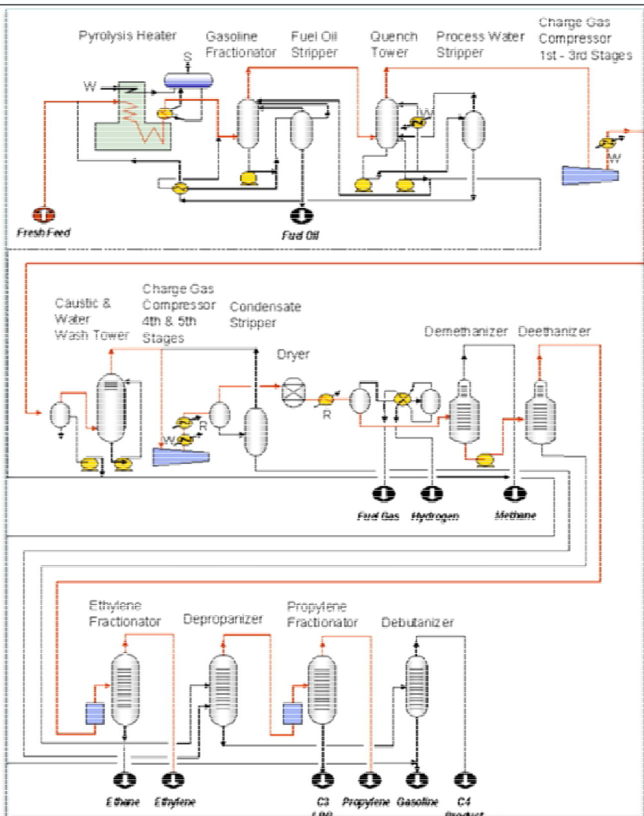
The Hydrocarbon Processing Industry – Olefins Plant



Current Process **gas** measurements

- GC 22
- Conventional (IR..) 18

Alternative Potential gas measurements

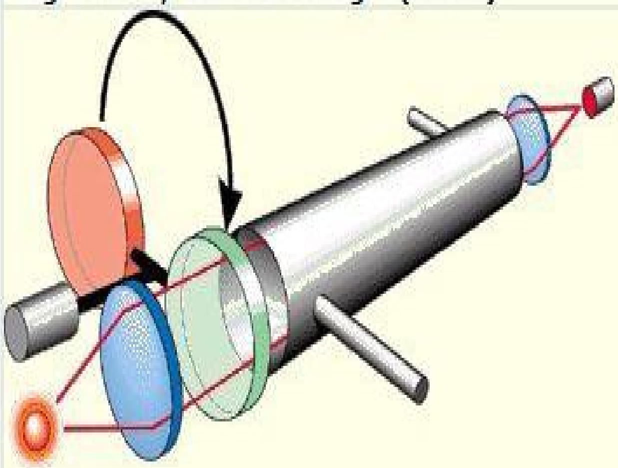
- TFS 16
- Conventional (IR…) 10-18
- Laser TDL 4
- TCD 6 (H_2)

Typical Application Detail and Interface to TDL/TCD/2500/Systems - Part Ethylene Plant (Hydrocarbon Sep)

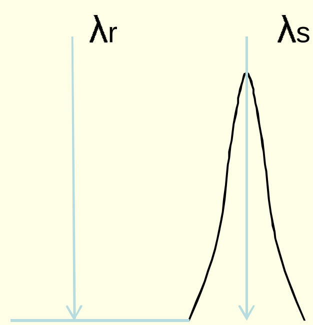
SAMPLE STREAM AND TASK	COMPONENTS MEASURED	TYPICAL RANGES	CURRENT METHODOLOGY	SOLUTION
Ethylene product for quality	C1, C2, C2=	300/10/1000ppm	PGC	Extractive TDL
	CO, CO2, NH3	2/5/1 ppm range	PGC	Conventional IR , GFC
	MeOH, PrOH, CO..	0-1ppm	PGC/IR	
To DeButaniser for process control	C1, C2, C2=	1000/10/1000ppm	PGC	Tuneable Filter
	CO, CO2, NH3	0-2/5/1 ppm	PGC	
	MeOH, PrOH, CO..	0-1ppm	PGC	
DePropaniser overhead for process control	C2, C3=, C3, C4+	%	PGC	Tuneable Filter IR
Propylene Product ,C3 split bottoms for quality	C3=, C4+. Propadiene (C3==)	%	PGc and IR	Tuneable Filter IR
	Propyne (methyl acetylene, MA)	Nb also trace ammonia, 5 ppm ,MA ,CO,CO2		Extractive TDL
Butene-1 product for process control	C2, C2=, C4, C4=, C6=	Ranges vary between 0-100ppm and 0-3000ppm	PGC	Tuneable Filter IR, TDLAS

SBMW…….Optical Filters

Single Beam, Dual Wavelength (SBDW)



Narrow wave bands –little energy but can reduce interference



λs / λr = very robust

<3% error for 50% transmission reduction

A pair of optical filters are mounted on a rotating motor. They pass through the beam of light alternately.
One filter (the measure filter) is chosen to pass light only at a wavelength that the gas to be measured absorbs, the other (the reference filter) to pass light at a wavelength unaffected by the gas to be measured.
The difference in absorbences is measured by the detector and provides a direct output of the gas concentration.

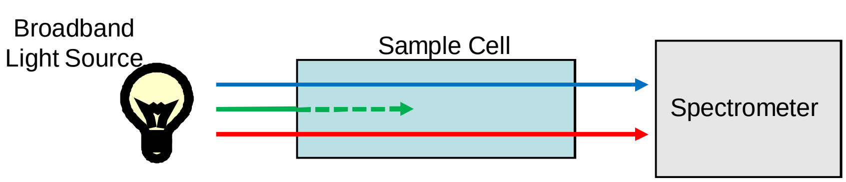
Setting the Standard for Automation™

Tunable Filter Spectrometer (TFS^{TM})

Analysis Solutions in Paradise……See us in Galveston 2013
The 58th Annual Symposium of the Analysis Division
Galveston, Texas, USA; 14-18 April 2013

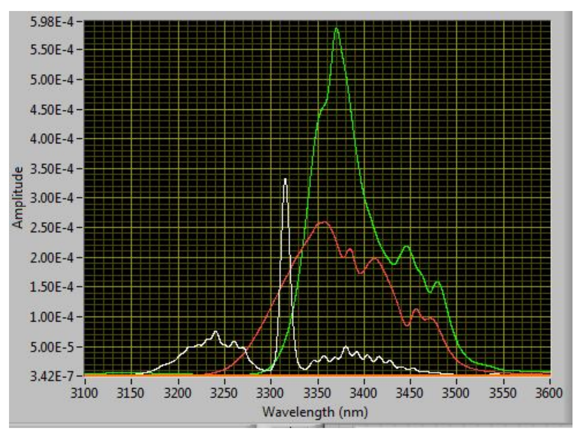
Measurement Principle

- Measurement in based on NIR/IR absorption spectroscopy with advanced spectral decomposition analysis
  - Molecules absorb light radiation at certain frequencies or wavelengths
  - Absorption spectrum of each hydrocarbon compound is unique => this acts as “fingerprint” and can be used to speciate compounds
  - Intensity of the absorption is proportional to the concentration of the molecules => this can be used to compute concentrations



No columns for compounds physical separations as in GC’s

Example absorption spectra, C1 – C3 alkanes



THE FABRE PEROT EFFECT

The Optical filters are rotated through the IR light source enabling spectral coverage of selected areas rather than just a narrow band “point” measurement

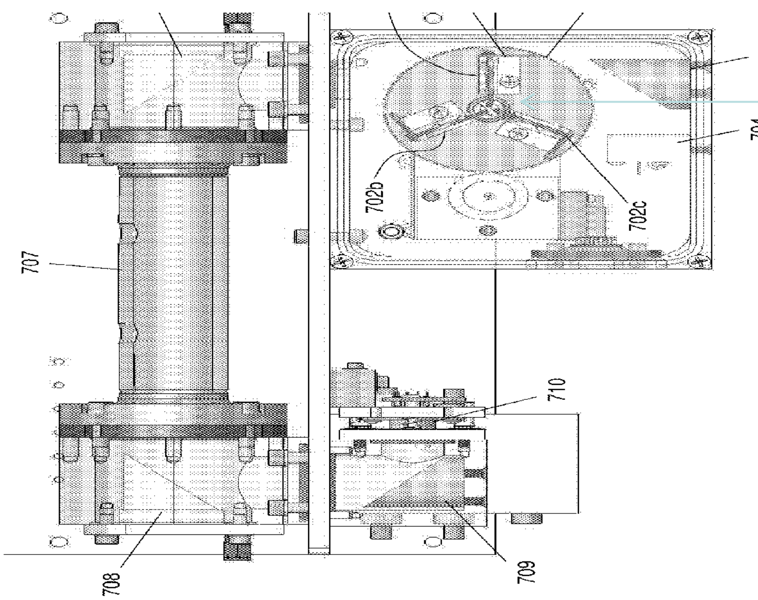
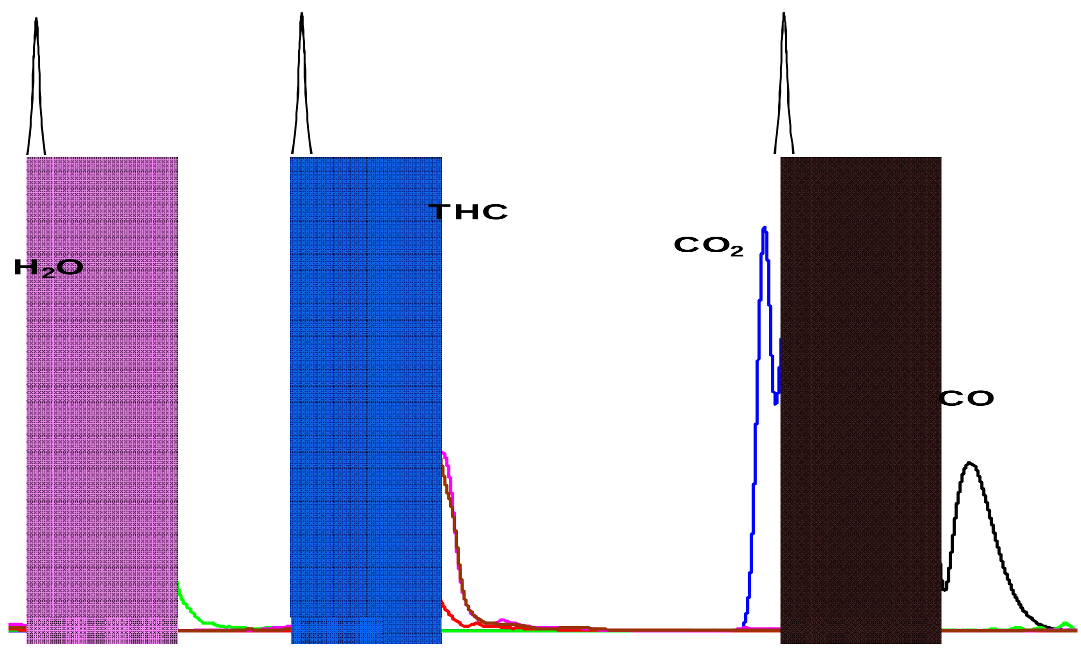


FIG. 7

Rotating optical filters

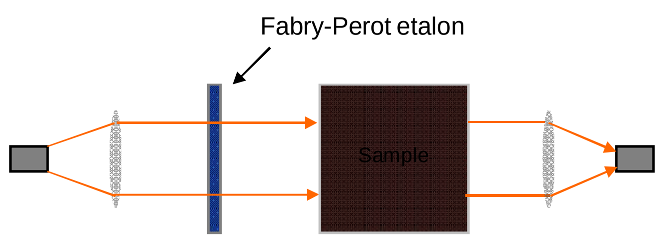
TFS™ Sensor Wavelength Scanning Technology

- Custom designed Fabry-Perot element
- Focused on relevant band(s)
- Wavelength scanning within the band(s)

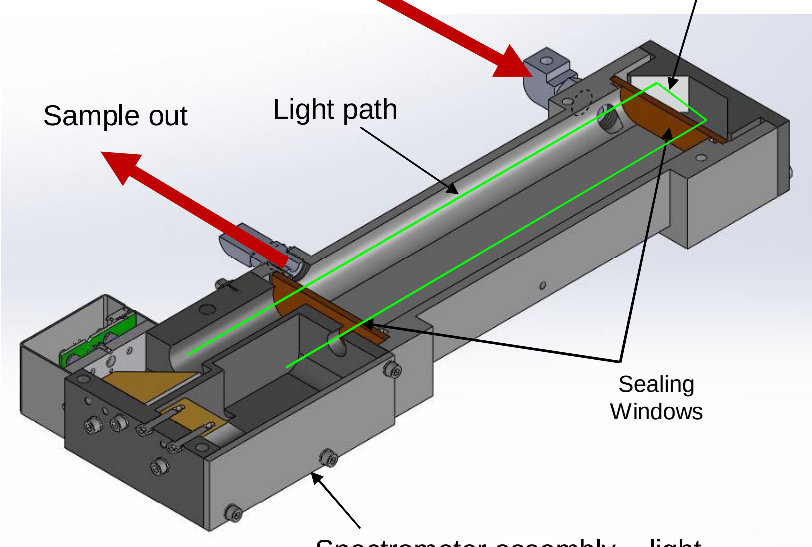


TFS – Wavelength Scanning Mechanism

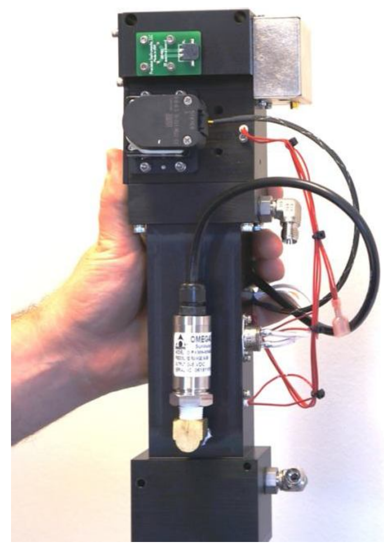
- Custom designed Fabry-Perot element
- Wavelength scanning within particular band(s)
- One rugged rotational element with low-precision requirement
  - “over engineered” with <1% of dynamic load capability used
- Patented technology



Core Sensor Platform Design



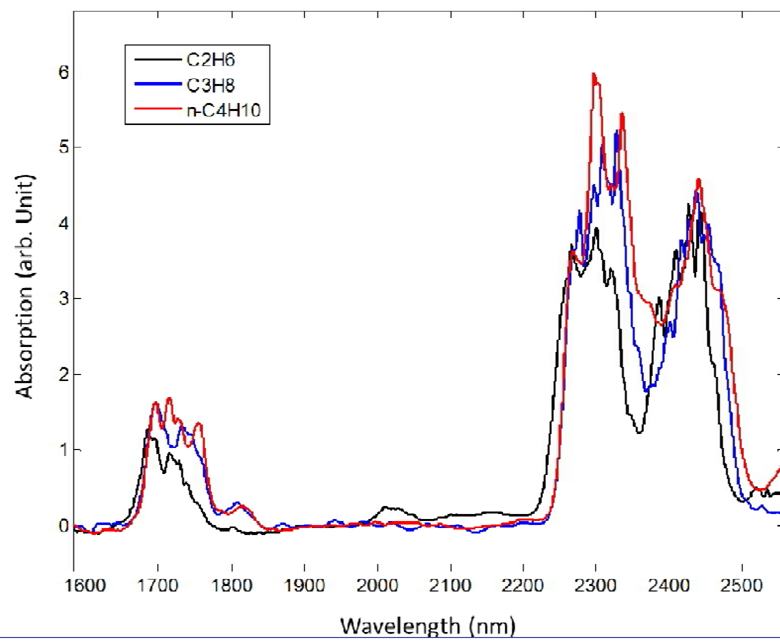
- Rugged, bolted-on-together design
- Patented spectrometer design



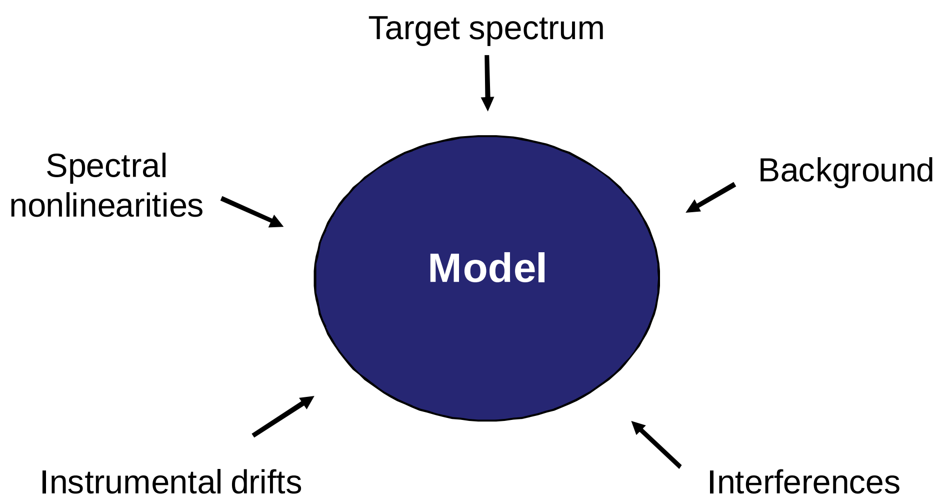
Challenges of Hydrocarbon Spectroscopic Analysis

- Overlapping spectra
- Presence of nonlinear behaviors
  - Peak shifts & other feature modification behaviors
  - Non-additive characteristics
  - Due to “real-world” conditions

Linear chemometrics won’t work robustly



Overcoming Challenges – Robust Modeling of Spectra



Real-time, On-Line, All-Optical Hydrocarbon Gas Analyzer

Hydrocarbon gas analyzer, providing:

- Individual component concentration, such as C1 – C4
- Calculated BTU/CV value
- Calculated Wobbe index value
- Calculated specific gravity
- Real-time measurement in seconds
- Low-cost installation and operation:
  - No carrier gas requirement
  - No calibration gases or “clean” air requirement
  - No “shelter” or air conditioning requirement
  - No sample drying or other sampling requirement

Methane	85.12
Ethane	6.53
Propane	2.35
n-Butane	1.05
iso-Butane	0.98

Setting the Standard for Automation™

Experimental Results

<u>*Analysis Solutions in Paradise……See us in Galveston 2013*</u>

The 58th Annual Symposium of the Analysis Division

Galveston, Texas, USA; 14-18 April 2013

Mixtures Test (example validation at Precisive)

Two independent certified mixtures

Mixture 1

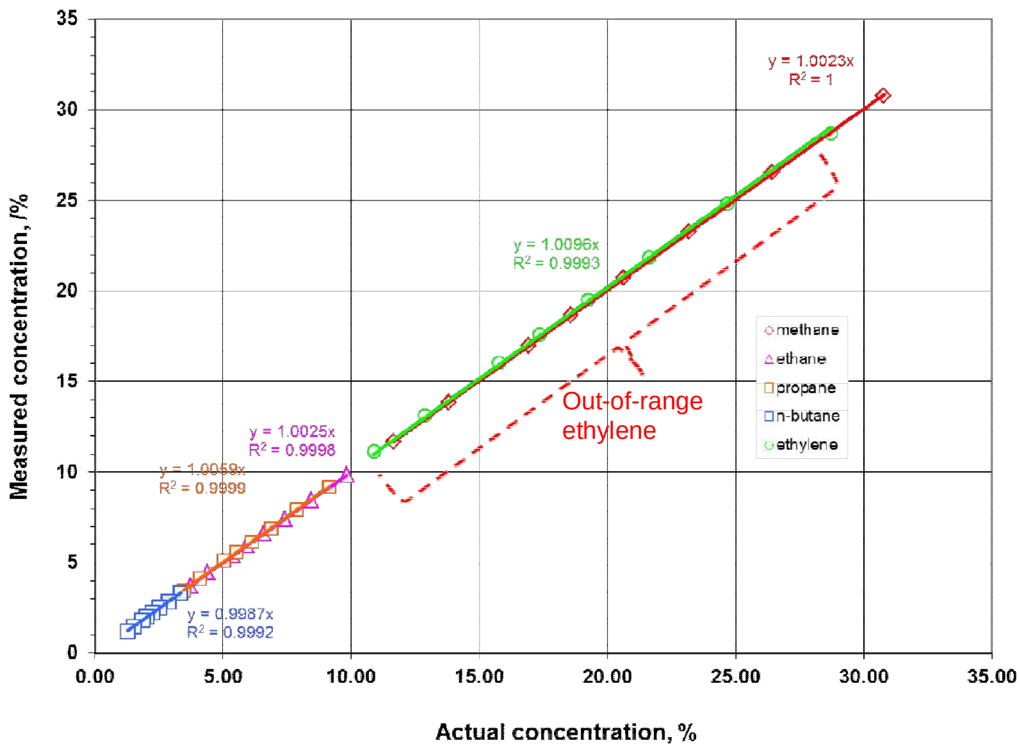
	Theoretical (%)	Reading (%)	Error (%)
Methane	92.01	91.95	-0.06
Ethane	2.97	3.03	0.06
Propane	0.99	1.00	0.01
Iso-Butane	0.31	0.28	-0.03
N-Butane	0.30	0.27	-0.03

Mixture 2

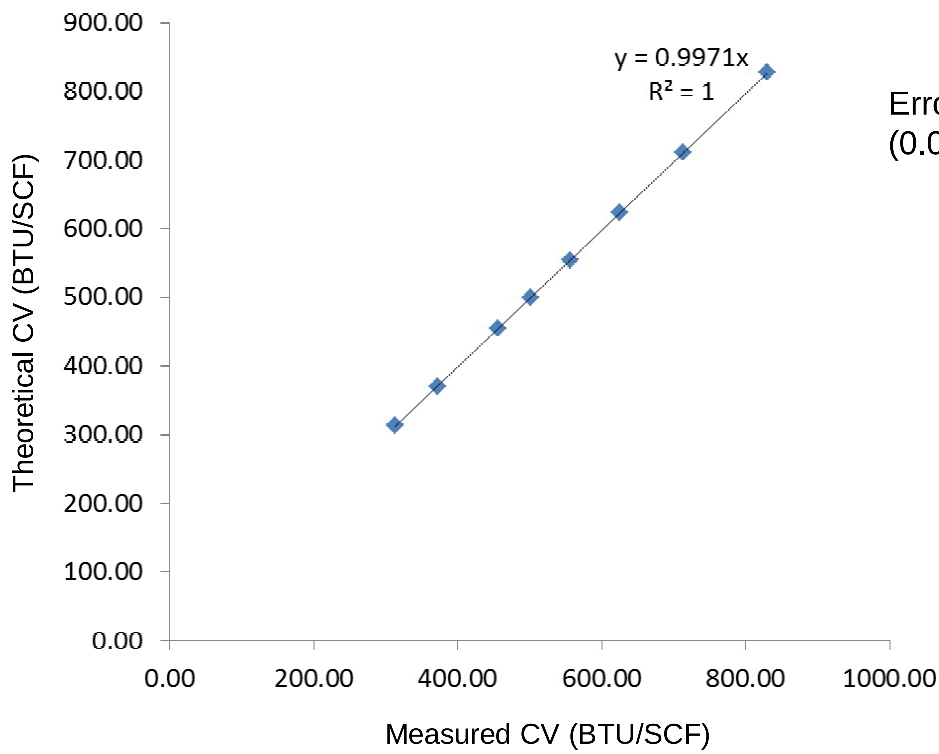
	Theoretical (%)	Reading (%)	Relative Error (%)
Methane	50.01	50.13	0.12
Ethane	10.0	10.03	0.03
Propane	10.0	9.93	-0.07
Iso-Butane	1.00	1.01	0.01
N-Butane	1.00	0.88	-0.12
Propylene	3.00	3.03	0.03
Ethylene	5.00	5.09	0.09

Accuracy – C1 to C4 alkanes and ethylene (continued)

Linearity



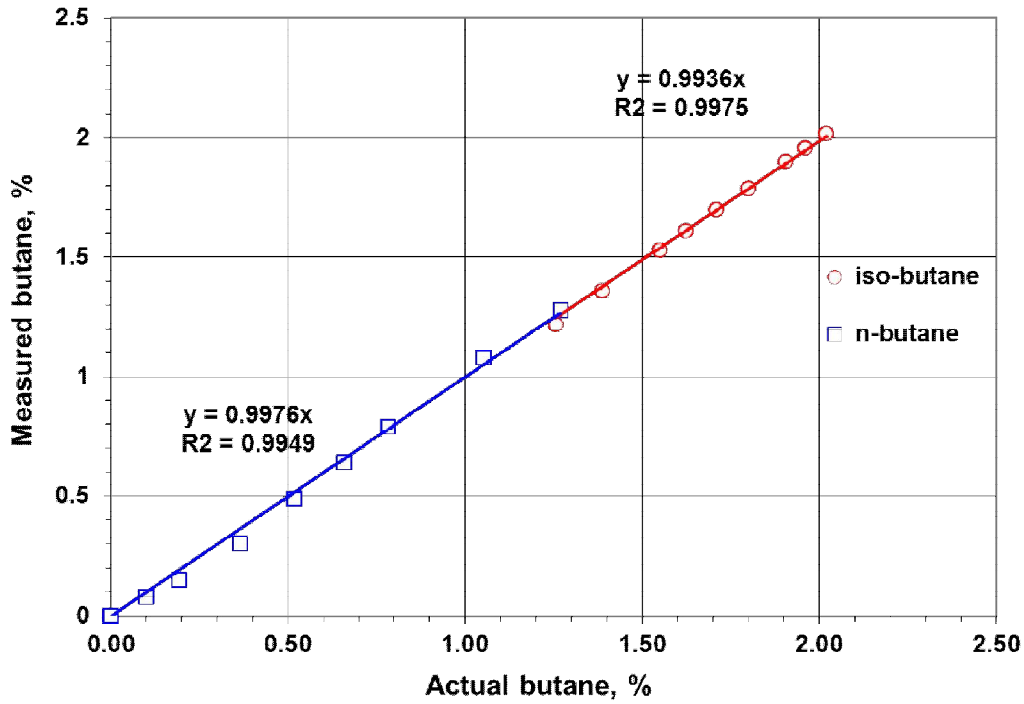
CV Measurement Linearity



Error (RSMEP): 1.8 BTU/SCF
(0.067 MJ/NM^3)

Accuracy – iso-butane

Linearity



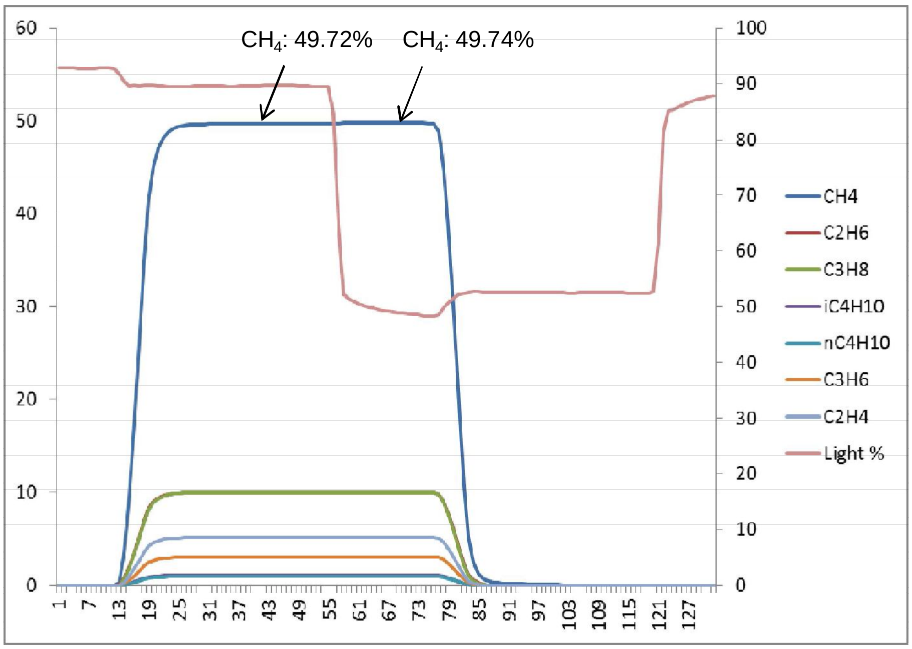
Stability – effects of source drifts

Test Procedure:

1. Zero the instrument (with pure N_2)
2. Flow sample mixture
3. Reduced light source intensity by ~ 50%
4. Flow back N_2

Results:

- Span drift due to ~50% light intensity reduction: < 0.03% on all channels
- Zero drift: virtually zero on all channels (< 0.01%)



CURRENT TFS AVAILABLE MEASUREMENTS

Channel	Gas	NATURAL GAS -AND CV		
1	CH4	0 – 100%	0 – 100%	0 – 100%
2	C2H6	0 – 25%	0 – 25%	0 – 25%
3	C3H8	0 – 25%	0 – 25%	0 – 25%
4	Iso C4H10	0 – 10%	0 – 10%	0 – 10%
5	N C4H10	0 – 10%	0 – 10%	0 – 10%
6	C3H6	0 – 50%	0 – 50%	0 – 50%
7	C2H4	0 – 50%	0 – 50%	0 – 50%
8	CO2	0 – 100%	0 – 100%	0 – 100%
9	C2H2	n/a	0 – 30%	0 – 30%
10	Iso-C5H12	n/a	0 – 10%	0 – 10%
11	1-Butene	n/a	n/a	0 – 10%
12	Cis-2-Butene	n/a	n/a	0 – 10%
13	Trans-2-Butene	n/a	n/a	0 – 10%
14	Isobutylene	n/a	n/a	0 – 10%
15	1,3 Butadiene	n/a	n/a	Can interfere C3s, cis butene

Summary

- Patented Tunable Filter Spectrometer with hydrocarbon speciation chemometrics
  - GC-like speciation performance (C1 – C5, alkanes, alkynes, alkenes)
  - Fast update rate (1 second)
  - No carrier gas or other consumables
  - Proven technology & platform with 1600+ units deployed with 160+ years of cumulative run time
- Test results
  - Robust baseline and span stability
  - Robust speciation performance
- An attractive alternative to GC, residual oxygen and refraction based analyzers in hydrocarbon/fuel gas analysis

Trace Gas Measurements using Tunable Diode Laser Absorption Spectroscopy

Jiwan Jain

SpectraSensors™

Outline

- SpectraSensors Introduction
- What are TDL analysers
- Absorption Spectrscopy
- Tunable Diode Laser and WMS
- Response Characteristics of TDL Analysers
- Technolgy implementation
- Application Examples: H2S and H2O
- Summary
- Questions

SpectraSensors,Inc.
An Introduction

SpectraSensors :

- An Endress+Hauser subsidiary
- Founded in 1999 by a group of NASA engineers
- Headquartered in Houston, Texas
- Production facility in California
- Pioneer in on-line Tunable Diode Laser Analyzers (TDLAS)

Over 5000 units installed to date

California Office

Houston Office

SpectraSensors™

Proven **Tunable Diode Laser (TDL)** Sensors for Measuring Conditions in Extreme Environments

Space

Deserts

Refineries

Aircraft

RELIABILITY

ROBUSTNESS

ACCURACY

RESPONSE TIME

SpectraSensors

Sampling of Some of SpectraSensors Current Customers

ExxonMobil
FORMOSA PLASTICS CORPORATION
PETRONAS
elpaso
RasGas
Duke Energy
Gas Transmission
ups
Chevron
Cheyenne Plains
Gas Pipeline Company, LLC
ENBRIDGE
Origin energy
DUPONT
Chesapeake
Natural Gas. Natural Advantages.
Saudi Aramco
PTT Public Company Limited
Dominion
It all starts here.
bp
Consumers Energy
Count on Us
KINDER MORGAN
ENERGY PARTNERS, L.P.
OG&E
TOTAL
Enterprise Products Partners L.P.
EAGLE MOUNTAIN PIPELINE
BR PETROBRAS
CCO CROSSCOUNTRY
AIR LIQUIDE
NORTHSTAR INDUSTRIES
NOAA
UCAR
Lufthansa
Bitter Creek Pipelines, LLC.
The Link between Producers and the Market
SpectraSensors

What Are TDL Analyzers?

- Like NDIR Analyzers* that users are already familiar with.
- But rather than using a lamp to produce IR light, TDL analyzers use a focused Laser beam.
- Laser Beam is generated by a Semiconductor Diode called Tunable Diode Laser (TDL).
- TDL technology is being driven by the fiber-optic telecom industry
- Goal is to retain the simplicity of NDIR analyzers while avoiding some of the measurement issues associated with IR analyzers

*** Note that TDL analyzers are available in IR and UV ranges depending on laser selected**

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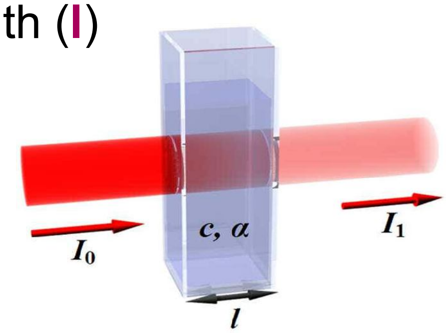
What are TDL analysers

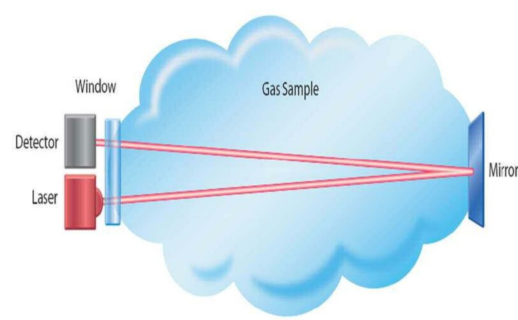
Measurement Mechanics Of Optical Spectroscopy

- Absorbance = f(conc, pathlength, and molar absorptivity)

$$A = c \cdot l \cdot \alpha$$

- Concentration increases Absorption increases (l , α are constant)
- If analyte concentration is low, increase **A** by increasing path length (**l**)





Concentration = $\dfrac{\textbf{(Amount of light absorbed (energy) thru the sample cell)}}{\textbf{(Absorption Coefficient for a species) x (its path length)}}$

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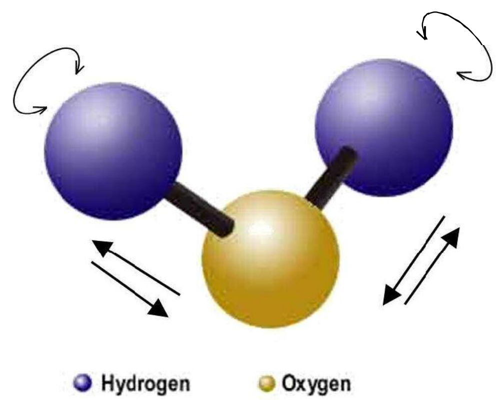
Absorption Spectroscopy:
IR Absorption By Molecules

- Light at certain harmonic wavelengths will cause the molecular bonds to twist or stretch.
- This “vibration” absorbs energy.
- Gas concentration can be accurately measured by the amount of light absorbed



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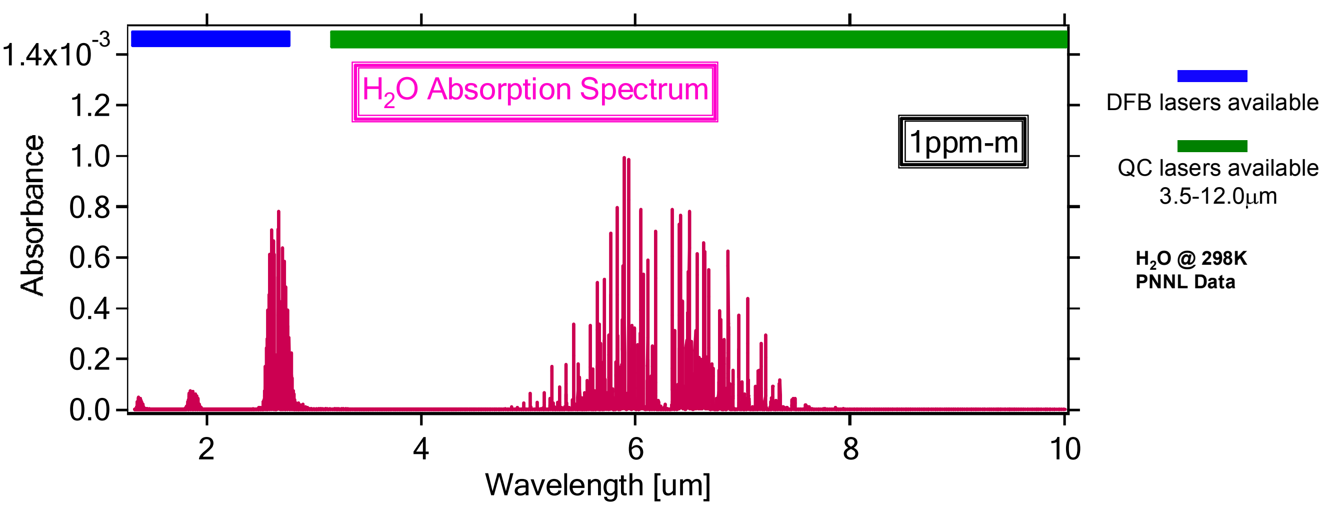
Absorption Spectroscopy:
Moisture spectrum example



- Over 26,000 individual absorption lines exist for H_2O between 1.3 and 3.0 microns
- TDL analyzers need only one line in that region that is free of interference to work successfully!
- SSI has special development software to search for the optimum wavelength based on concentrations and background gases

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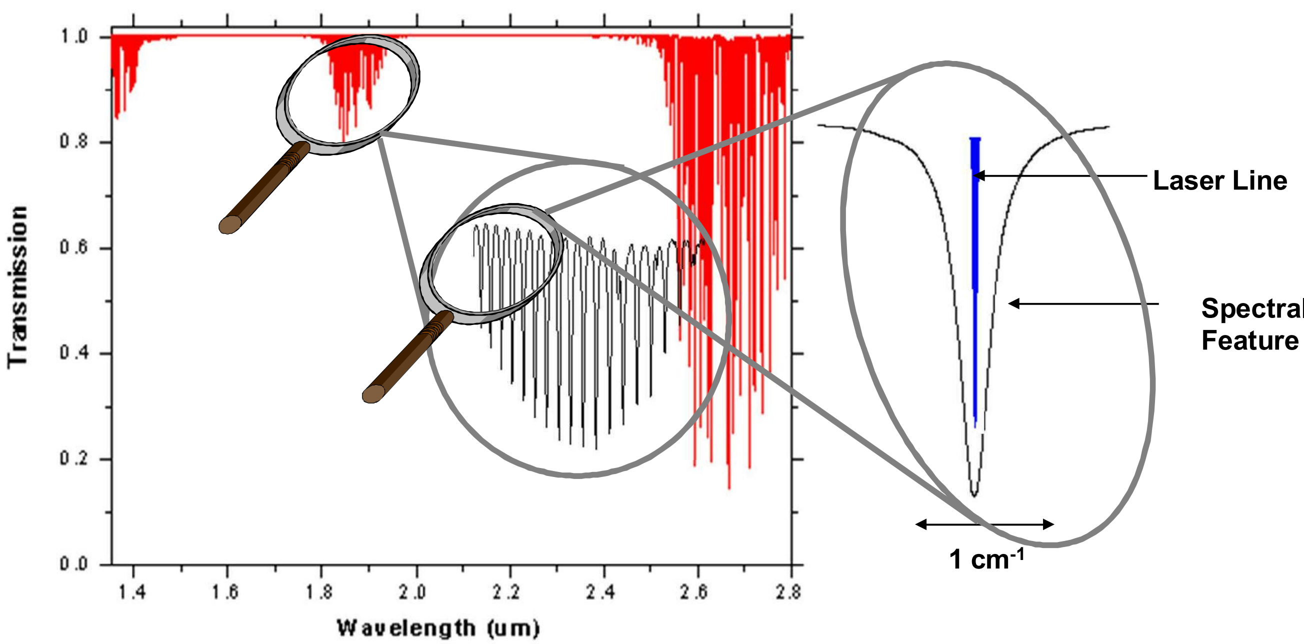
Absorption Spectroscopy:
Reading The Fine Print Of Spectral Signatures



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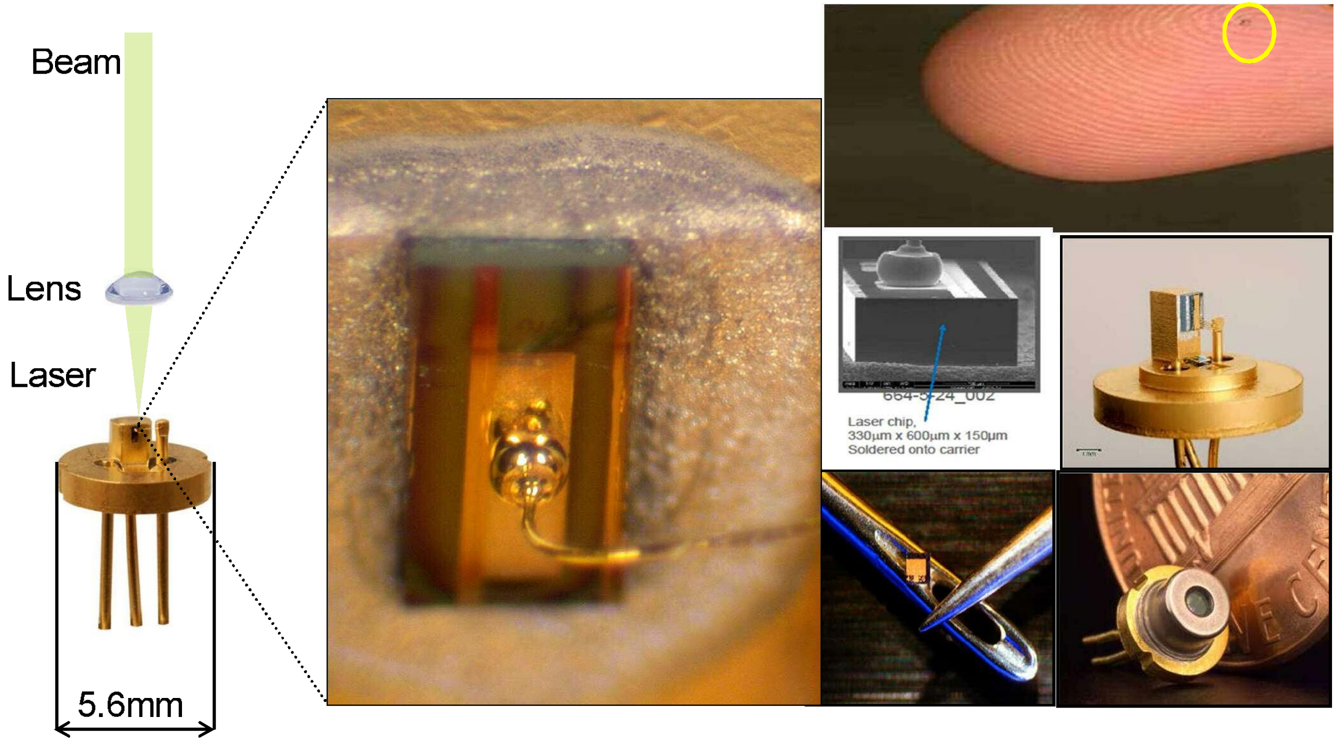
Tunable Diode Laser:
How does a Tunable Diode Laser (TDL) looks like?



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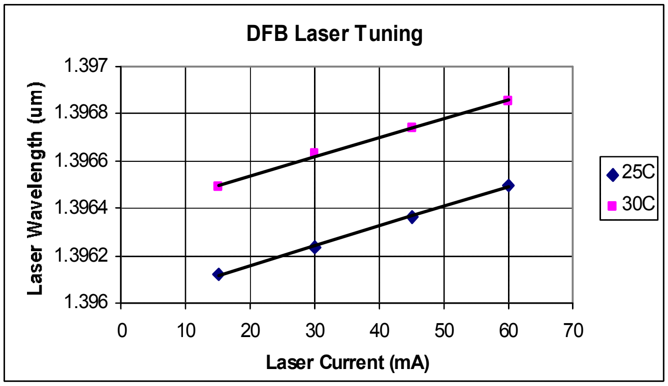
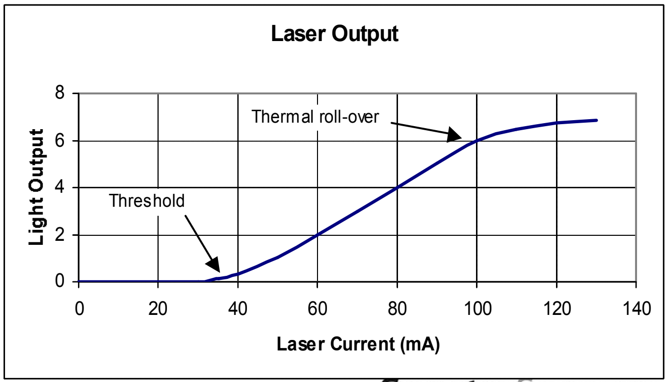
Tunable Diode Laser:
Tuning TDL: Multiple IR Wavelengths with One TDL

- Most TDLs are in the Near InfraRed (NIR) wavelength range:
  0.7 to 3.0 microns
- Laser Wavelengths can be changed by:
  Laser construction
  Temperature control
  Current (fine tuning)
- For Analysis:
  - Temperature of laser is held constant and the current flowing through it is varied
  Tunable range is ~3 nanometers





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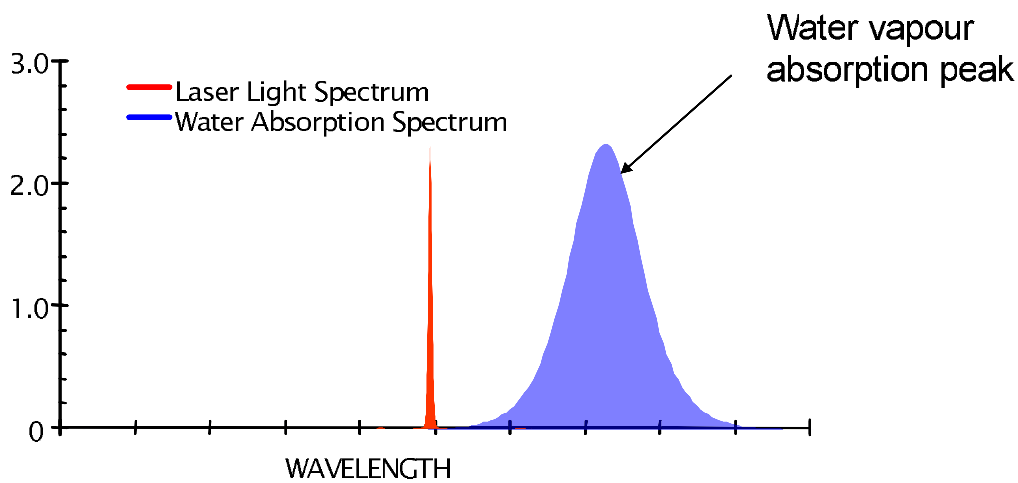
Tunable Diode Laser:
Laser Scan



Tunable range 3 nanometers

Measures 250 discrete wavelengths

Scanning 4 times per second

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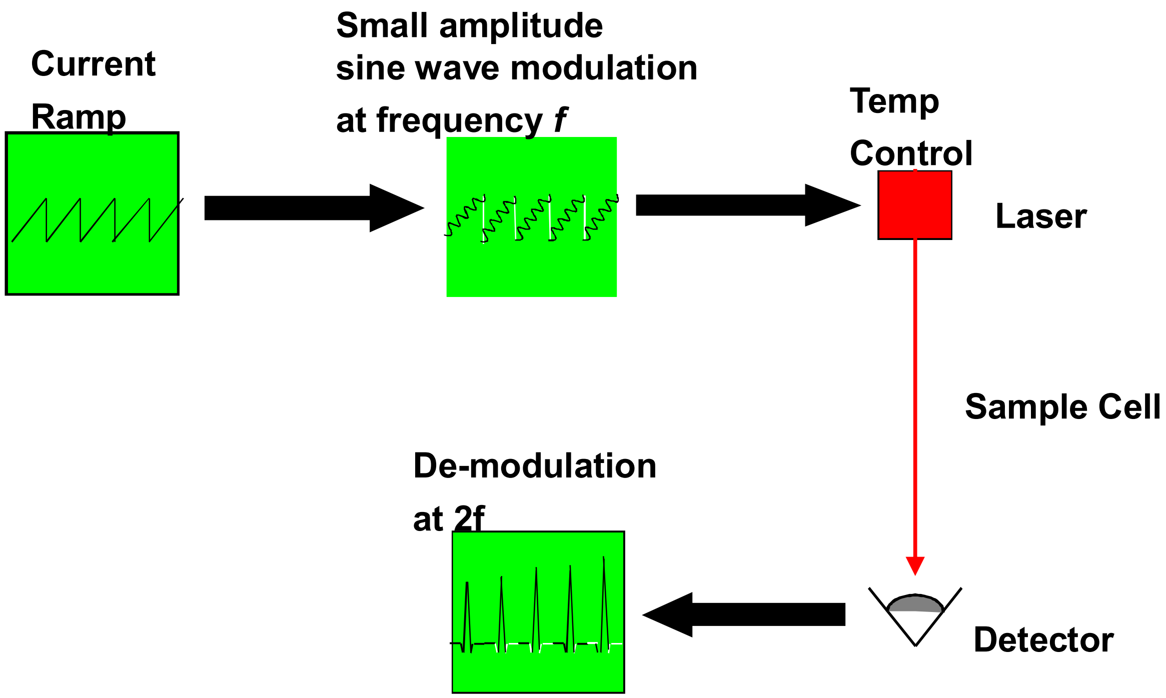
Tunable Diode Laser:
Wavelength Modulation Spectroscopy (WMS)



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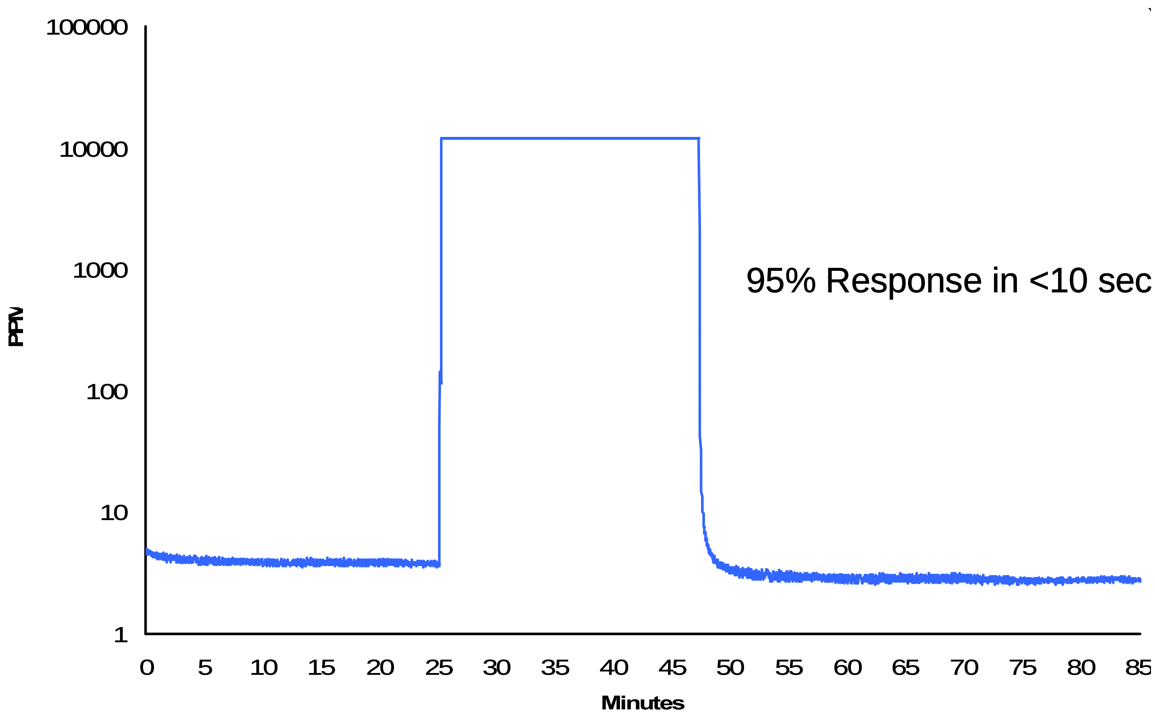
Response Characteristics:
Extremely Fast Speed of Response



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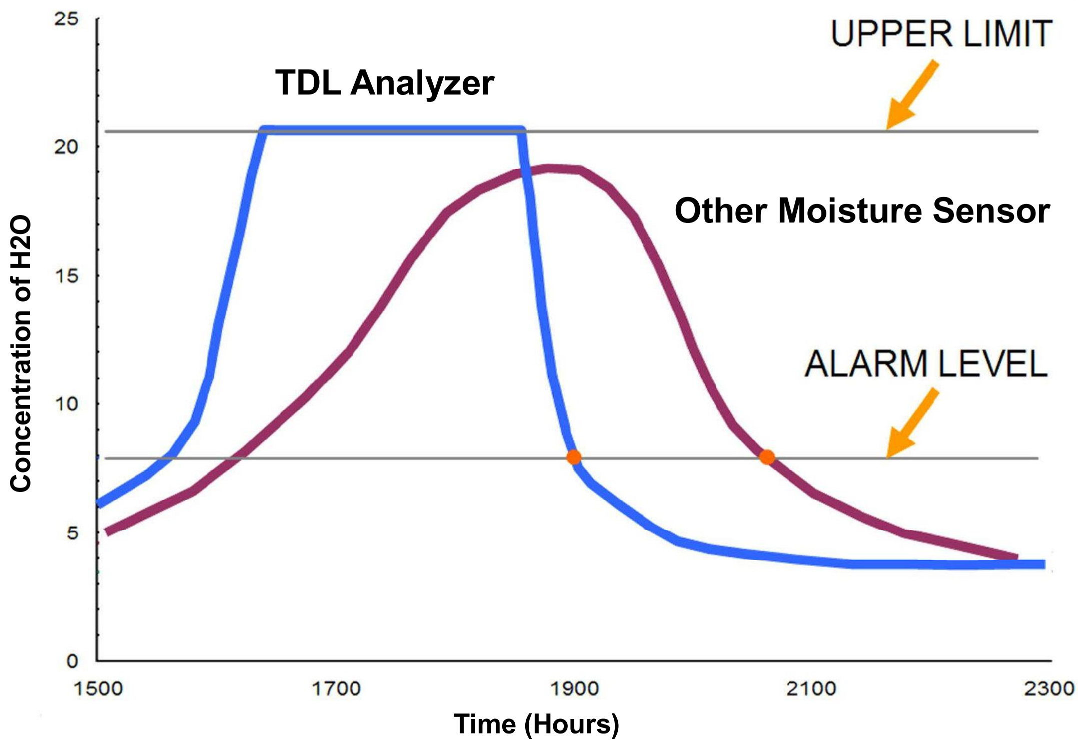
Response Characteristics:
Faster Recovery From Process Upsets



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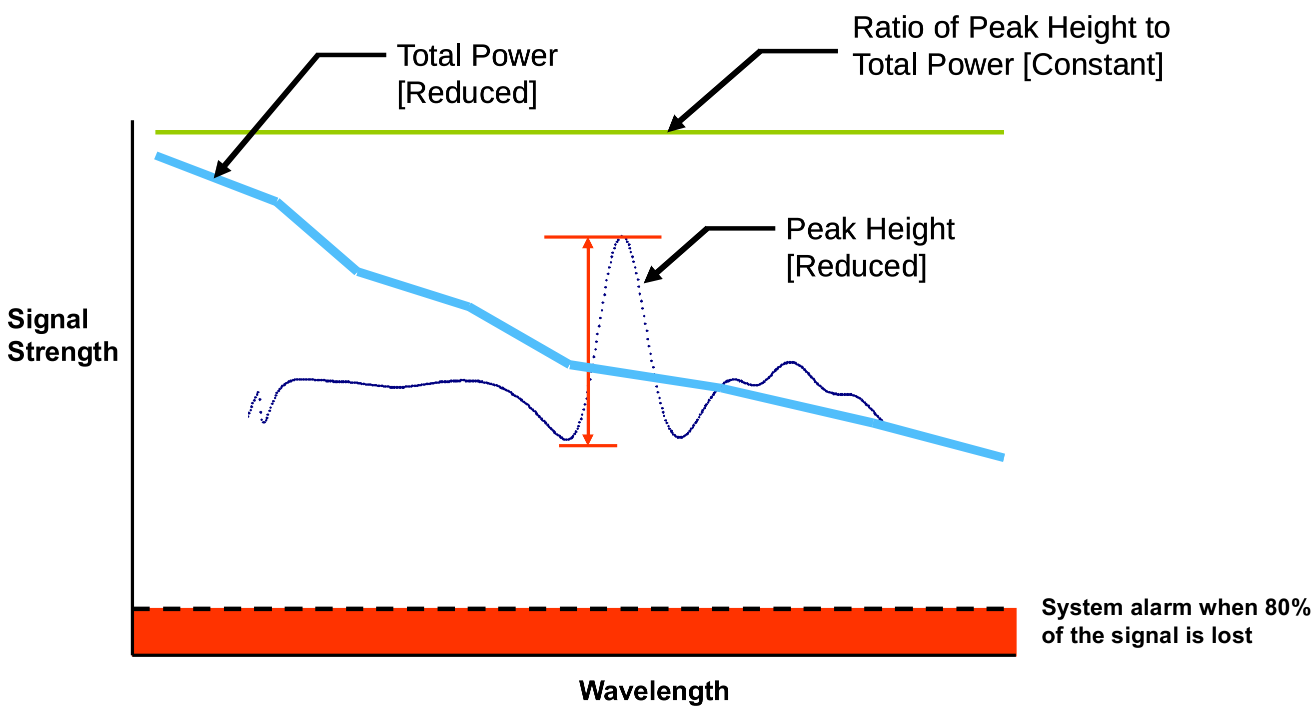
Response Characteristics:

Window Contamination: Not a problem because of ratio measurement



Technology Implementation

Variety Of On-Line TDL Analyzers On Market

- **Cross Stack design**

  Used to measure components in a combustion process; e.g., stack gases

- **Open Air design**

  Used to measure components in ambient air monitoring; eg, toxic and flammable gases

- **Portable design**

  Used to measure components in air or processes; e.g., moisture in natural gas

- **Extractive design**

  Used to measure components in chemical processes; e.g., gas purity applications

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Technology implementation
SpectraSensors Analyzers

- Flexible analytical hardware
  - Choice of IR lasers
  - Single and dual channel configurations
  - Multi-pass cells available
  - Heated cell cabinets available
- Extremely low cost of ownership
  - No routine maintenance
  - No routine calibration needed
- Fast measurement response
  - Most applications are done in 1 second

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Application Examples

H_2S Measurement: Use of spectral Subtraction

Background gases are nearly impossible to predict due to changing nature of the Fuel Gas

- Fuel Gas can have anything from H_2 to C_4+ at any time
  - Sample composition changes preclude avoiding of interferences
- TDL system assumes there are always interferences present
- Process sample flows through an H_2S scrubber to take snap-shots of interferences
- Software then subtracts these interferences to give precise H_2S measurements

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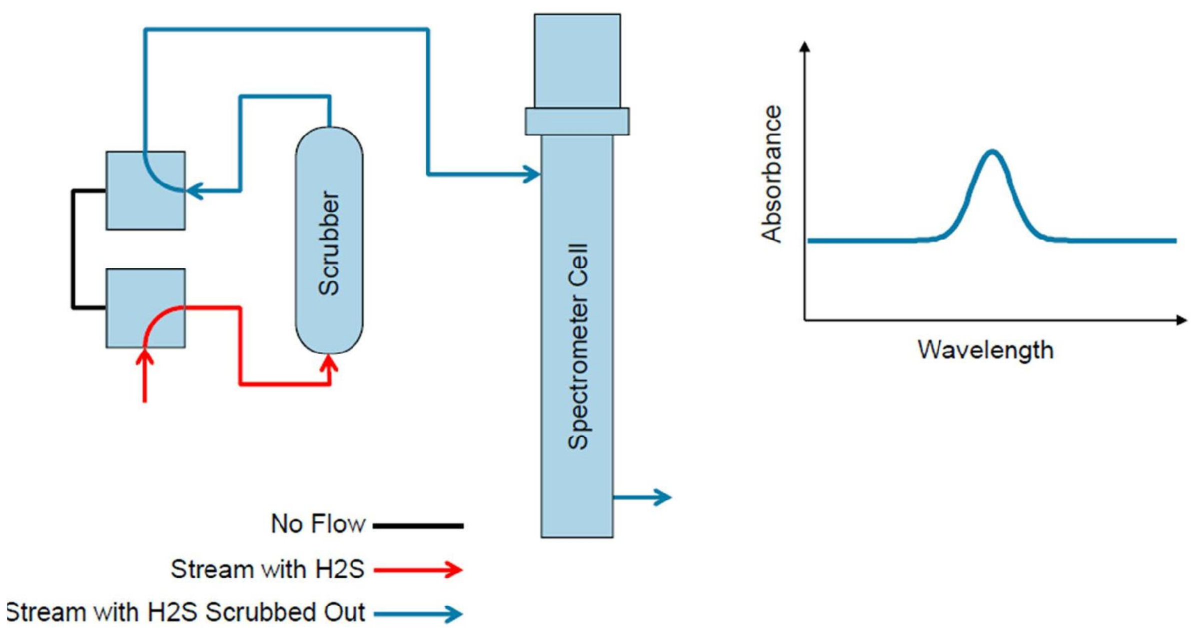
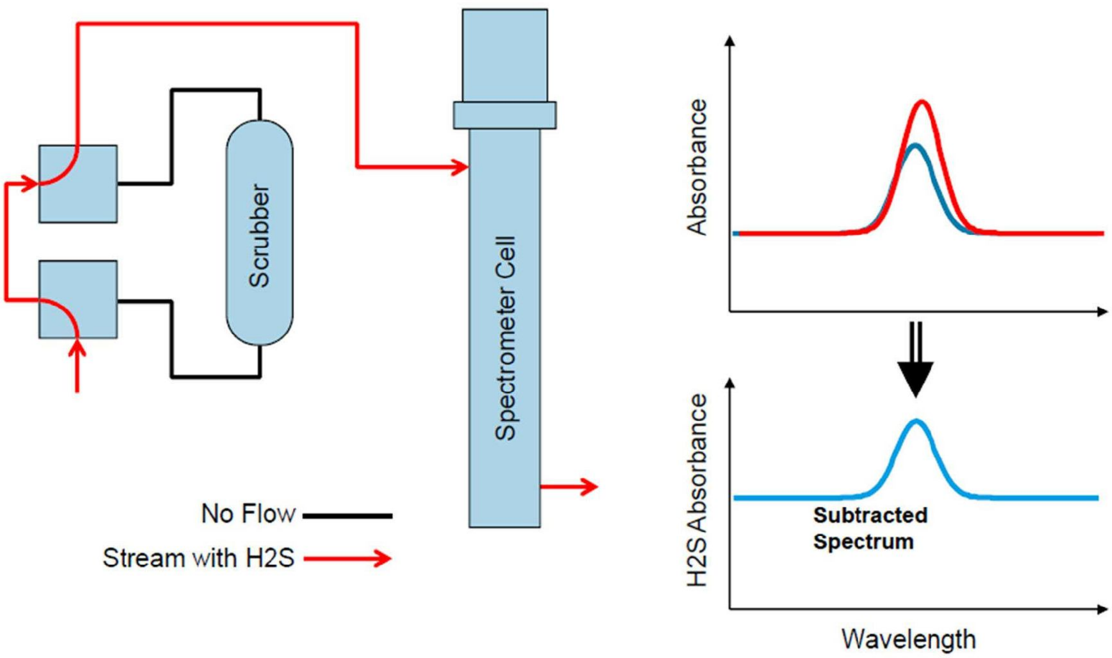
Application Examples

H_2S Measurement: Use of spectral Subtraction

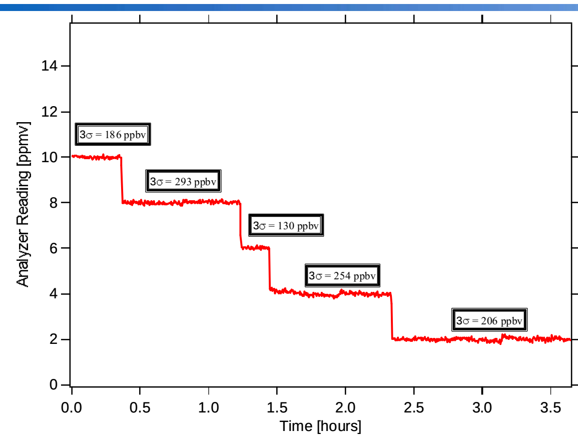


Application Example

H2S measurement: Use of spectral subtraction



Application Example
H2S measurement Performance

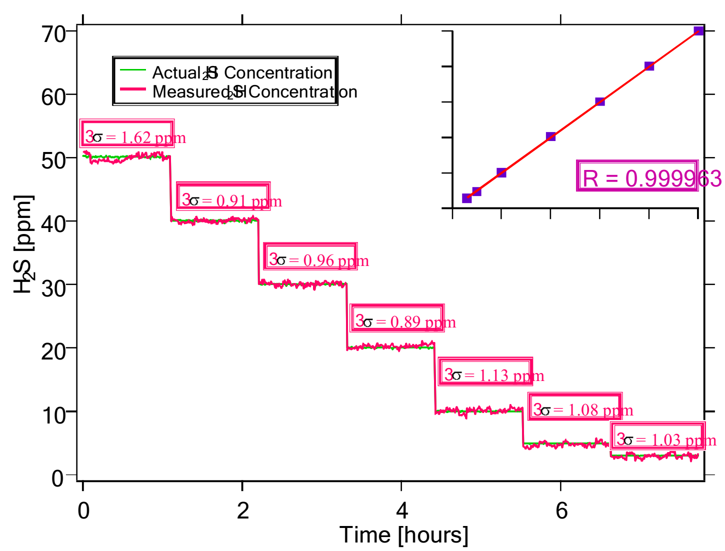


H_2S in Propane (0-10ppm Range)

- Repeatability of <±300 ppb (3 sigma)

H_2S in Fuel Gas Background (0-300ppm Range)

- Repeatability of <±2 ppm (3 sigma) gas



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Application Example

Speed of Response: Moisture Measurement

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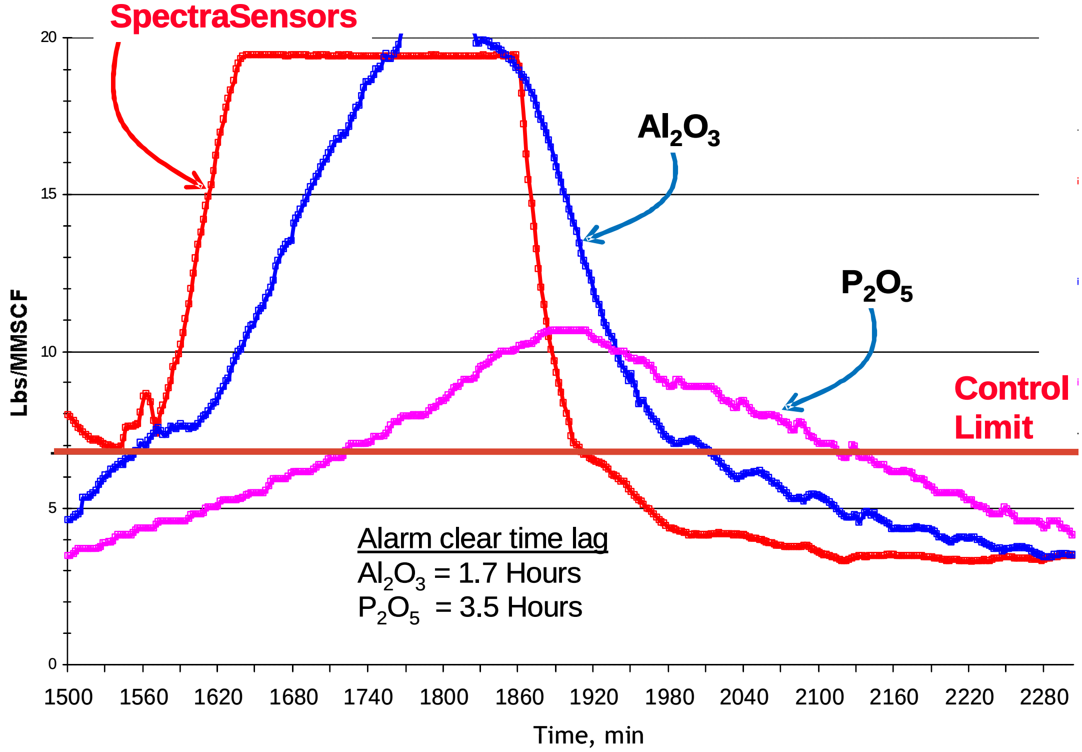

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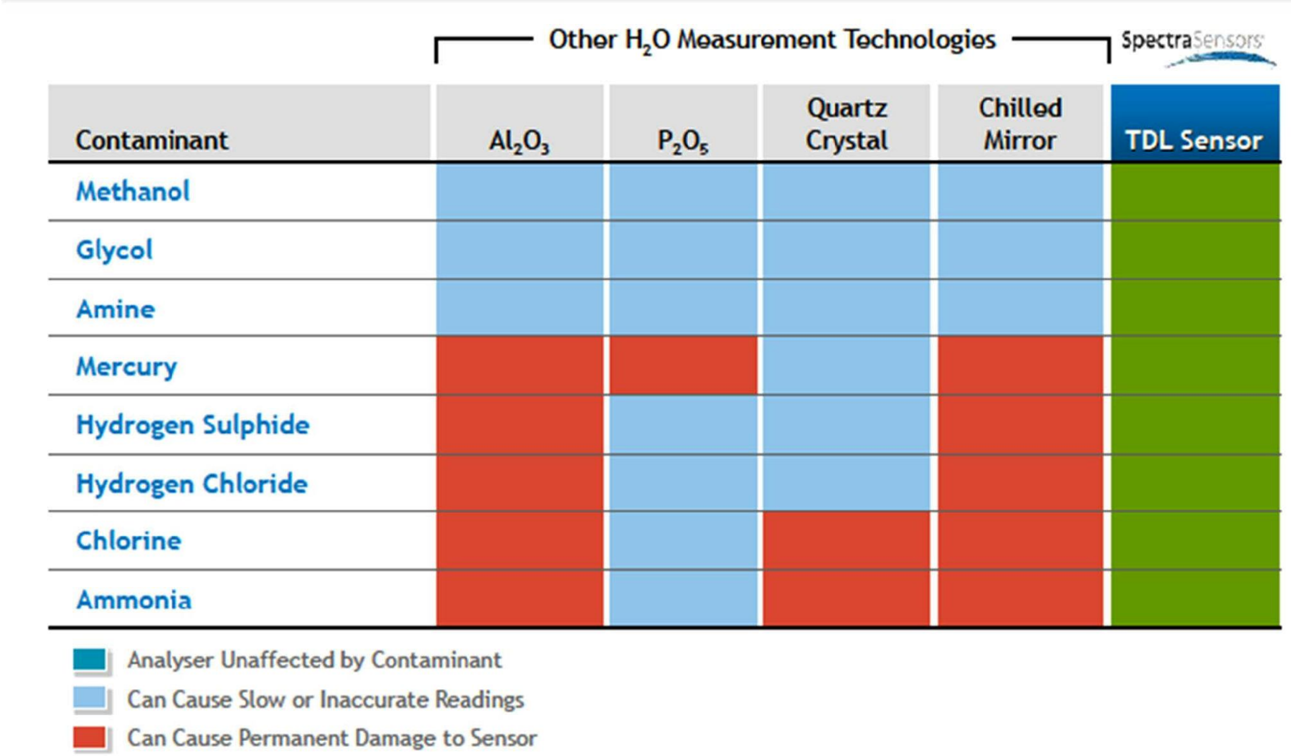
Application Example

Superior Availability of TDL moisture analysers



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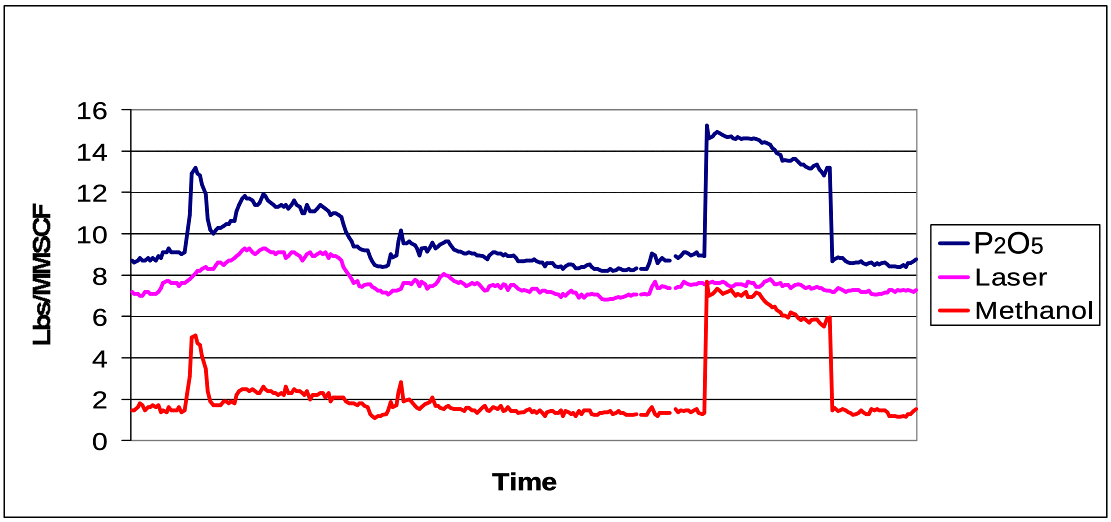
Application Example

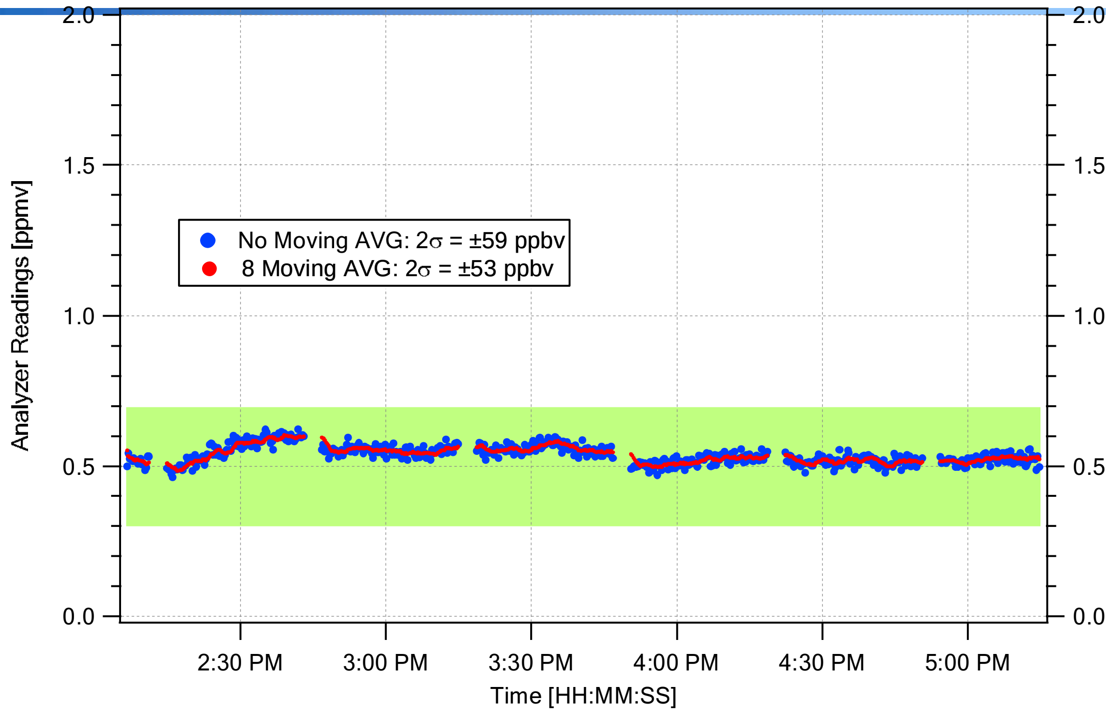
Moisture Performance: Water and Methanol in Natural Gas



Here, moisture concentration is monitored by two analyzers, as methanol is injected, the TDL analyzer does not register a change while the P2O5 analyzer sees the Methanol as though it were moisture. This is a big problem for operators that inject methanol and need to read moisture

Application Example

Moisture Performance: 0.5ppm H_2O in Ethylene



- The 3hour long term test shows repeatability (2σ) is well within the ±200 ppb spec.

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Applications: Refinery and Petrochem

INDUSTRY	PROCESS	STREAM	ANALYTE	TYPICAL CONC. RANGE
REFINING	UOP CATALYTIC REFORMER	HYDROGEN RECYCLE	H2O	CONTROL 0-10 PPM MONITOR 0-500 PPM
			H2S	0-100 PPM UPTO 0-500 PPM
	PROPANE PRODUCTION	PROPANE , LO PURITY	H2S	0-4000 PPM
	FEED PURITY FOR PROPYLENE PRODUCTION	PROPANE	H2S H2O	0-10 PPM 0-10 PPM
		FUEL GAS (<C4) FLARE GAS (< C4)	H2S	0-300 PPM 0-300 PPM
OLEFINS	PRODUCT OR PROCESS FEED	ETHYLENE , PROPANE, & PROPYLENE	H2O	0-10 PPM CONTROL AT <1PPM
	MID BED BACK END ACETYLENE CONVERTER	ETHYLENE	C2H2	0-5000 PPM
	PRODUCT OR PROCESS FEED	ETHYLENE	NH3	0-10 PPM CONTROL AT <1PPM

SpectraSensors™

Applications: Natural Gas Processing & LNG

INDUSTRY	PROCESS	STREAM	ANALYTE	TYPICAL CONC. RANGE
GAS PROCESSING	DRYER OUTLET OR TURBOEXPANDER FEED	NATURAL GAS	H2O	0-10 PPM
	VARIOUS	NATURAL GAS	CO2	0-100 PPM
	DOWNSTREAM FROM GAS CONDITIONING OPERATIONS	NATURAL GAS	H2S	0-10 PPM AND HIGHER
	LIQUEFACTION & FRACTIONATION OUTPUTS (<C4)	NATURAL GAS LIQUIDS	H2S	0-10 PPM AND HIGHER
	GAS PROCESSING PLANTS & SRU	FEED STREAMS	H2S	PERCENTAGE LEVELS e.g. 0-30%
LNG	DRYER OUTLET OR TURBOEXPANDER FEED	NATURAL GAS	H2O	0-10 PPM
	TURBOEXPANDER FEED	NATURAL GAS	CO2	0-100 PPM
SYNGAS		AMINE SCRUBBER INLET	H2O	0-10 PPM
		AMINE SCRUBBER OUTLET	CO2	PPM LEVELS
BULK & SPECIALITY GASES		AIR, NITROGEN, HELIUM, ETC.	H2O CO2, H2S	0-10 PPM 0-10 PPM 0-100 PPM

SpectraSensors™

Summary:
TDL Spectroscopy Technology

- SpectraSensors TDL analyzers are responsive
  - Fast response to concentration step-changes
  - Possible because TDL measures a fundamental property of the molecule (interaction with light) rather than a derived effect
- SpectraSensors TDL scanning technology is selective
  - Isolates the measured molecule signal amidst the dominant hydrocarbon background
- SpectraSensors TDL spectrometers are precise
- SpectraSensors TDL analyzer systems are reliable
  - Pre-calibrated at the factory
  - The intrinsic stability of the technology eliminates the need for field calibration
  - Very low maintenance due to absence of moving parts
  - Validation only is required to verify that the original certificate of calibration remains valid

SpectraSensors™

Summary:
Superior TDL Technology

HIGHER QUALITY Output with LOWER COST of Ownership

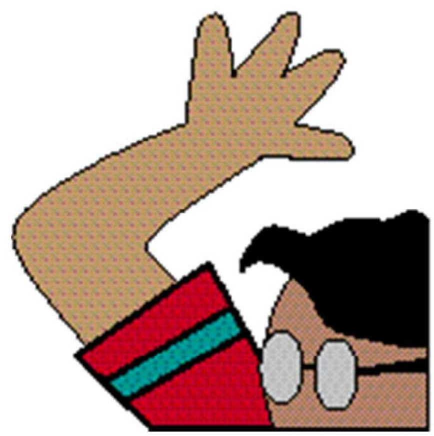
- Greater Accuracy
- No Routine Maintenance or Field Calibration
- No Degradation Due to Sample Contaminants
- Measurement Updates Every Second, Across Concentration Ranges

Fewer Components	No Moving Parts	No Consumables	Non Contact Model

SpectraSensors TDL Platform Design

SpectraSensors™

Any Questions??



Please contact:
Endress+Hauser India Pvt. Ltd.
Raj Plaza, Wings A&B,
5th Floor, LBS Marg, Vikhroli (W),
Mumbai-400083
Tel: 022-6648 1111 / Mobile: 9769 1775 28
E-mail: jiwan.jain@in.endress.com

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