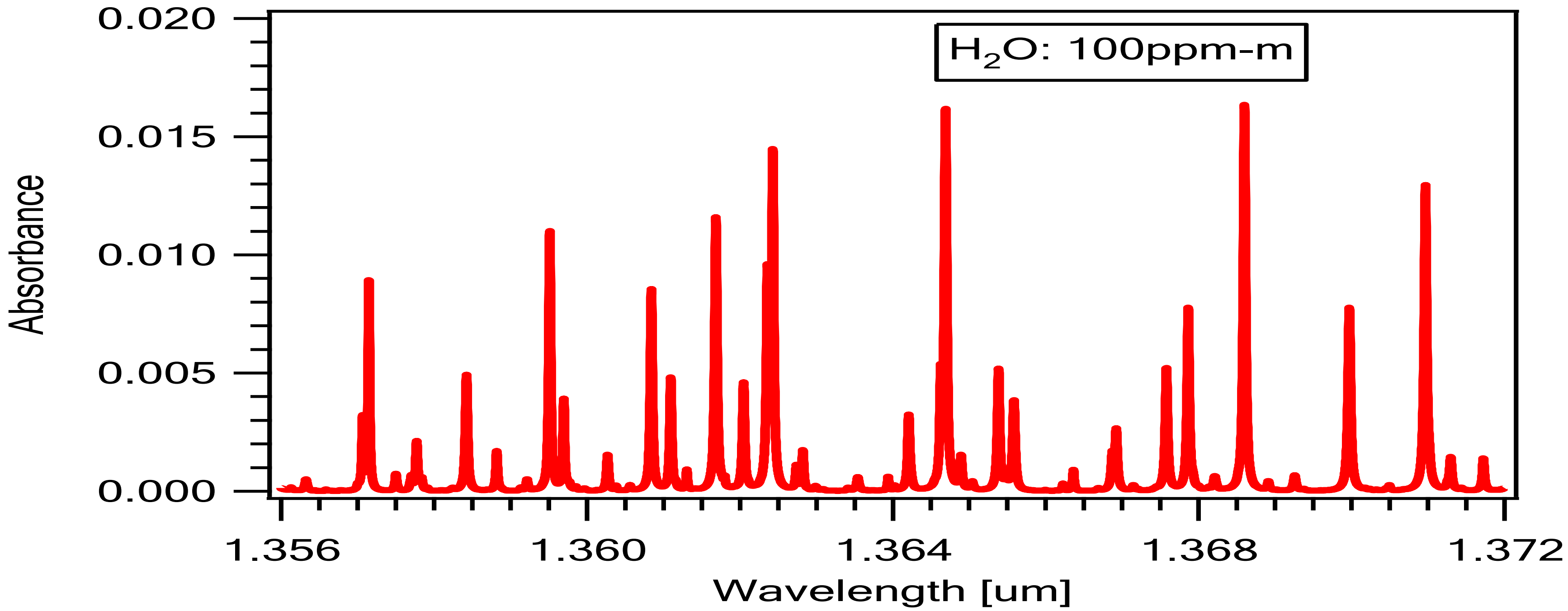
$I_1 < I_0$



Light detector

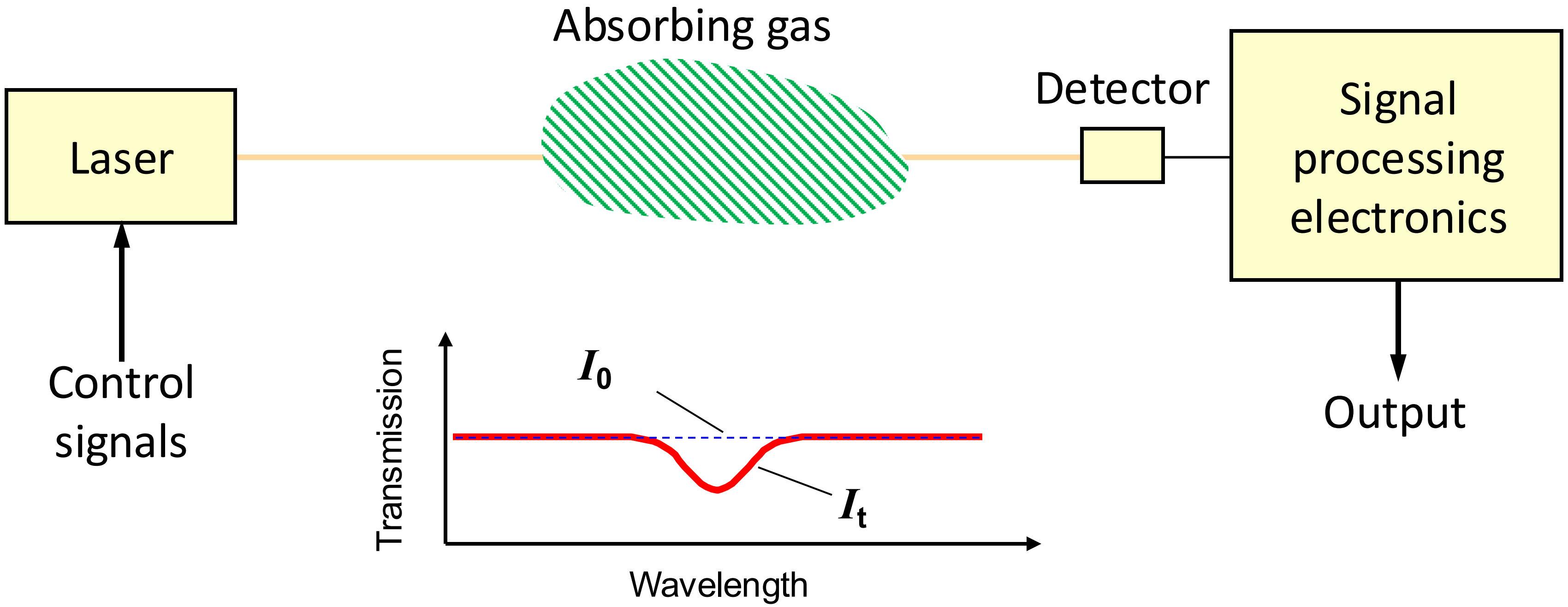
Definition of spectroscopy – (II)

- A **spectrum** is a plot of the interaction as a function of wavelength or frequency

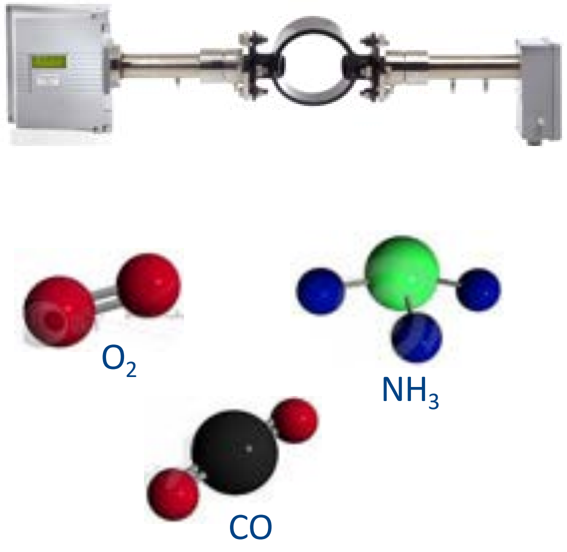


CGA Energy Nexus & Annual Technical Conference 2025

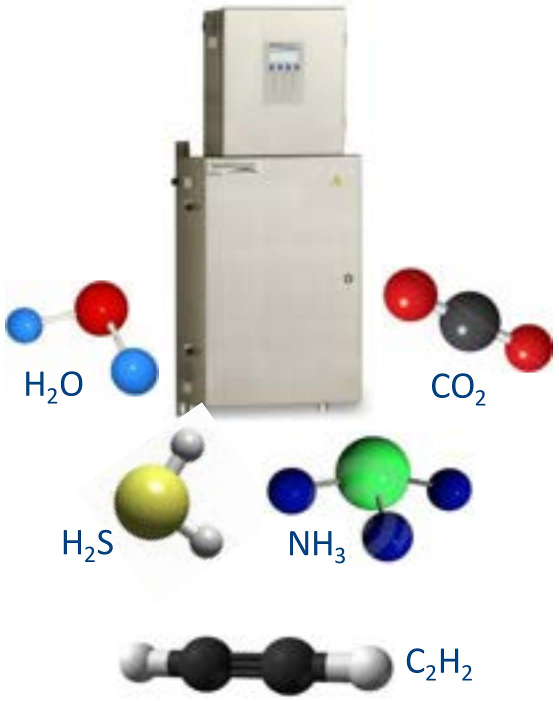
- **T**unable **d**iode **l**aser (the light source)
- **a**bsorption **s**pectroscopy



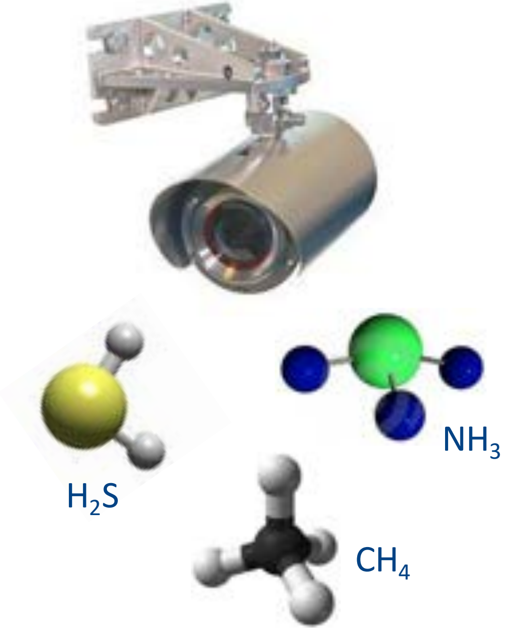
TDLAS gas analyzers - 3 flavors



Cross stack/cross pipe/extractive-cross pipe TDLAS



Extractive
fixed path length TDLAS



In situ &
open path
TDLAS

CGA Energy Nexus & Annual Technical Conference 2025

TDLAS gas analyzer – proven technology for reliable H_2O measurement

Analyzer systems

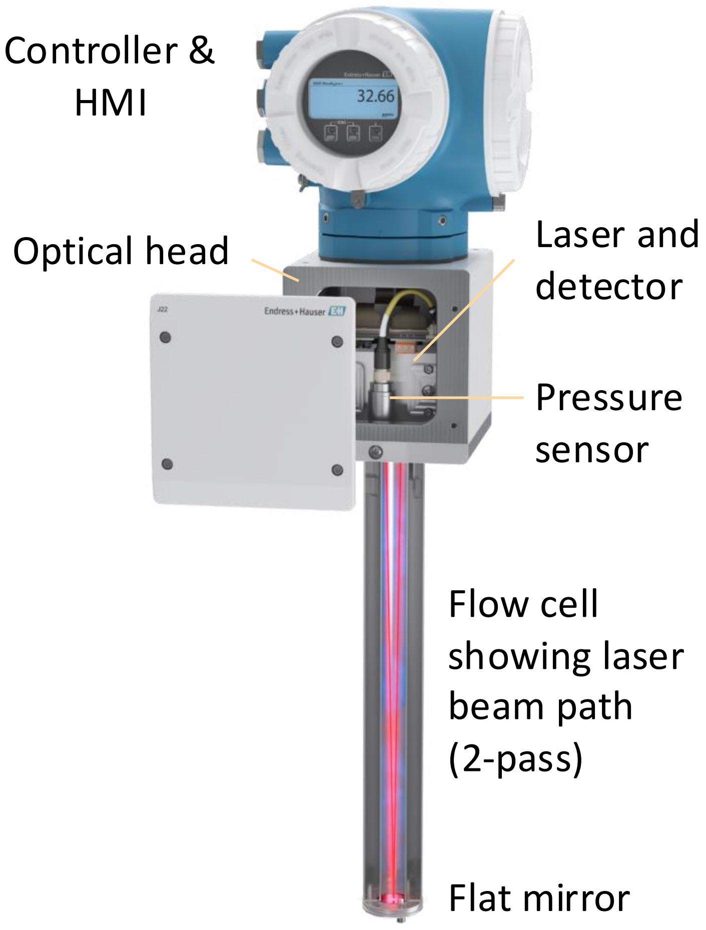
- Proven reliability and real-time moisture measurement guarantees continuous gas deliveries and eliminates disputes
- Highest analyzer availability and low maintenance significantly reduces operational costs
- Diagnostics support reliable automation of natural gas quality control

Distinguishing features

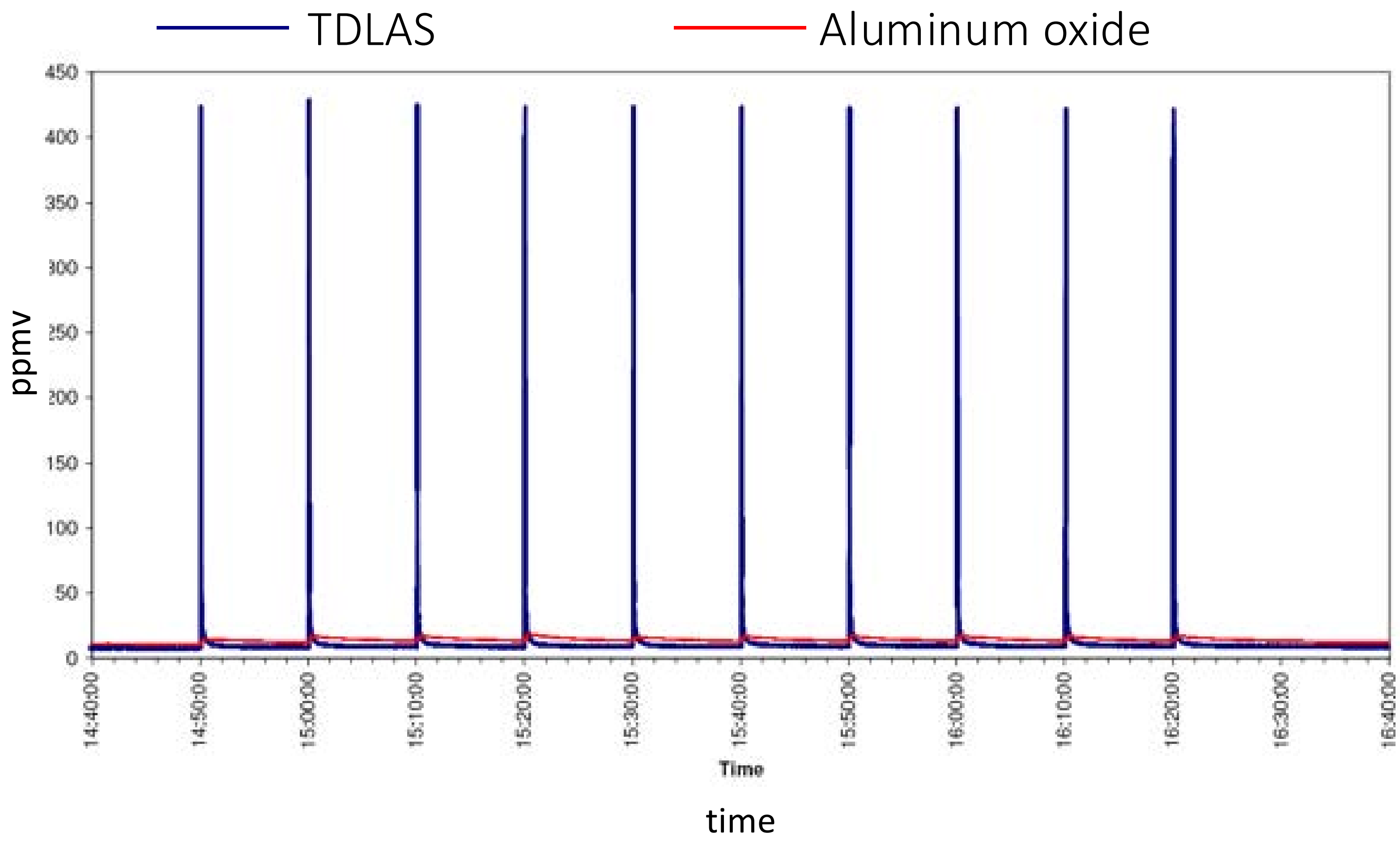
- Onboard analytics
- Web server / web browser for service software
- Data, history, and spectrum logging
- Easy to service optics and electronics in the field
- Does not require field recalibration

TDLAS (tunable diode laser absorption spectroscopy) analyzers

- TDLAS analyzers employ tunable diode lasers (TDL) to inject a beam of near-infrared light into the gas sample
- Light absorbed by moisture is measured by the detector
- Moisture concentration is correlated to the absorption
- Gas pressure and temperature are measured to compensate for their impact on the measurement

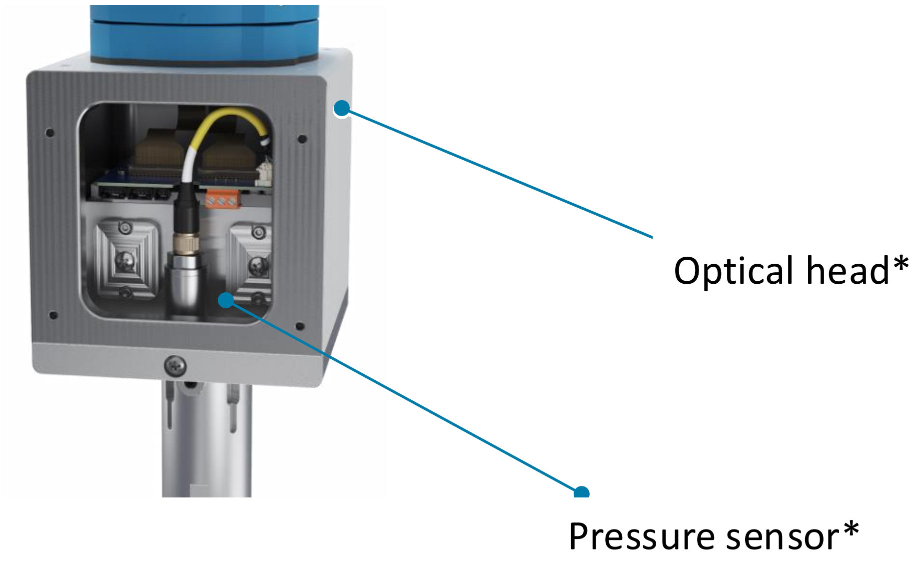


CGA Energy Nexus & Annual Technical Conference 2025

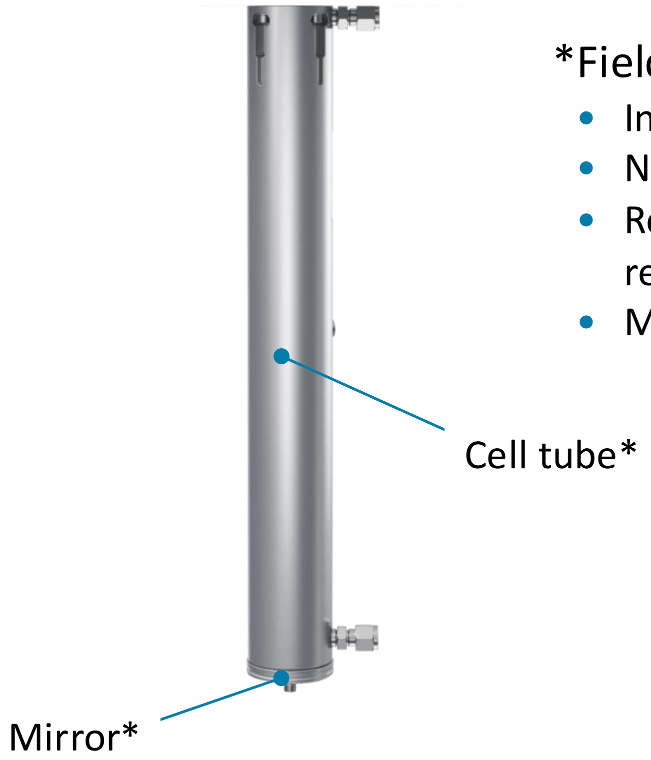


- In this 2-hour test, the aluminum oxide analyzer barely recognized H_2O slugs because it is too slow. The TDLAS catches moisture slugs and dries down quickly.

TDLAS gas analyzer - ease of service (optics)



Optical head enclosure
(OHE)



*Field-replaceable:

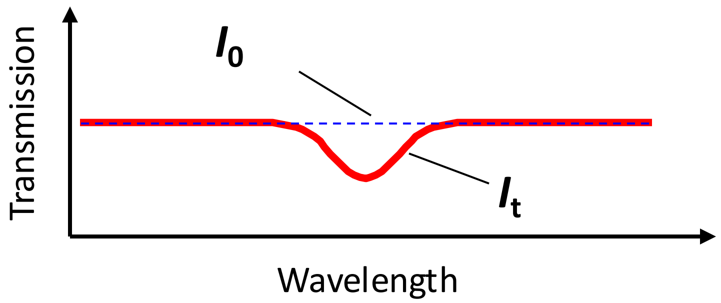
- Interchangeable
- No recalibration required
- Requires simple tools to remove and replace
- Minimized downtime

TDLAS gas analyzer measurement ranges for applications

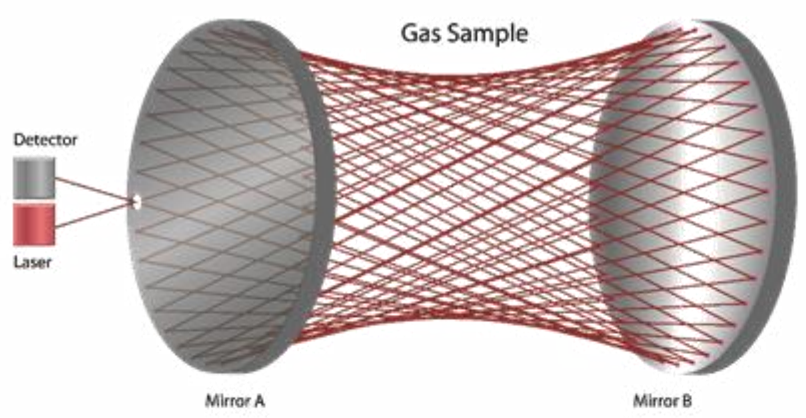
Typical H_2S measurement ranges

• LNG	0-10 to 0-20 ppm
• NGL fractionation	0-20 ppm
• Refining production	0-10 ppm to 0-300 ppmNatural gas 0-10 ppm to 0-500 ppm
• Natural gas pipeline	0-10 ppm to 0-500 ppm
• Energy transition	0-10 ppm to 0-500 ppm
• Gas processing	0-10 ppm to 0-500 ppm
• Petrochemical	0-500 ppm

Beer-Lambert law



Two pass

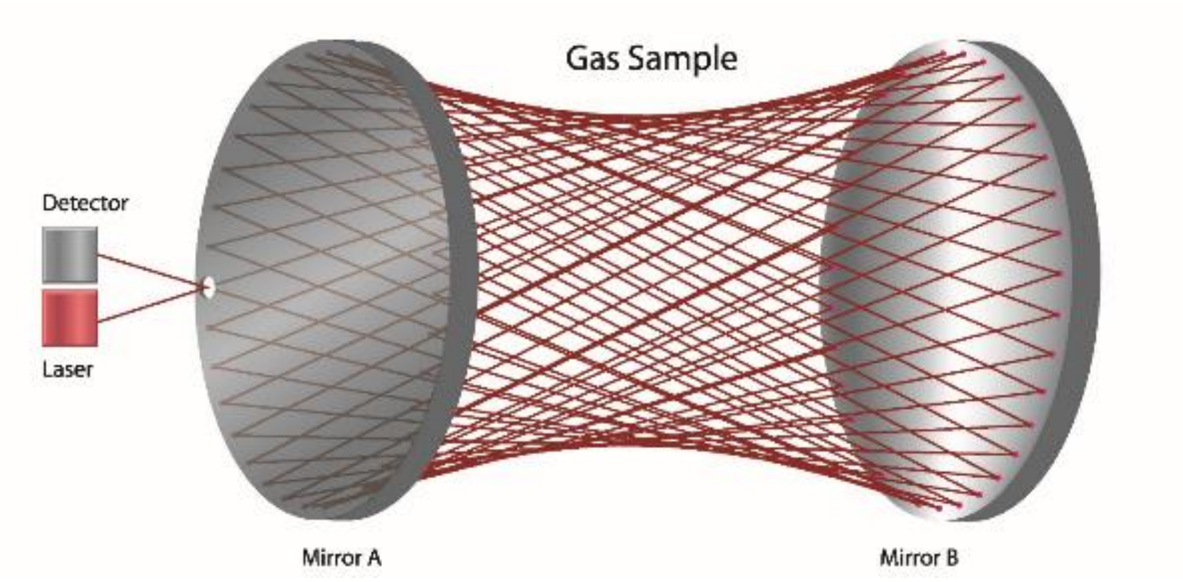


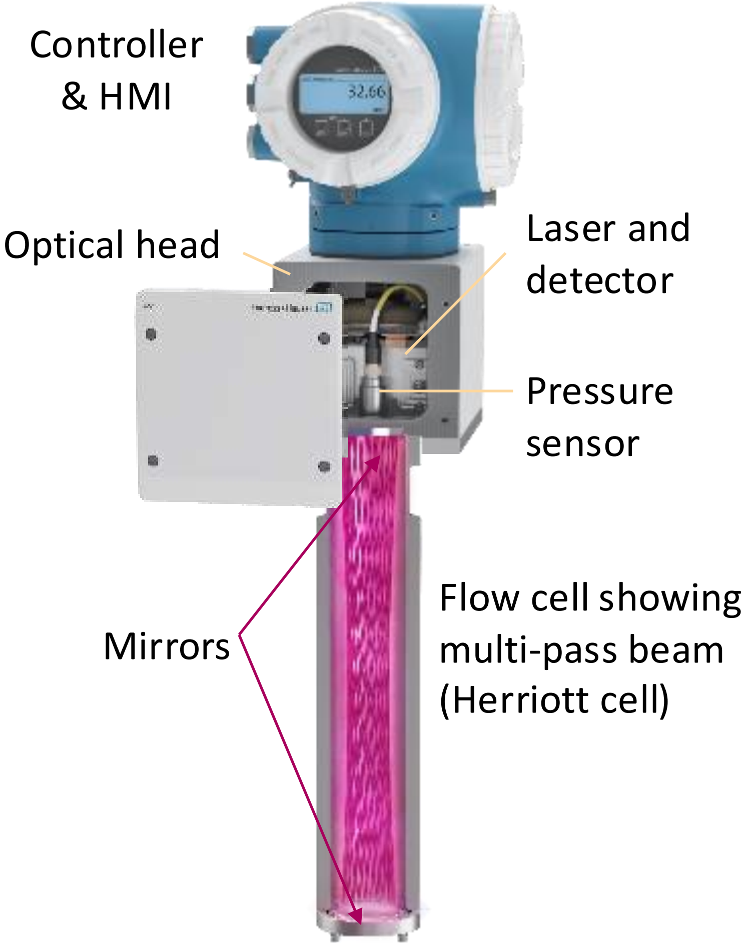
Multi pass

Absorbance = function of (concentration, path-length, and molar absorptivity)

CGA Energy Nexus & Annual Technical Conference 2025

- The TDLAS analyzers employs tunable diode lasers (TDL) to inject a beam of near-infrared light into the gas sample.
- Light absorbed by H_2S is measured by the detector.
- H_2S concentration is correlated to the absorption augmented by **differential** spectroscopy.
- Gas pressure and temperature are measured to compensate for their impact on the measurement

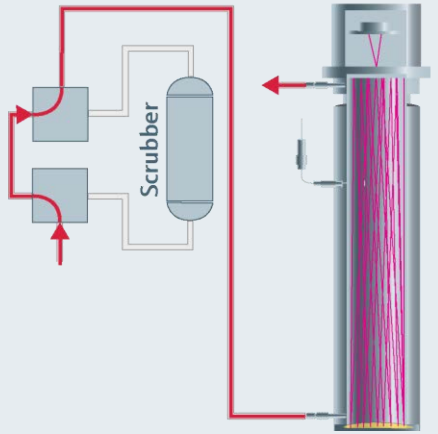




H2S Spectrometer

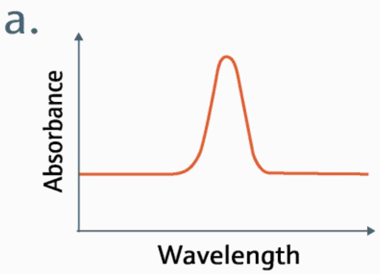
TDLAS gas analyzer - differential spectroscopy

Gas with analyte

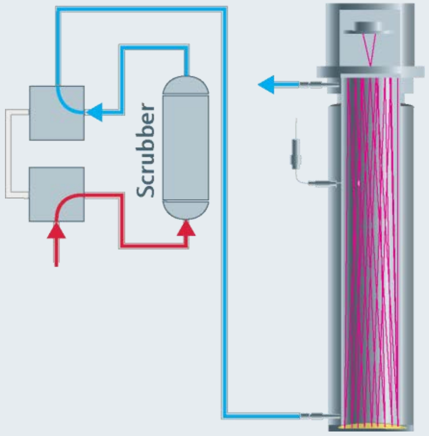


Process

Spectrum with analyte

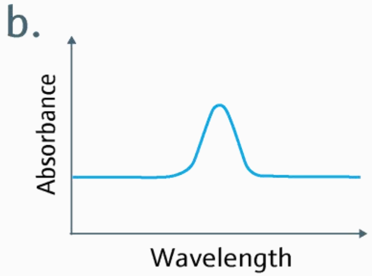


Gas without analyte



Zero spectrum

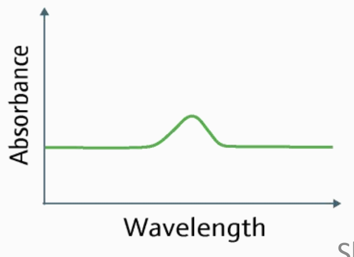
Spectrum without analyte



Analyte concentration
is calculated from the differential
spectrum

Differential measurement

a - b = analyte spectrum



Comparison of Al_2O_3 Sensor vs. TDLAS Analyzer for Trace H_2O

Design / Performance Characteristic	Al_2O_3 Aluminum Oxide	TDLAS Analyzer
Direct contact with process gas	Yes	No – laser and detector are isolated and protected from gas
Analyte-specific measurement	No – responds to other polar compounds (MeOH, glycols, H_2S)	Yes – absorption at analyte specific wavelength
On-stream factor > 95% (analyzer availability)	No – must be removed from service for factory recalibration	Yes
Analyzer response time to H_2O concentration changes	Several minutes - much longer for dry down (hours or days)	< 1 minute

Comparison of Lead Acetate Tape Analyzer vs. TDLAS Analyzer

Design / Performance Characteristic	Lead Acetate Tape Analyzer	TDLAS Analyzer
Consumable Items for Operation	Proprietary paper tape / cartridges Acetic acid reagent	None
On-stream factor > 95% (analyzer availability)	No	Yes
Mechanical components required for operation	Yes – tape drive system for paper reels / cartridges	No
Waste generated from operation	Lead tape is classified as a hazardous waste requires disposal	None

Comparison of UV Photometer vs. TDLAS Analyzer for H_2S

Design / Performance Characteristic	UV Photometer	TDLAS Analyzer
Analyte-specific measurement	No – interferences from sulfur compounds and aromatics	Yes
Calibration	A daily zero calibration is required to correct for drift from decreasing UV lamp output	No field calibration required Periodic validation checks confirm proper analyzer operation
Analyzer light source	UV lamp output decreases in continuous 24/7 operation requiring replacement	Solid-state, tunable diode laser operates continuously with no diminution in NIR output
Consumable Parts for operation	UV Lamp (one or more per year)	None

QCM Analyzer vs. TDLAS Analyzer for Trace H_2O Measurement

Design / Performance Characteristic	QCM Quartz Crystal Microbalance	TDLAS Analyzer
Direct contact with process gas	Yes	No – laser and detector are isolated and protected from gas
Analyte-specific measurement	No – responds to other compounds (MeOH, glycols, H_2S, compressor oil, etc)	Yes – absorption at analyte specific wavelength
On-stream factor > 95% (analyzer availability)	No	Yes
Analyzer response time to H_2O concentration changes	Several minutes (longer for dry down)	< 1 minute

CGA Energy Nexus & Annual Technical Conference 2025

Resistance to contamination - measurement method comparison

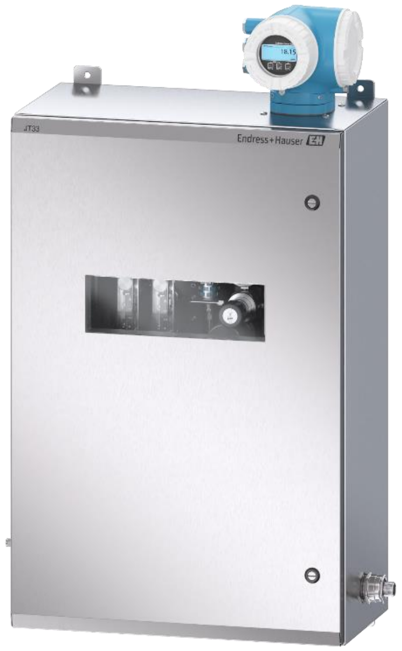
Gas phase contaminant	Al_2O_3	P_2O_5	Quartz crystal	Chilled mirror	TDLAS
Methanol	◗	◗	◗	◗	✓
Glycol	◗	◗	◗	◗	✓
Amine	◗	◗	◗	◗	✓
Mercury	●	✓	✓	✓	✓
Hydrogen sulfide	●	◗	◗	▯	✓
Hydrogen chloride	●	◗	◗	▯	✓
Chlorine	●	◗	●	▯	✓
Ammonia	●	◗	●	▯	✓

✓ = Analyzer unaffected

● = Can cause permanent damage to sensor

◗ = Can cause slow or inaccurate readings

TDLAS gas analyzer – proven technology for reliable measurement



TDLAS analyzer systems

- Reliable measurement guarantees continuous gas deliveries for natural gas pipeline operators, biomethane, and carbon capture plant owners, with continuous, real-time measurements to prevent pipeline corrosion and minimize the risk of an uncontrollable event
- Proven differential technology, tolerating contaminants, and allowing for stream changes for a dependable measurement ensures specifications are met and documented
- Highest analyzer availability and low maintenance with easy field serviceability significantly reduces operational costs
- Advanced diagnostics and measurement algorithms enable reliable automation of gas quality control

Summarized

- Reliable in critical applications
- Tolerant to changing conditions
- Exceptional analyzer availability
- Advanced diagnostics