# Raman Spektroskopi som nytt og enkelt måleprinsipp for olje og gass

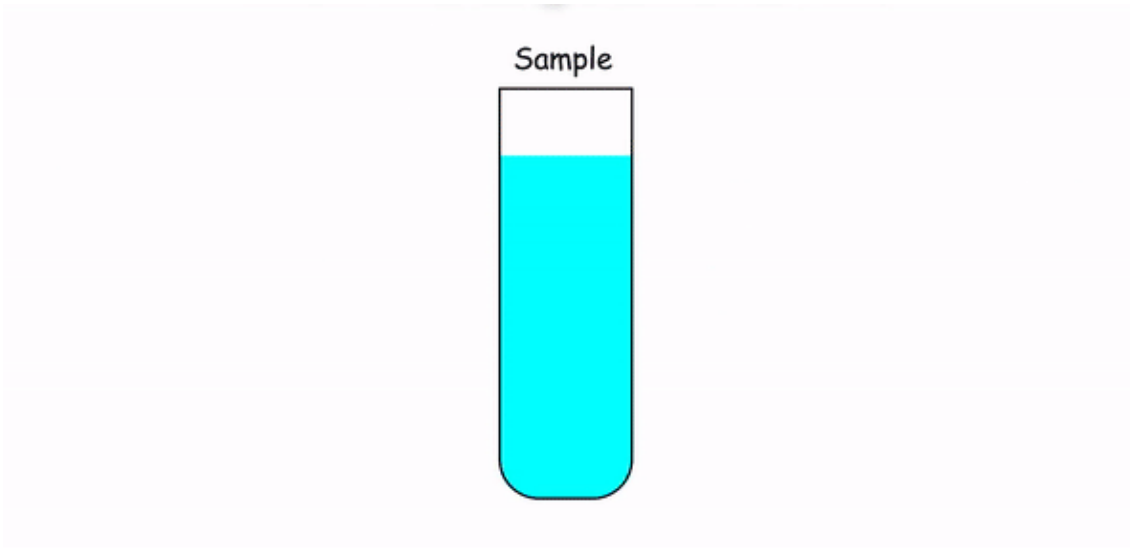
Robert Biederbick, Endress+Hauser AS

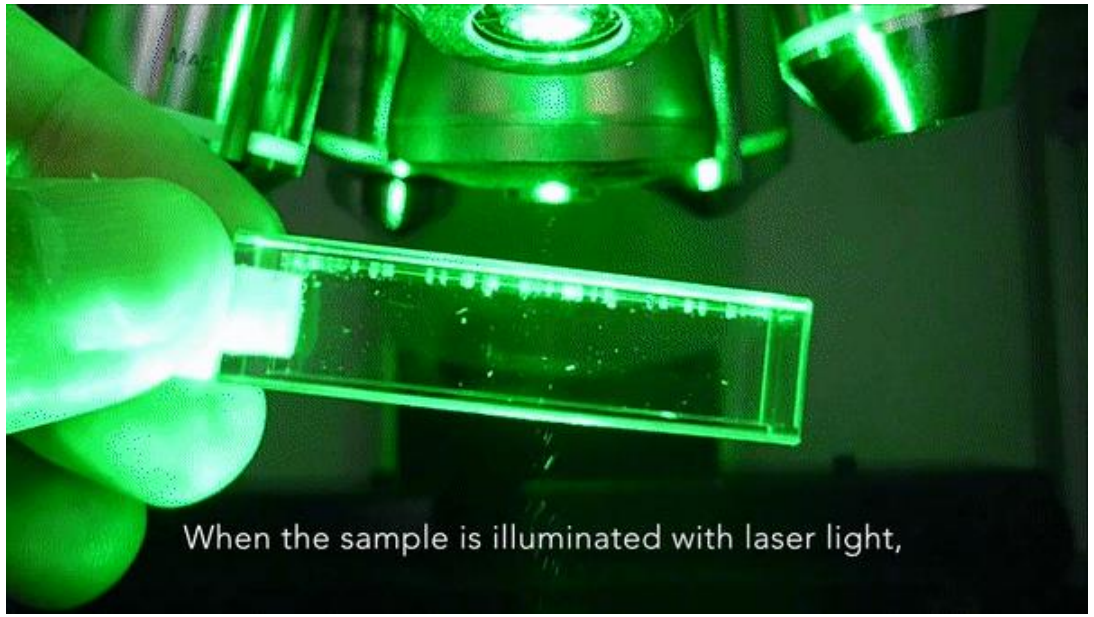
# Why is the water blue?

# History of Raman Spectroscopy

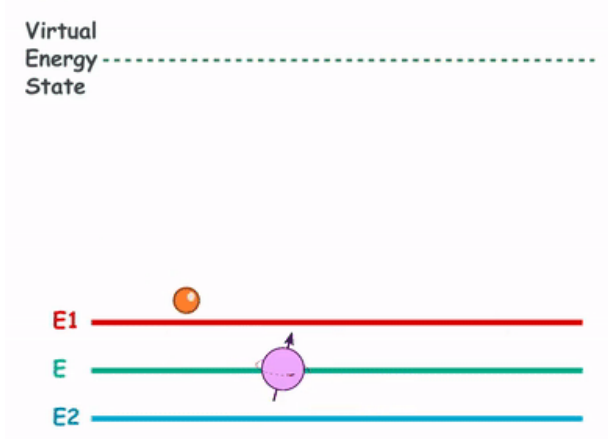
- 1921, C.V. Raman undertakes tour of Europe as a delegate of Universities' congress
- 1928 Raman and Krishnan discover "a new type of secondary radiation" → Raman effect.
- Only 1 in 1,000,000 (0.0001%) photons are scattered inelastically.
- In the 1930s, Raman became the principal means of non-destructive chemical analysis.
- 1939-1945 Perkin Elmer develop the first commercial IR.
- After WWII, commercial IR surpassed Raman in this role.
- Advent of lasers in the 1960s revived interest in Raman to some extent. – First Raman renaissance – lasers, photon counting, double monochromators.

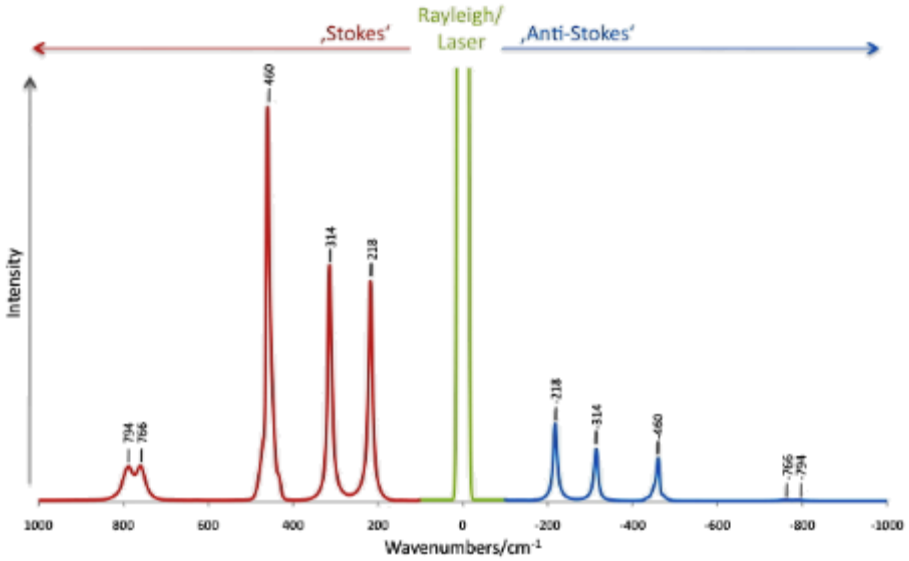
# Understanding the Raman Effect



# What Does a Raman Spectrum Look Like?



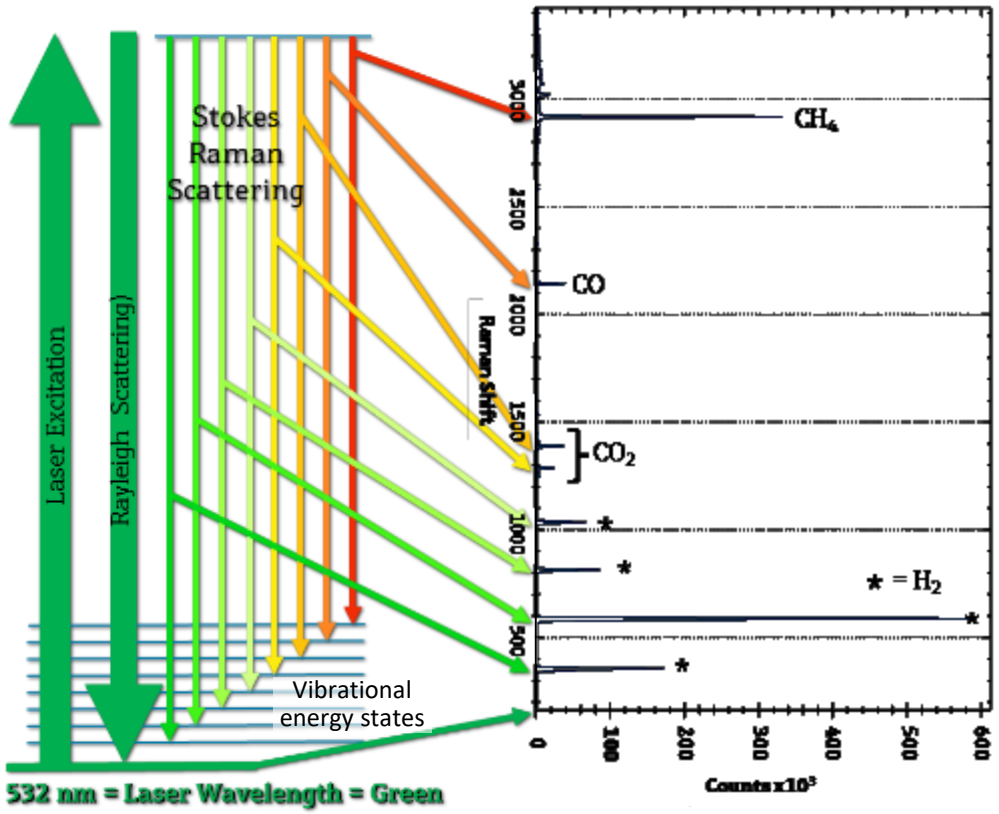




- Raman data are plotted as Raman Shift versus Intensity
- Raman shift is the amount of energy transferred to a bond
- Rayleigh scatter has no energy transfer, so has a Raman Shift of 0.
- Stokes and Anti-stokes lines have the same Raman Shift values
- Anti-stokes peaks are less intense

**Stokes and Anti-Stokes Raman Spectrum of $CCl_4$**

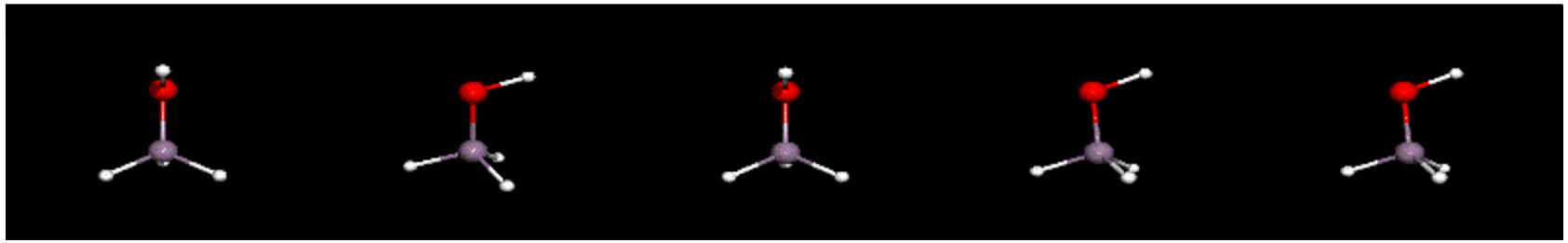
# What about the Raman Spectrum of a Gas Mixture?

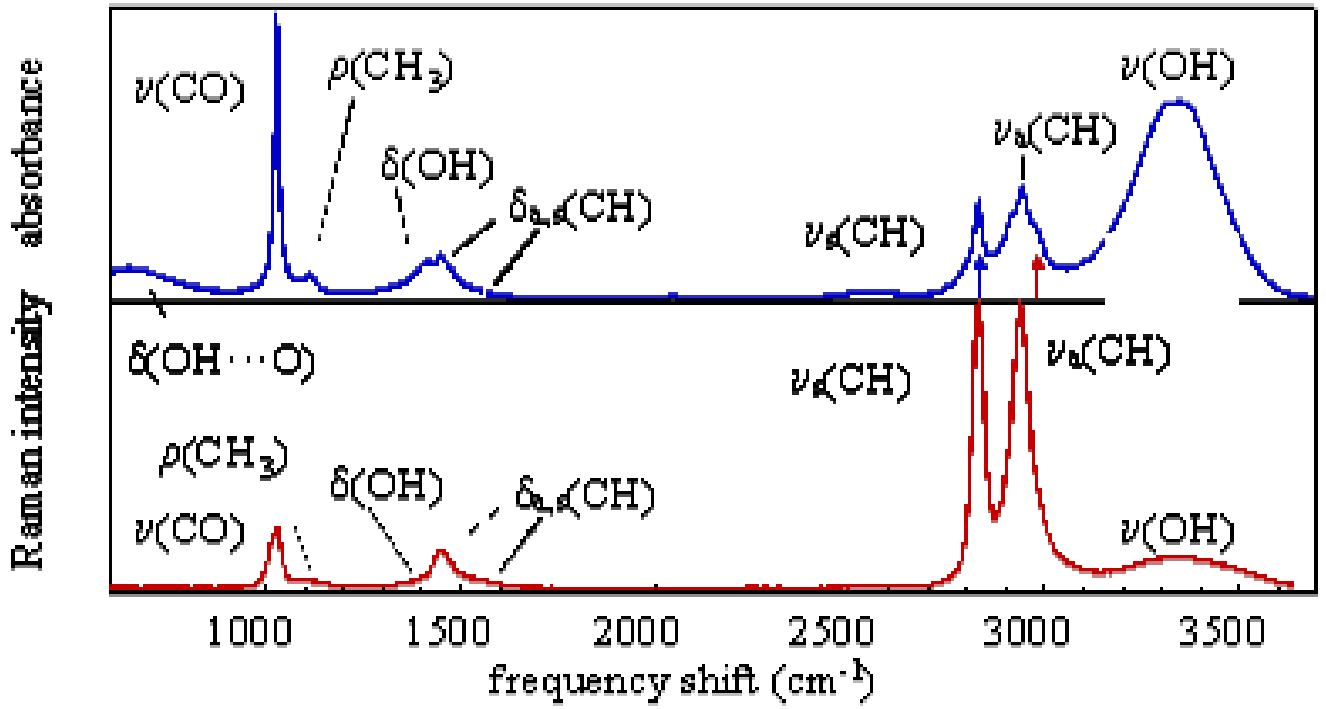
*'One Color In, Multiple Colors Out'*




- Simple molecular gases (e.g. CO, $CO_2$, $H_2$, $N_2$, $NH_3$) have simple Raman spectra, often a single peak
- Raman scatter from each type of molecule in the sample results in a different wavelength (color) of light emitted from the sample
- The Raman analyzer measures all of these gases simultaneously, separating them 'by color'
- Simple spectra allow for the use of simple 'Method-based' analysis of mixtures

# Most Molecules Have Multiple Vibrational Modes





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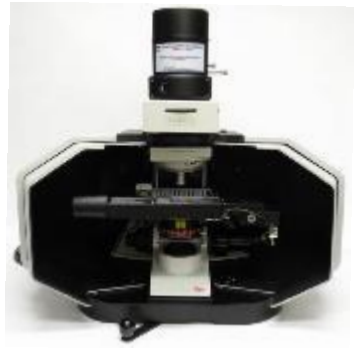
# History of Raman Spectroscopy

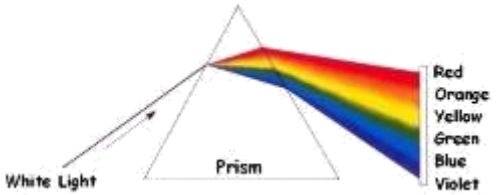
Response time 1930: 1-2 hours / spectrogram on photo plate

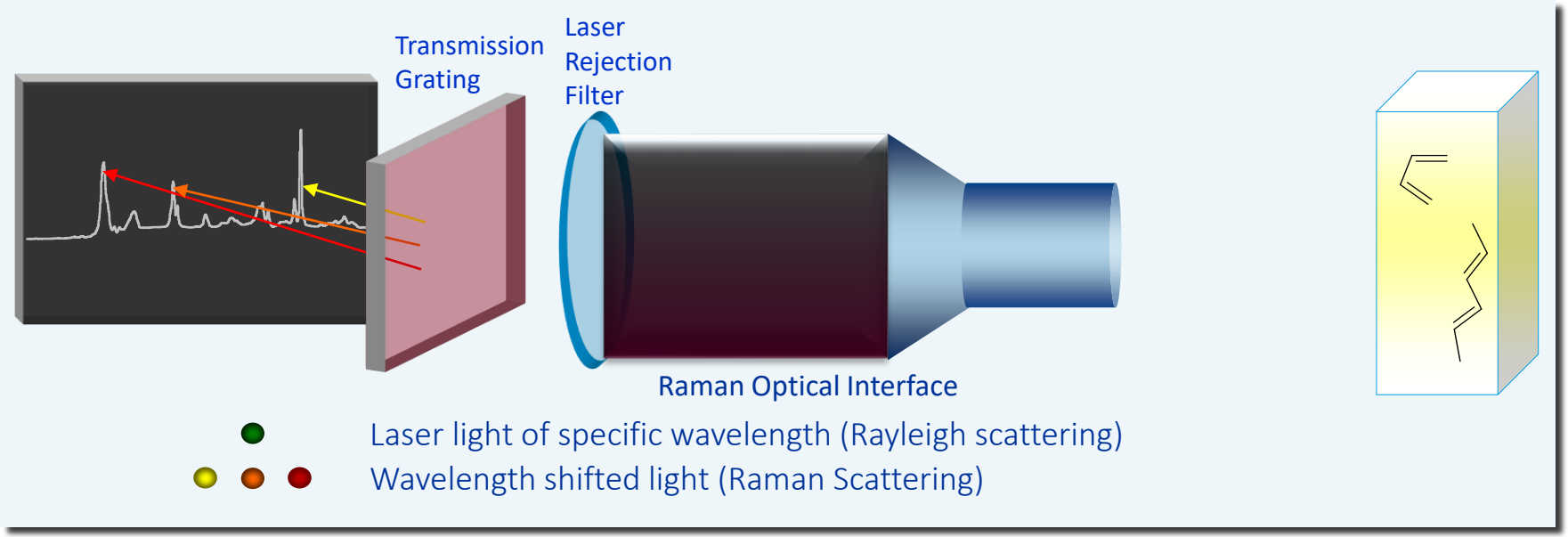


Response time today: 2-3 seconds / spectrogram life on screen

# Raman Scattering – How is Raman Data Collected?

- Only back scattered photons are collected
- Laser Rejection Filter removes original laser light
- Light is spatially separated using a Transmission Holographic Grating, like a Prism separates sunlight into colors
- Raman photons are simultaneously detected with a CCD detector



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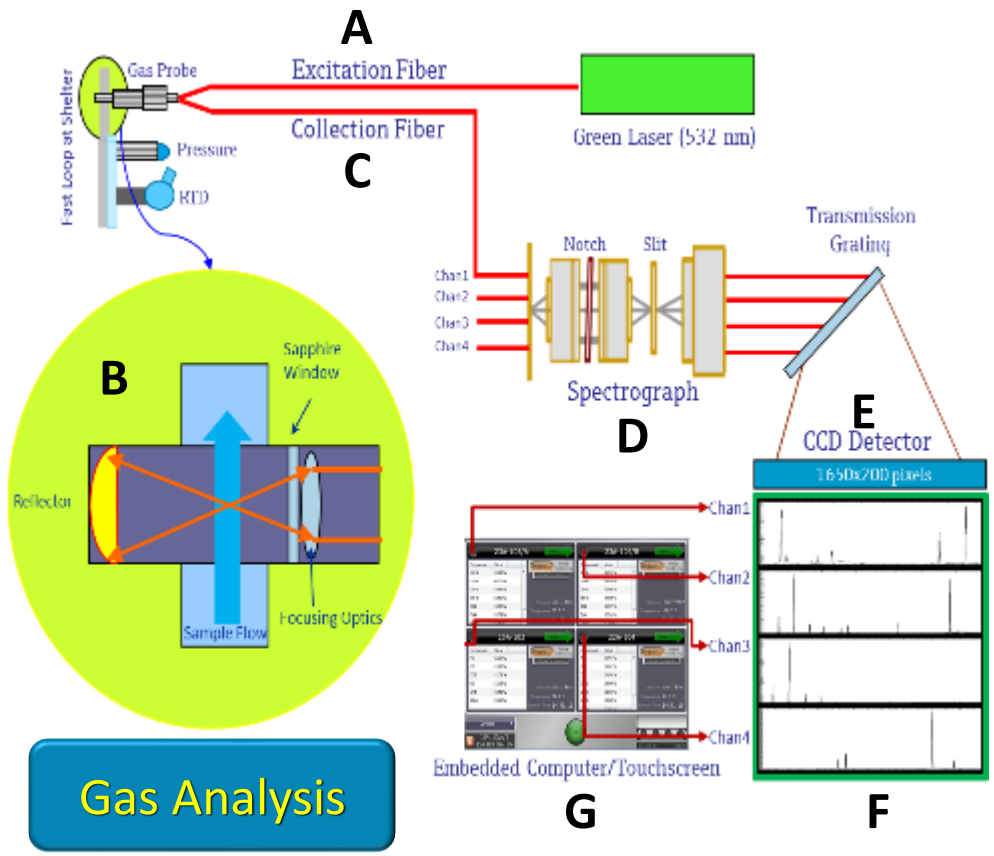
# Optograf Analyzer: Gas Optics Schematic



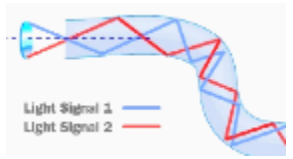

- **(A)** Green laser light travels along the Excitation Fiber to the gas probe (AirHead™ probe)
- **(B)** Sample flows past the Sapphire Window of the probe. The laser light is focused into that sample
- **(C)** Scattered light of multiple colors is transmitted along the Collection Fiber to the Spectrograph
- **(D)** The Spectrograph separates the colors (like a prism)
- **(E)** The CCD detector collects the light. 4 independent gas probes can be connected to one spectrograph
- **(F)** A Plot of the signal versus wavelength is the Optogram
- **(G)** Each peak area in the Optogram corresponds to the concentration of a different gas in the sample. Results are shown on the LCD display

# The “Optograf” Analyzer for Process Gas Analysis

**Optograf Base Unit**
**(18”W x 10”D x 32”H)**

Fiberoptic Sensor = Sample Interface
**Pipe-centric Enabler**






**Fiber Sensor**

- 4 Sensors(4 Lasers)
  - Operate in parallel
  - No Multiplexing
- Wetted Materials
  - 316 SS, Teflon, sapphire
- Pressure
  - Up to 1000 psi
- Temperature
  - 150º C at tip
  - 80º C at cable entry
- Size
  - Fits 1” Swagelok X-Tee

**Sensor Cables**

- Rule of Thumb: Up to 150 meters in length
- Can be installed in cable trays (conduit not required)
- Replaces heat-traced sample transport lines to the analyzer shelter



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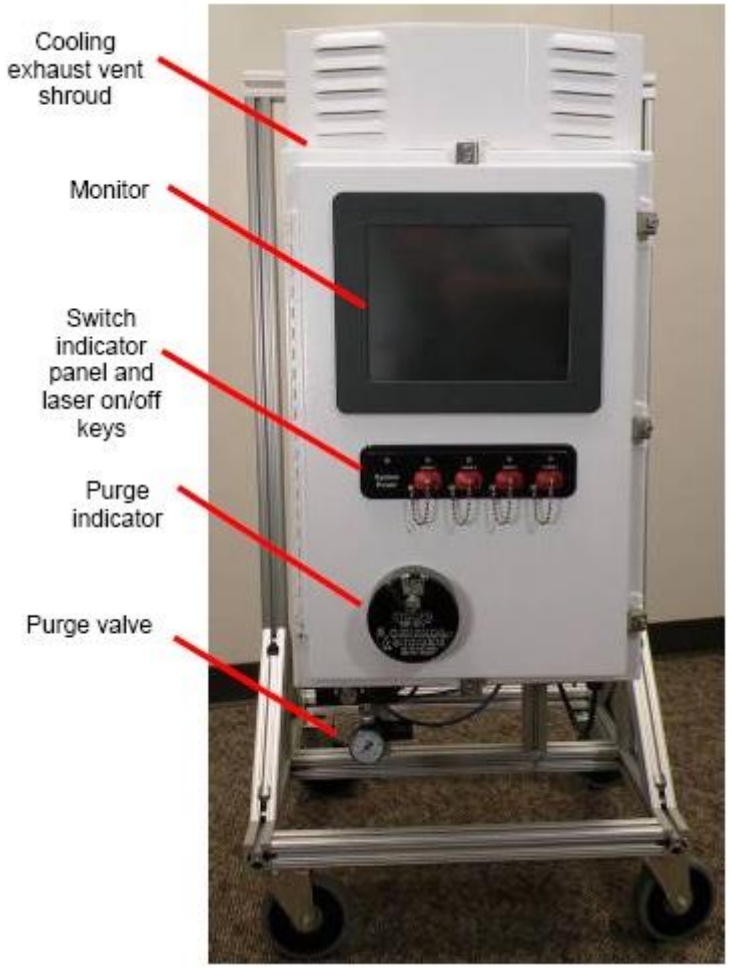
# Exterior Views – Front, Side and Top




# GUI – Stream Detail Analysis Tab


**Most recent analysis Optogram**

**Most recent analysis composition**

**Three Tab Options**

- **Analysis**
- **Trends**
- **Settings**

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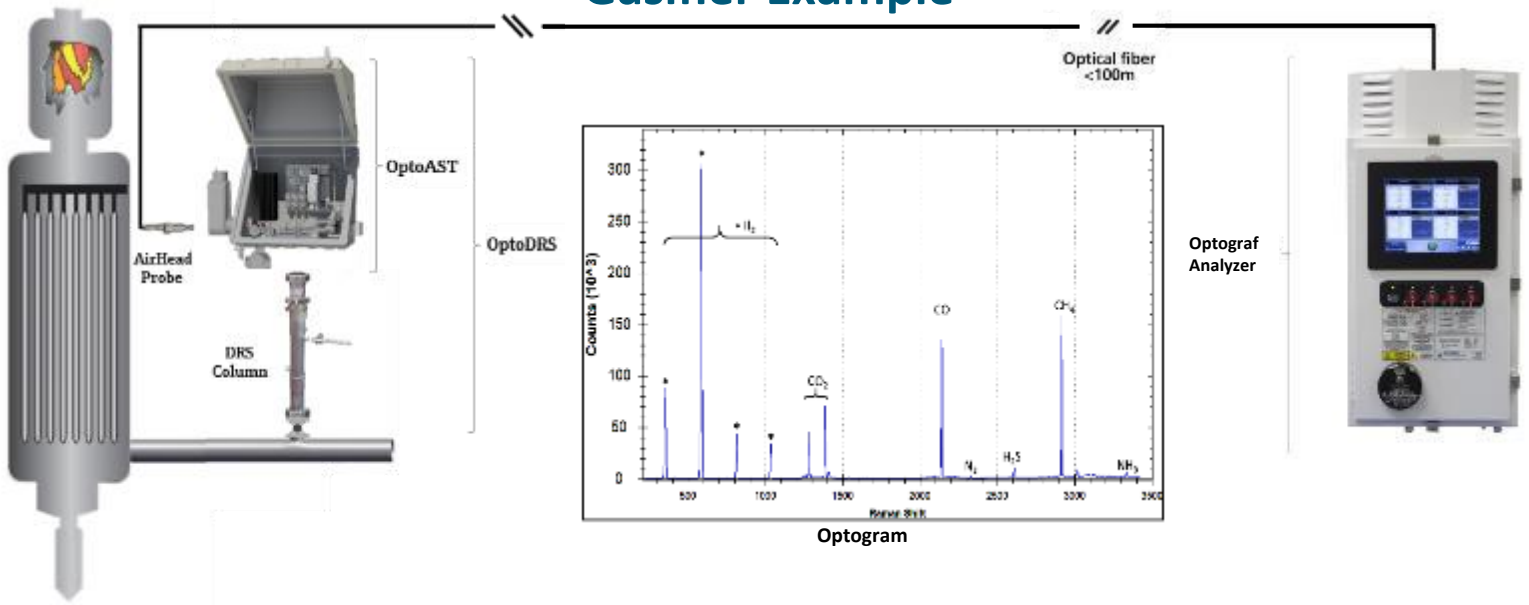
# The Optograf™ Analyzer Is a Complete Analysis Solution

## Gasifier Example




### Sample Streams

- Installed at the sample tap
- Sample Streams include
  - Reformers
  - Gasifiers
  - Shift Converters
  - PSA
  - Methanators
  - Synthesis Loops
    - Ammonia
    - Methanol

### Sample Interface

- Non-extractive Optical Probe
- Multiple Options
  - Conventional
  - OptoAST
    - Moderate Temp and Dry
  - OptoDRS
    - Particle-laden, Hot, Wet
- Works at process P and T
- No Flare
- Class 1/Div 1; Zone 1

### Analysis Result

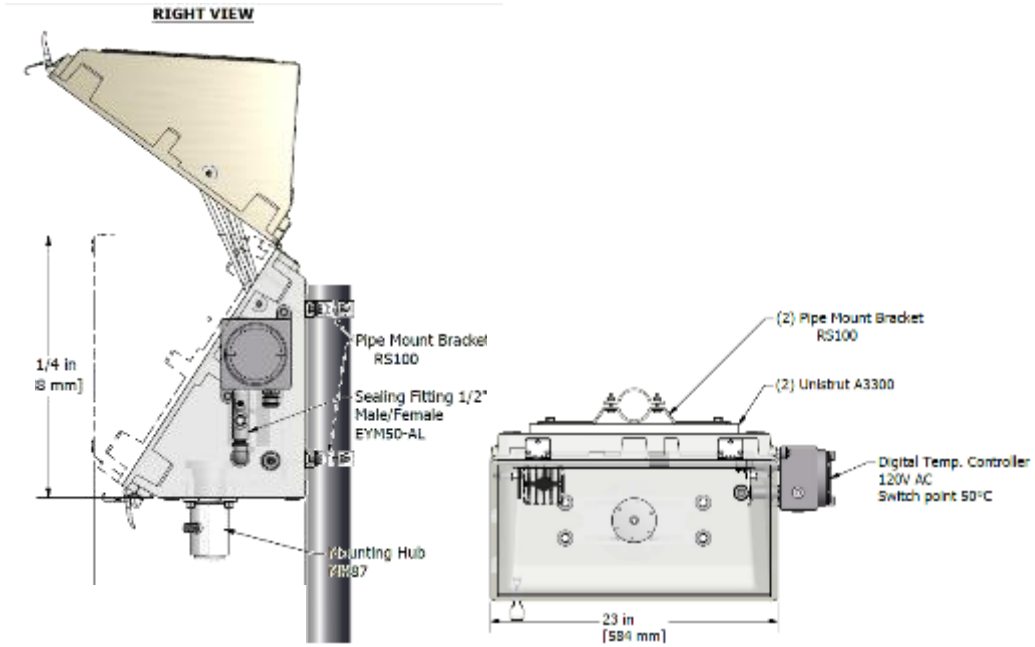
- Full stream composition
- Baseline peak separation
- Peak areas proportional to concentration
- Simple method-based analysis (no complex models)
- Can output BTU, Wobbe Index as derived values

### Base Unit

- Laser-based analyzer
- No columns
- No stream switching
- No sample transport
- No carrier gas
- Analyze 4 independent streams at one time
- Class 1/Div 2; Zone 2

# OptoAST™ and OptoDRS™ Sample Interfaces – Mounting Update

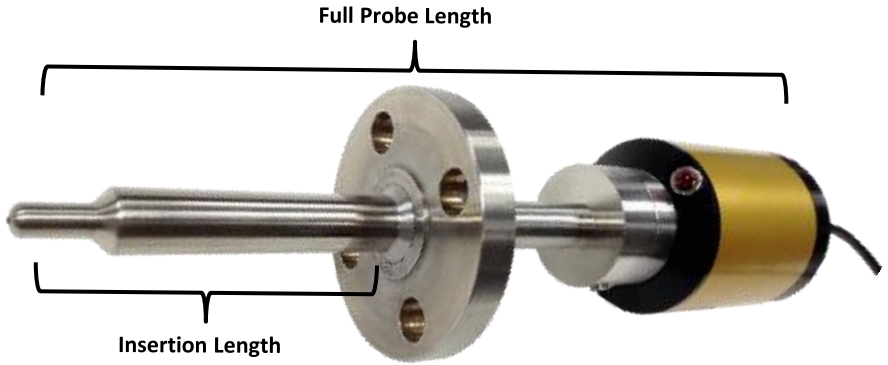
## OptoAST™ Sample Interface – Pole or Wall Mount 'Near Sample Tap' is the standard configuration




## OptoDRS™ Sample Interface – Direct on Isolation Valve

# Pilot™ Probe for LNG Installation – Interface Options

## Pilot™ Probe for Cryogenic Liquids




Probe Inserted 3-4” into Pipe

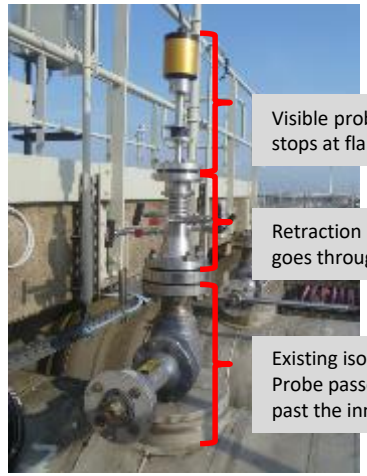
## Fast Loop


## Direct Pipe Flange

Insulated

Non-Insulated

## Fully Retractable



Visible probe portion stops at flange

Retraction interface. Probe goes through this.

Existing isolation valve on the pipe. Probe passes through this and 1-2” past the inner pipe surface.



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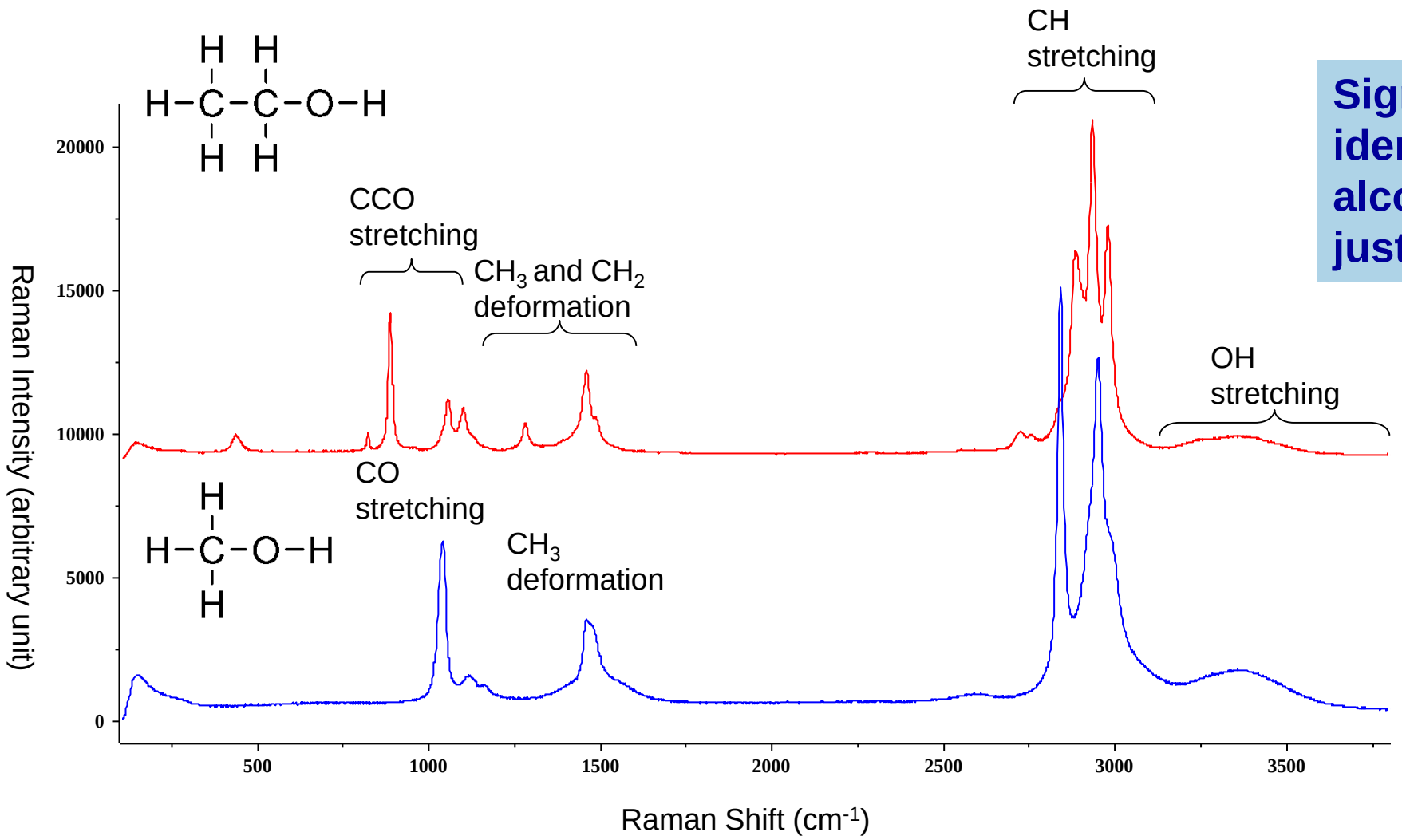
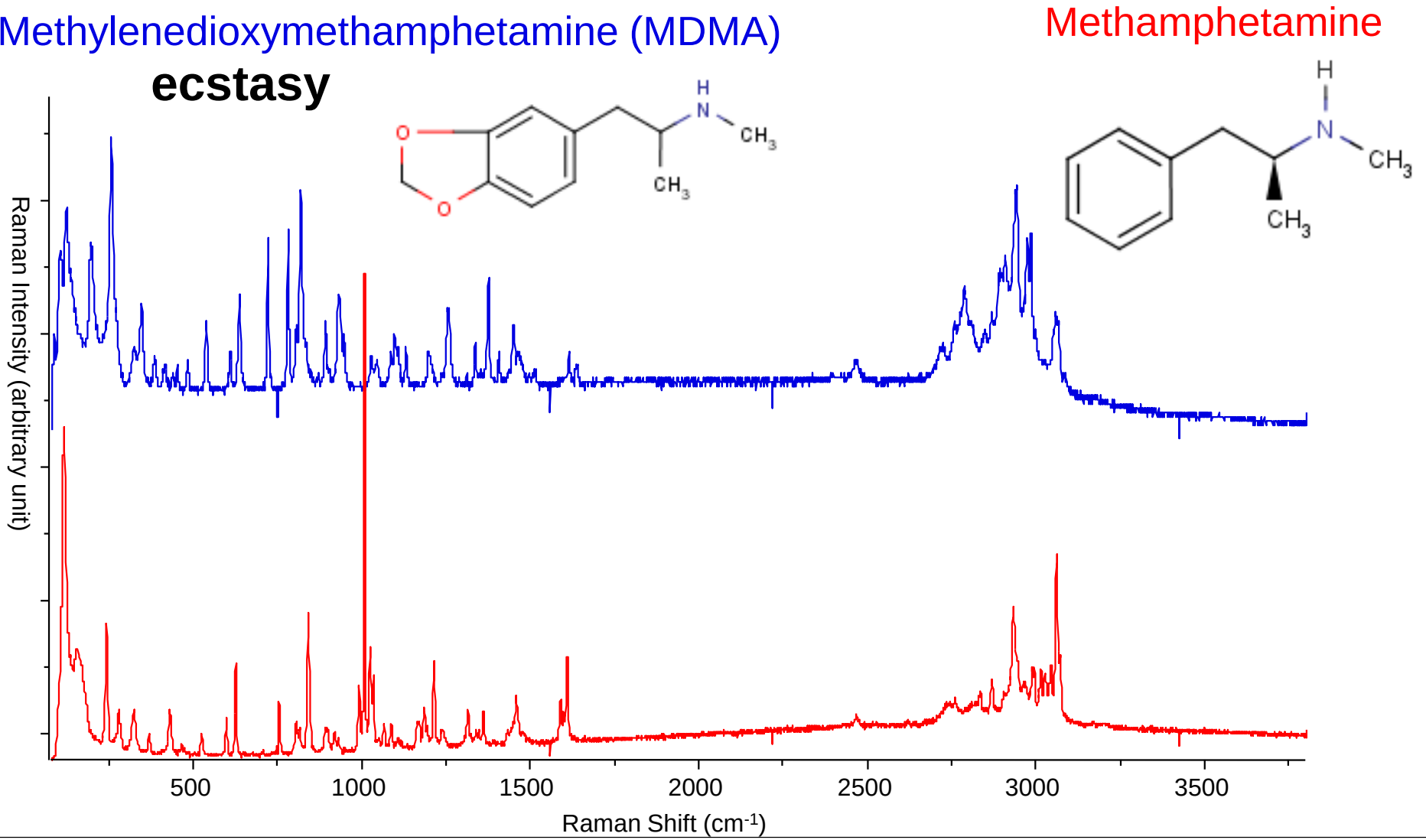
# Raman Analyzer Application Basics

# Raman Spectra of Methanol and Ethanol




**Significant identification of alcohols which differ just in one $CH_2$-group**

# Peak position – Chemical identity – Similar Structures



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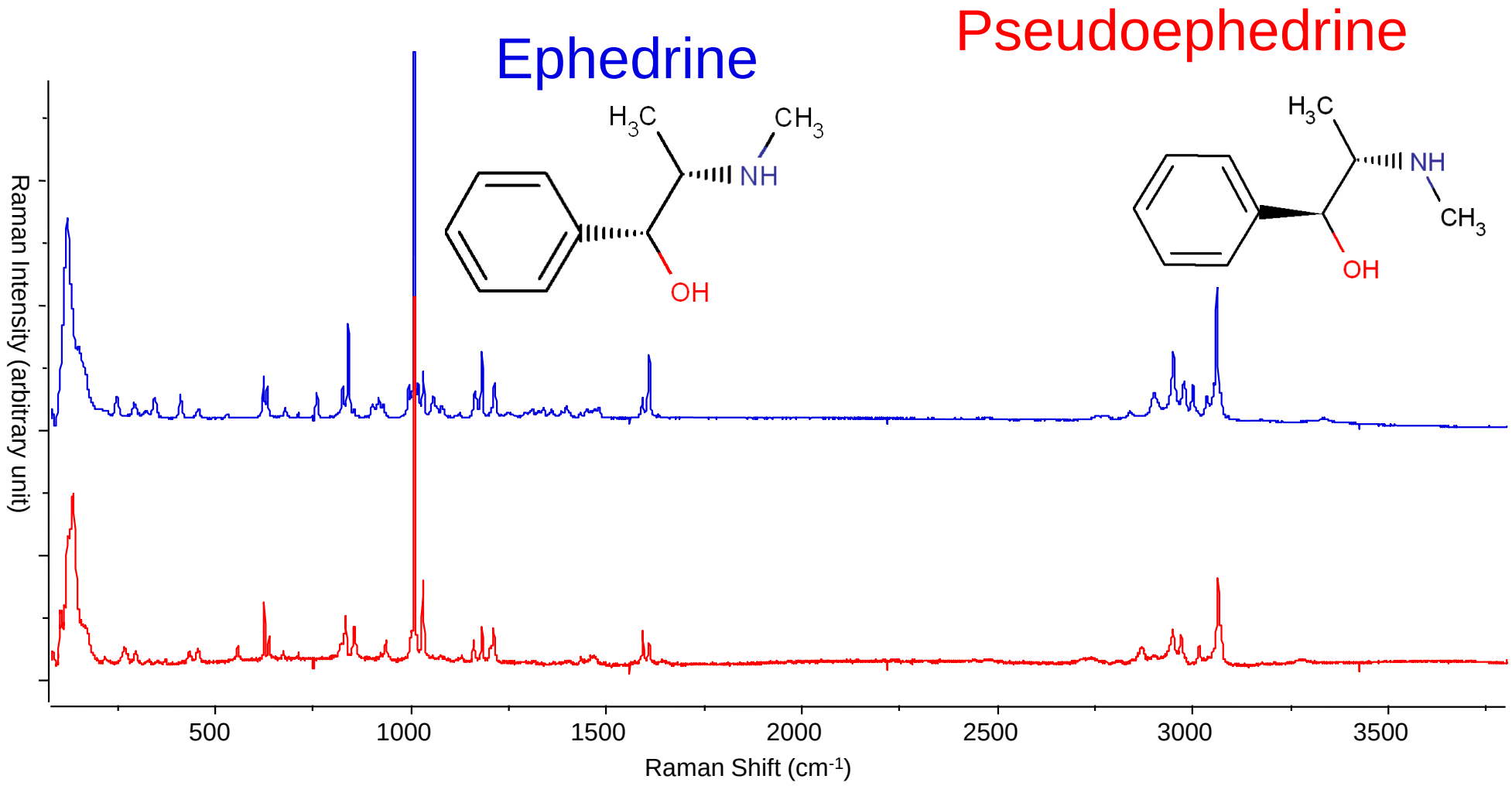
# Peak positions – Chemical identity - Diasteromers



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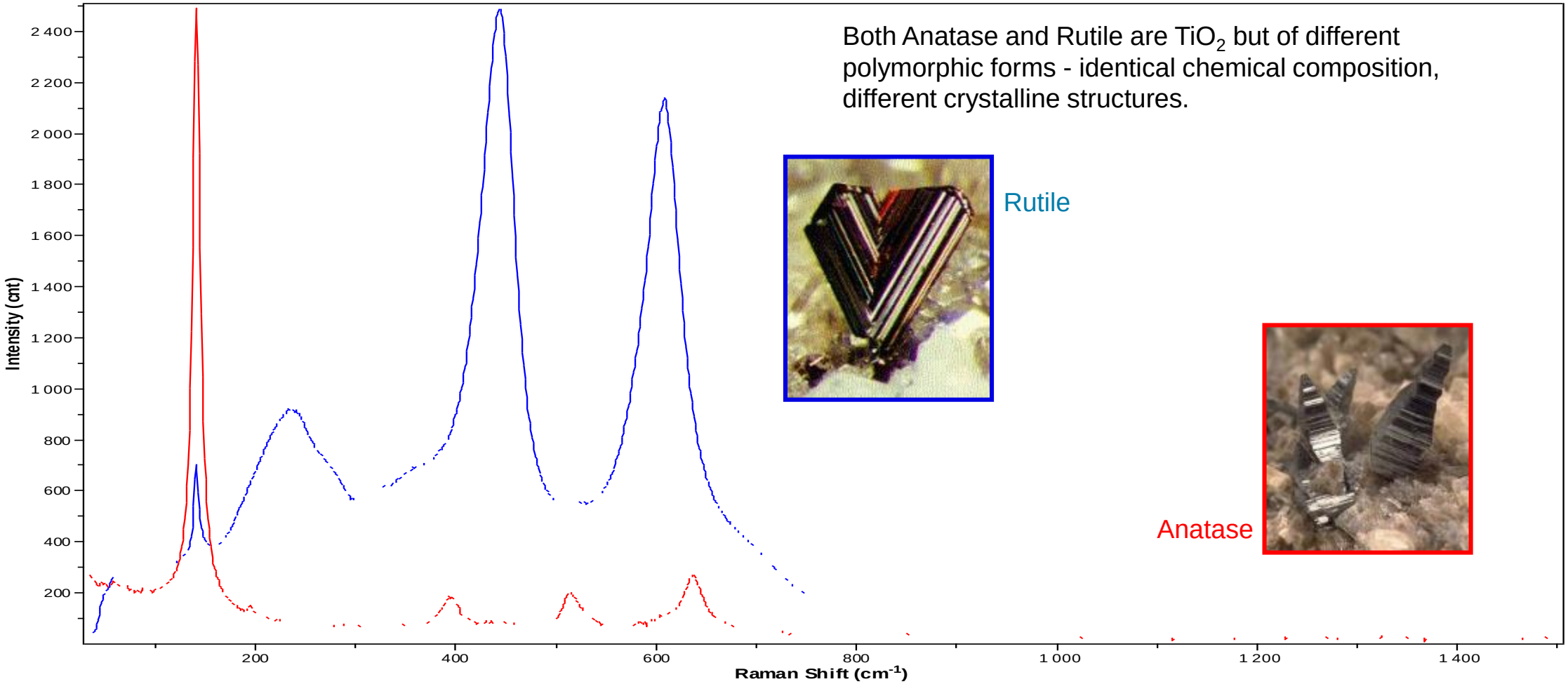
# Crystalline Structure on Raman Spectra




Both Anatase and Rutile are $TiO_2$ but of different polymorphic forms - identical chemical composition, different crystalline structures.



Rutile

Anatase





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# Optograf Analyzer – selected Applications

- Gasification/ Syngas
- Key Accounts/Quotes*
  - Coffeyville
  - POSCO
  - CNOOC (Huizhou)
  - Reliance (Jamnagar)*

*Typically multi-base unit sales*


- $H_2$ Recycle/Refining
- Key Accounts/Quotes
  - Chevron (Richmond)
  - Chevron (El Segundo)
  - Hyundai (Oil Bank)

*Strong synergy with TDLAS*


- $H_2$ Purity (PSA)/HyCO
- Key Accounts/Quotes*
  - Chevron (Richmond)
  - Chevron (Salt Lake)*

*Strong competitive position and value*


- LNG (Custody Transfer, Blending, Retail/SS LNG)
- Key Accounts/Quotes
  - AGL, NNG* (US, truck loading)
  - Grain LNG (UK, ballasting)
  - Osaka Gas (Japan, blending)
  - Wartsila (Bunkering)*

*Lower barrier to entry than large plants*


* Represent quotes/orders, not installed base

# Optograf Analyzer – Application Initiative: Syngas

- Gasification/ Syngas
- Key Accounts/Quotes*
  - Coffeyville
  - POSCO
  - CNOOC (Huizhou)
  - Reliance (Jamnagar)*

- $H_2$ Recycle/Refining
- Key Accounts/Quotes
  - Chevron (Richmond)
  - Chevron (El Segundo)
  - Hyundai (Oil Bank)

- $H_2$ Purity (PSA)/HyCO
- Key Accounts/Quotes*
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  - Wartsila (Bunkering)*

*Typically multi-base unit sales*


*Strong synergy with TDLAS*


*Strong competitive position and value*


*Lower barrier to entry than large plants*


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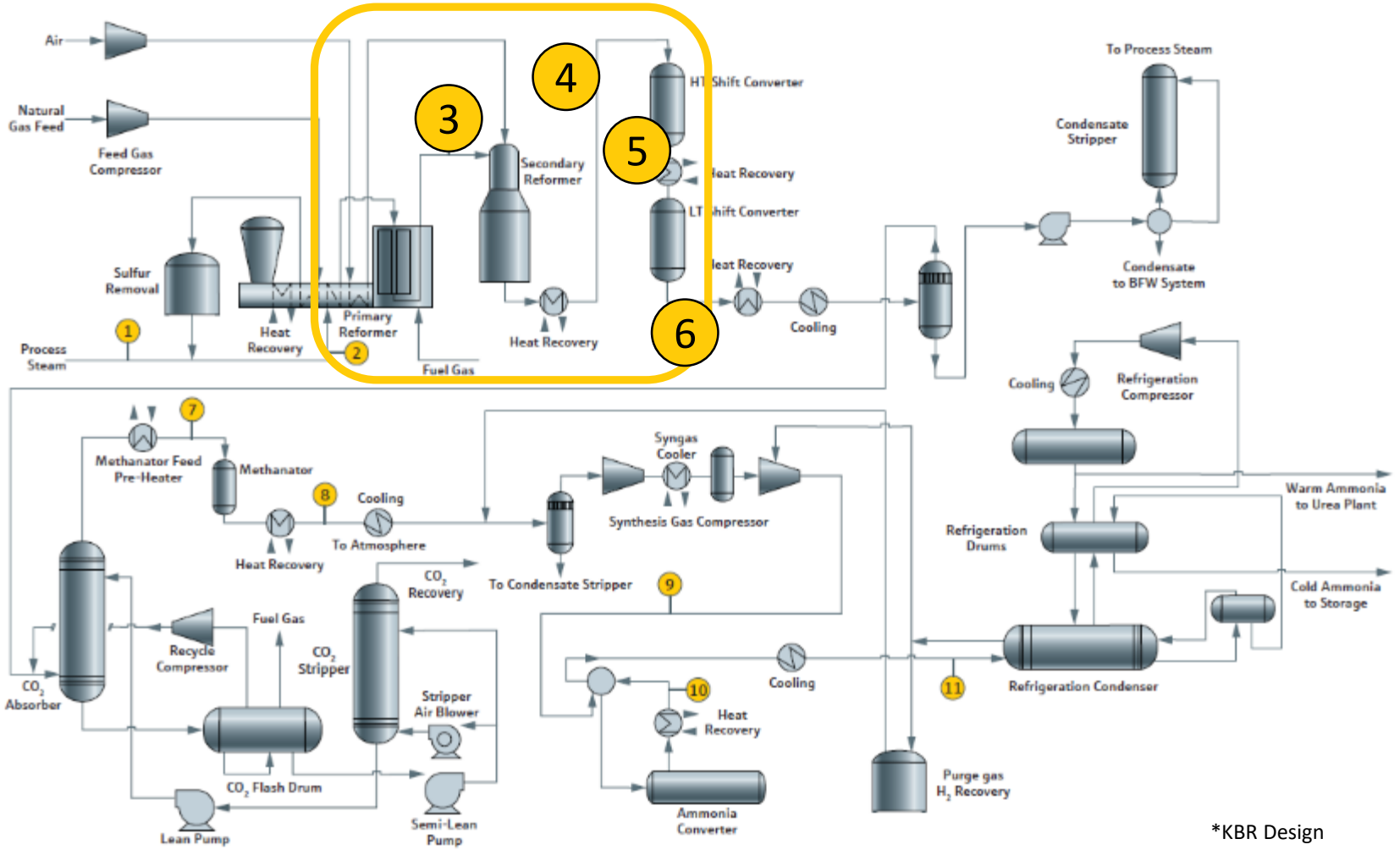
# Optograf Applications – Ammonia Production*




*KBR Design



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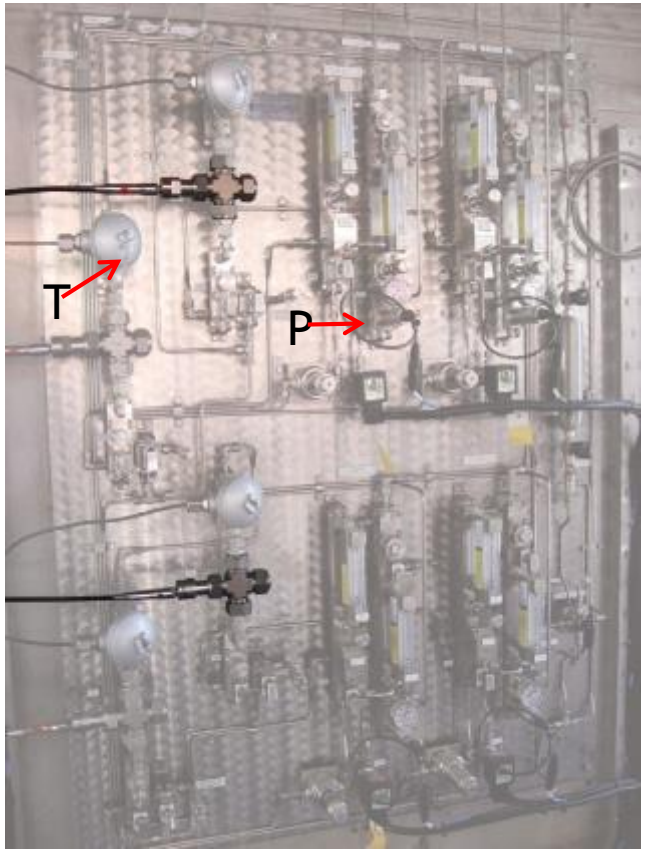
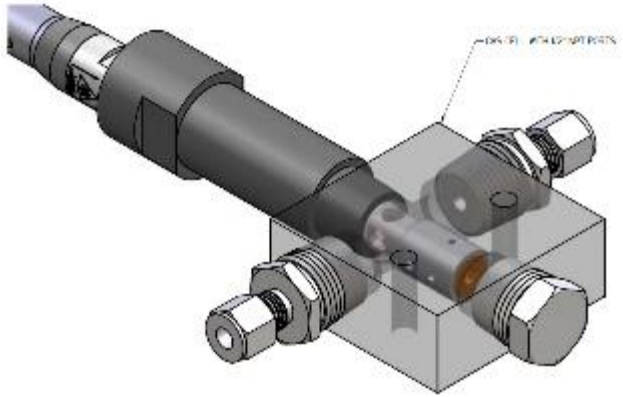
# Syngas Installation Example – AirHead™ Probe Cross T




AirHead™ Probe installed in a conventional sampling system at Coal Gasification Plant for Syngas Analysis

**Simple In-line Probe Installation**





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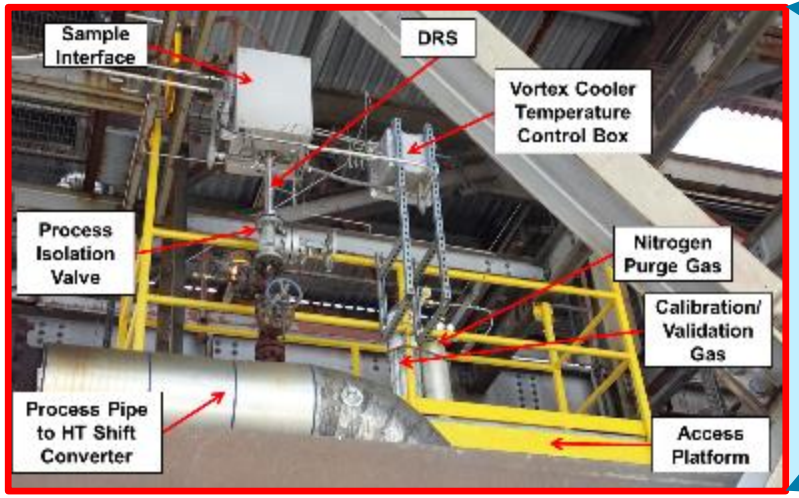
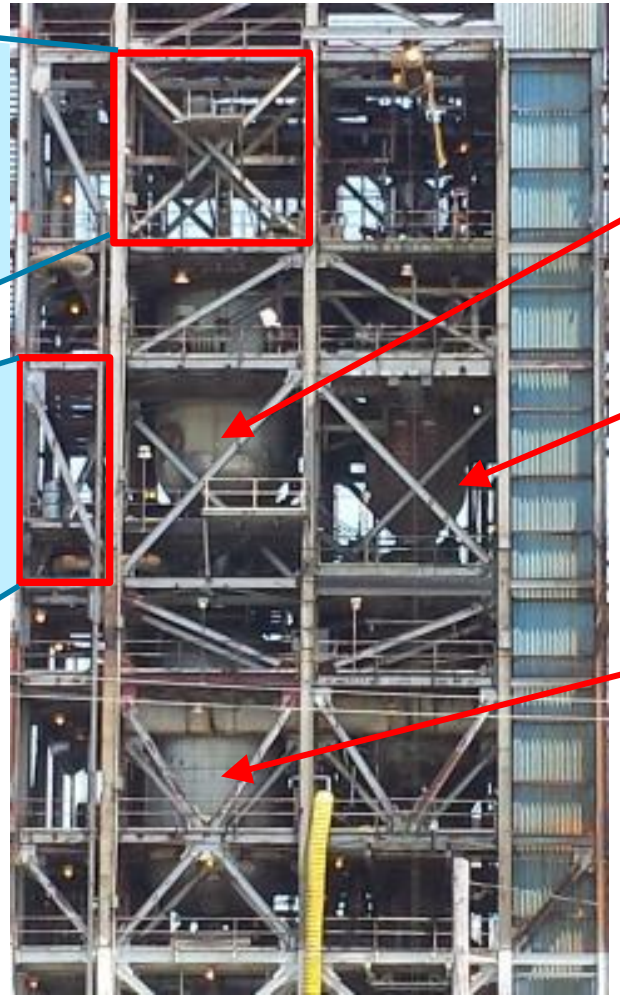
# Installation in a Gasifier Tower of the Coffeyville Ammonia Plant




Sample Interface + Access Platform

Raman Instrument



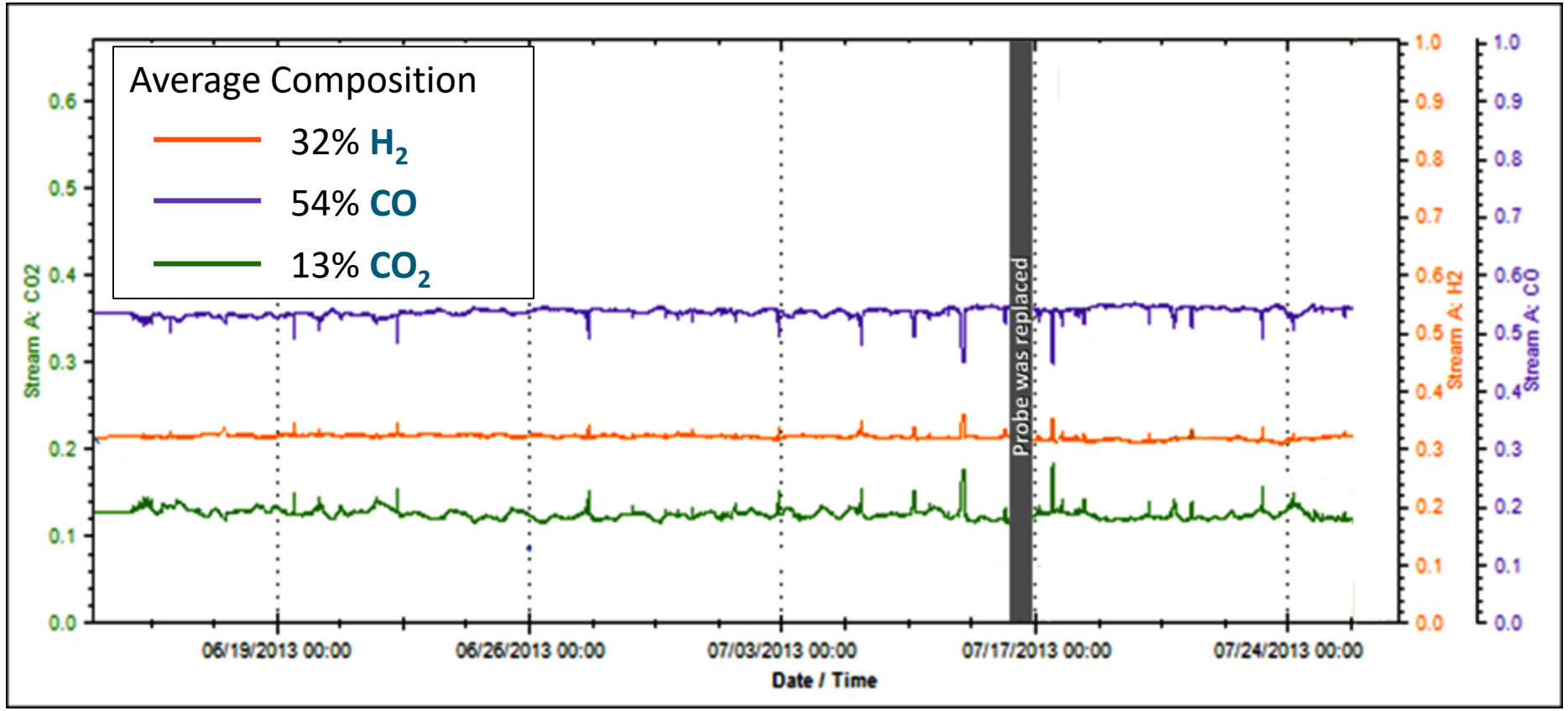
Primary Shift Converter

Gasifier

Secondary Shift Converter

# CH1 Scrubber Outlet – Process Data

Pressure: 580 psig  Update Time: 180 seconds



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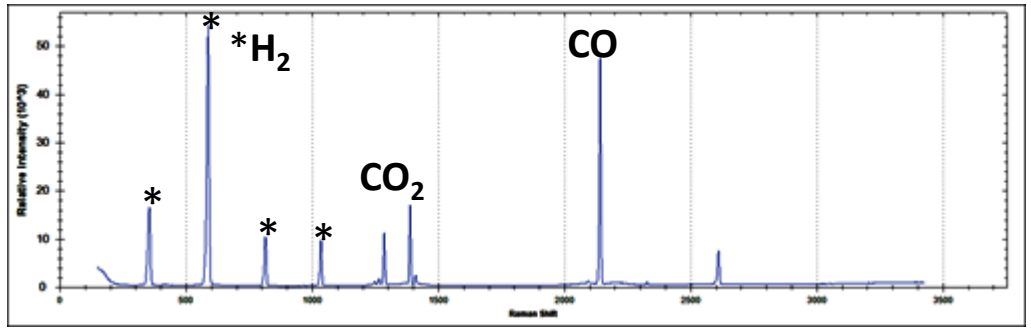
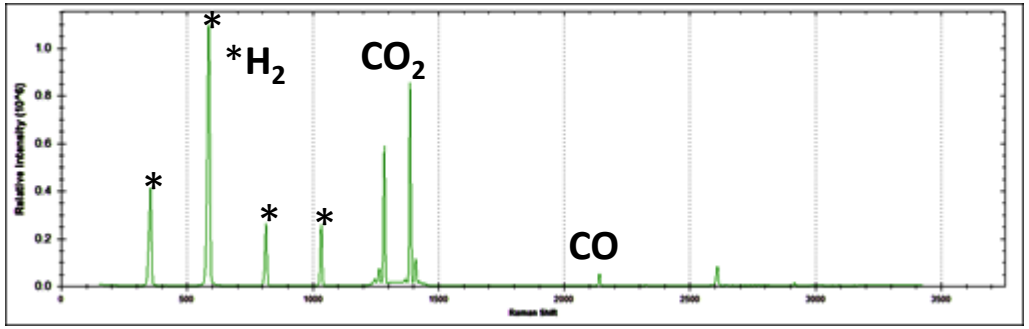
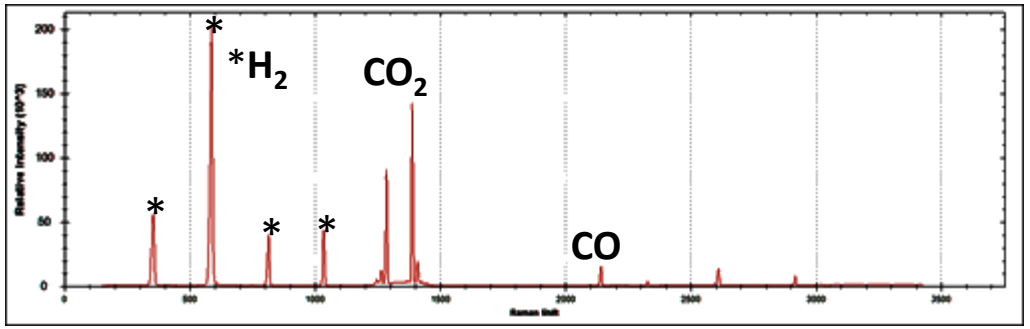
# Simultaneous Measurement of the Sour Gas Shift Process




| Scrubber Outlet (CH 1) | | |
|---|---|---|
| Gas | Expected | Measured |
| $H_2$ | 33.27 | 32.21 |
| $CO_2$ | 12.30 | 12.20 |
| CO | 53.85 | 53.46 |

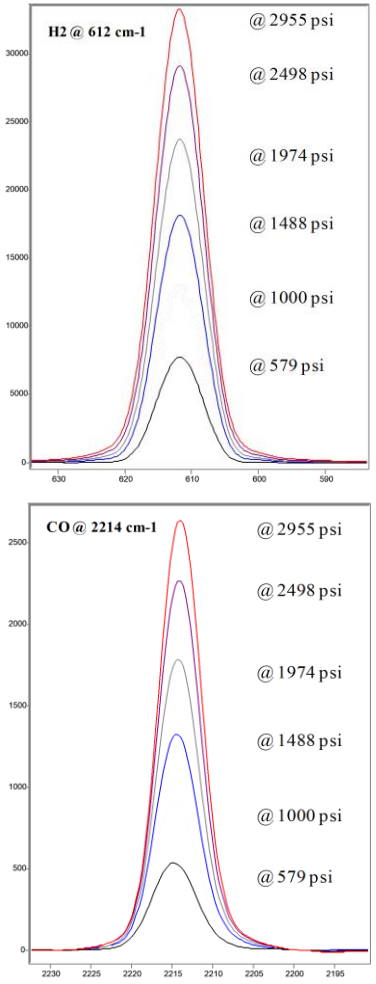



| 1st Shift Outlet (CH 2) | | |
|---|---|---|
| Gas | Expected | Measured |
| $H_2$ | 54.62 | 52.56 |
| $CO_2$ | 40.51 | 41.85 |
| CO | 3.75 | 4.00 |

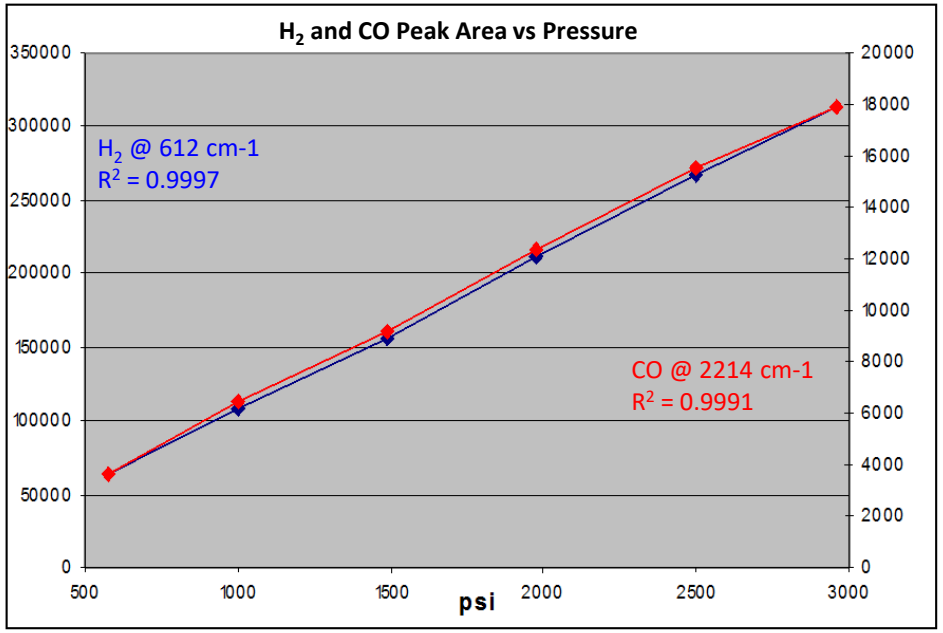



| 2nd Shift Inlet (CH 3) | | |
|---|---|---|
| Gas | Expected | Measured |
| $H_2$ | 50.38 | 53.01 |
| $CO_2$ | 33.87 | 37.89 |
| CO | 13.25 | 6.52 |

# Optograf Performance – Linearity with Sample Pressure




- Mixture of $H_2$ and CO (syngas)
- Pressure varied from 580 to 3000 psi
- Peak areas are used to calculate gas composition
- Peak areas are linear with pressure



# Recycle and Reuse of Hydrogen in Refineries

# Optograf Analyzer – 2018 Key Applications Initiative: $H_2$ Recycle

- Gasification/ Syngas
- Key Accounts/Quotes*
  - Coffeyville
  - POSCO
  - CNOOC (Huizhou)
  - Reliance (Jamnagar)*

*Typically multi-base unit sales*


- $H_2$ Recycle/Refining
- Key Accounts/Quotes
  - Chevron (Richmond)
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  - Hyundai (Oil Bank)

*Strong synergy with TDLAS*


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*Lower barrier to entry than large plants*


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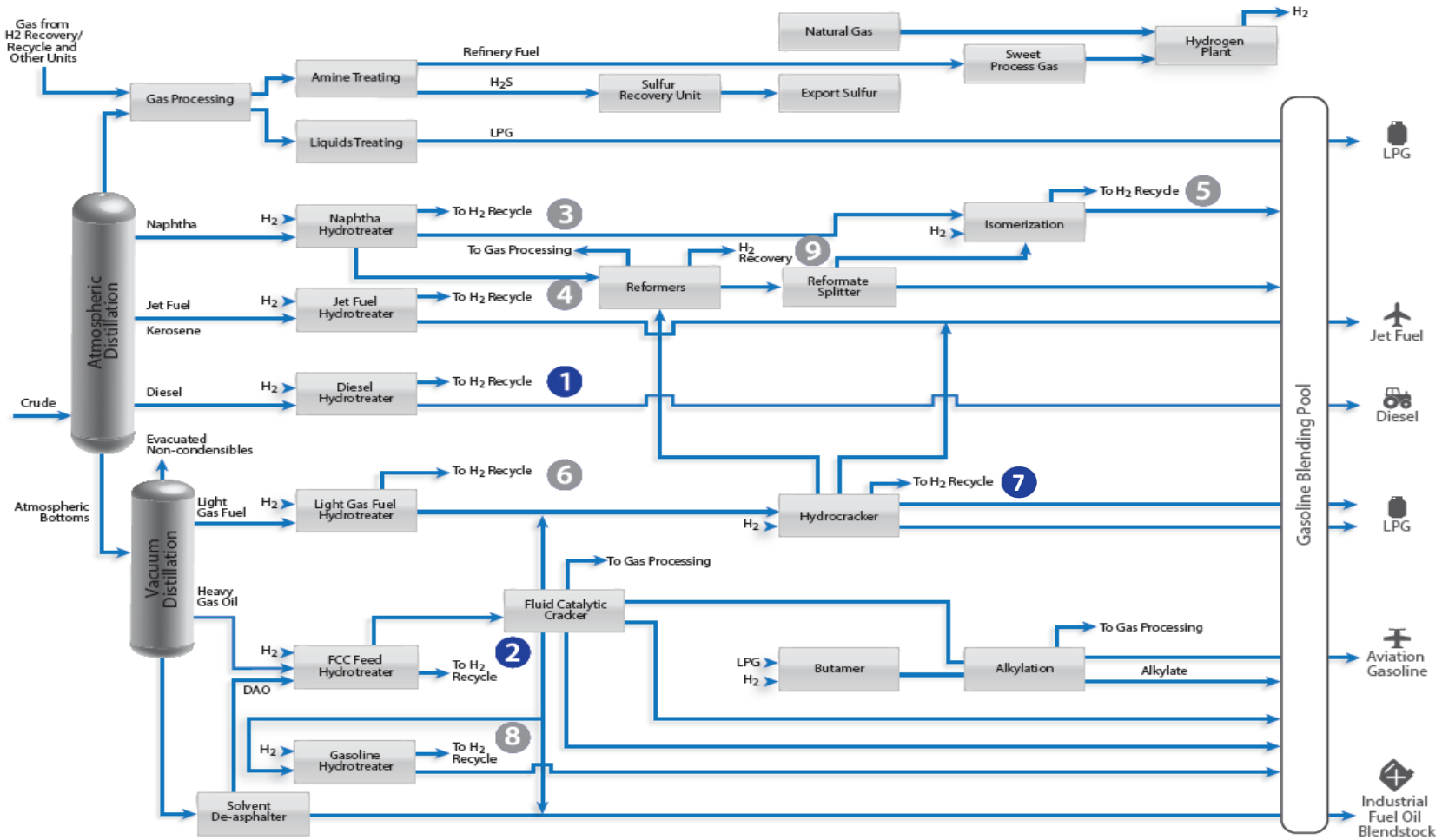
# Raman Applications – Hydrogen Recycle/Recovery (Refinery)



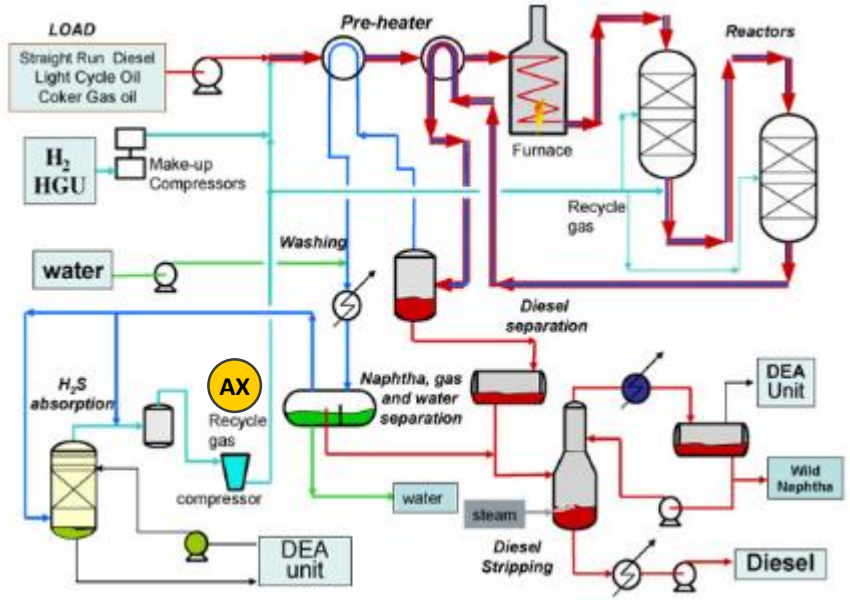
# Raman Applications – Hydrogen Recycle/Recovery (Refinery)

| | Stream Service | Key Measurement Parameter | Pressure* (barg) | Temperature* (°C) | Recommended Sampling Interface |
|---|---|---|---|---|---|
| 1 | Diesel Hydrotreater Recycle | $H_2/H_2S$ | 350 | 20-60 | OptoAST |
| 2 | DAO/FCC Feed Hydrotreater Recycle | $H_2/H_2S$ | 400 | 20-60 | OptoAST |
| 3 | Naphtha Hydrotreater Recycle | $H_2/H_2S$ | | | OptoAST |
| 4 | Jet Fuel/Kerosene Hydrotreater Recycle | $H_2/H_2S$ | | | OptoAST |
| 5 | Isomerization Unit Recycle | $H_2/H_2S$ | | | OptoAST |
| 6 | Light Gasoil Hydrotreater | $H_2/H_2S$ | | | OptoAST |
| 7 | **Hydrocracker Recycle** | **$H_2$** | | | **OptoAST** |
| 8 | Gasoline Hydrotreater Recycle | $H_2/H_2S$ | | | OptoAST |
| 9 | Reformer Hydrogen Recovery | $H_2$ | | | OptoAST |

# Hydrogen Recycle in Refinery Diesel Hydrotreater


| Refineries | Capacity (000 b/d) | Troughput (000 b/d) |
|---|---|---|
| Paulínia - Replan (SP) | 365 | 348 |
| Landulpho Alves - Rlam (BA) | 323 | 261 |
| Duque de Caxias -Reduc (RJ) | 242 | 243 |
| Henrique Lage - Revap (SP) | 251 | 236 |
| Alberto Pasqualini - Refap (RS) | 189 | 148 |
| Pres. Getúlio Vargas - Repar (PR) | 189 | 169 |
| Pres. Bernardes - RPBC (SP) | 170 | 153 |
| Gabriel Passos - Regap (MG) | 151 | 132 |
| Manaus - Reman (AM) | 46 | 41 |
| Capuava - Recap (SP) | 53 | 42 |
| Fortaleza - Lubnor (CE) | 7 | 6 |
| TOTAL BRAZIL | 1,986 | 1,779 |

- Production capacity of 360,000 bpd
- 20% of Brazil's oil refining capacity
- Test at Replan Refinery
- $H_2$ Recycle on Diesel Hydrotreater
- 30 Day Evaluation to compare with GC



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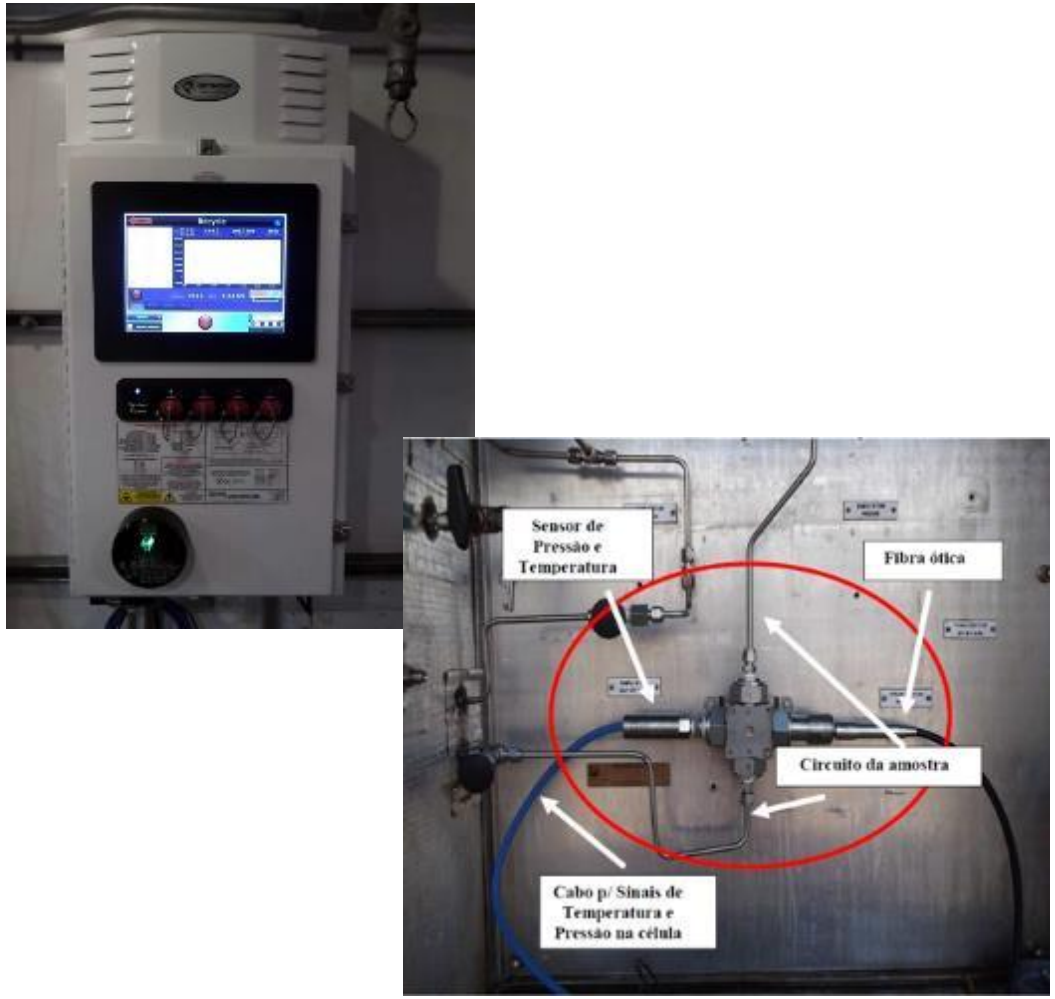
# Hydrogen Recycle in Refinery Diesel Hydrotreater - Installation




- **<u>Unit installed and operational in under 2 hours</u>**
- Simple Union Cross sample interface
- **<u>Operating pressure at probe was only 14 psi</u>**, integrating into existing GC sampling system
- “It can be installed directly on the gas line in the field”
- “Low maintenance frequency during the test, even in … conditions of installation”
- Final report highlighted need for better sample conditioning and temperature control for future installations

# Hydrogen Recycle in Refinery Diesel Hydrotreater – Results

| Calibração | | Padrão | Leitura do Padrão |
|---|---|---|---|
| | H2 | 0,979 | 0,979 |
| | H2S | 0,003 | 0,003 |
| | CH4 | 0,010 | 0,010 |
| | C2H6 | 0,002 | 0,002 |
| | C3H8 | 0,002 | 0,003 |
| | N2 | 0,001 | 0,001 |
| | iC4H10 | 0,001 | 0,000 |
| | nC4H10 | 0,001 | 0,001 |
| | iC5H12 | 0,001 | 0,000 |
| | nC5H12 | 0,001 | 0,001 |
| | Other | 0,000 | 0,000 |

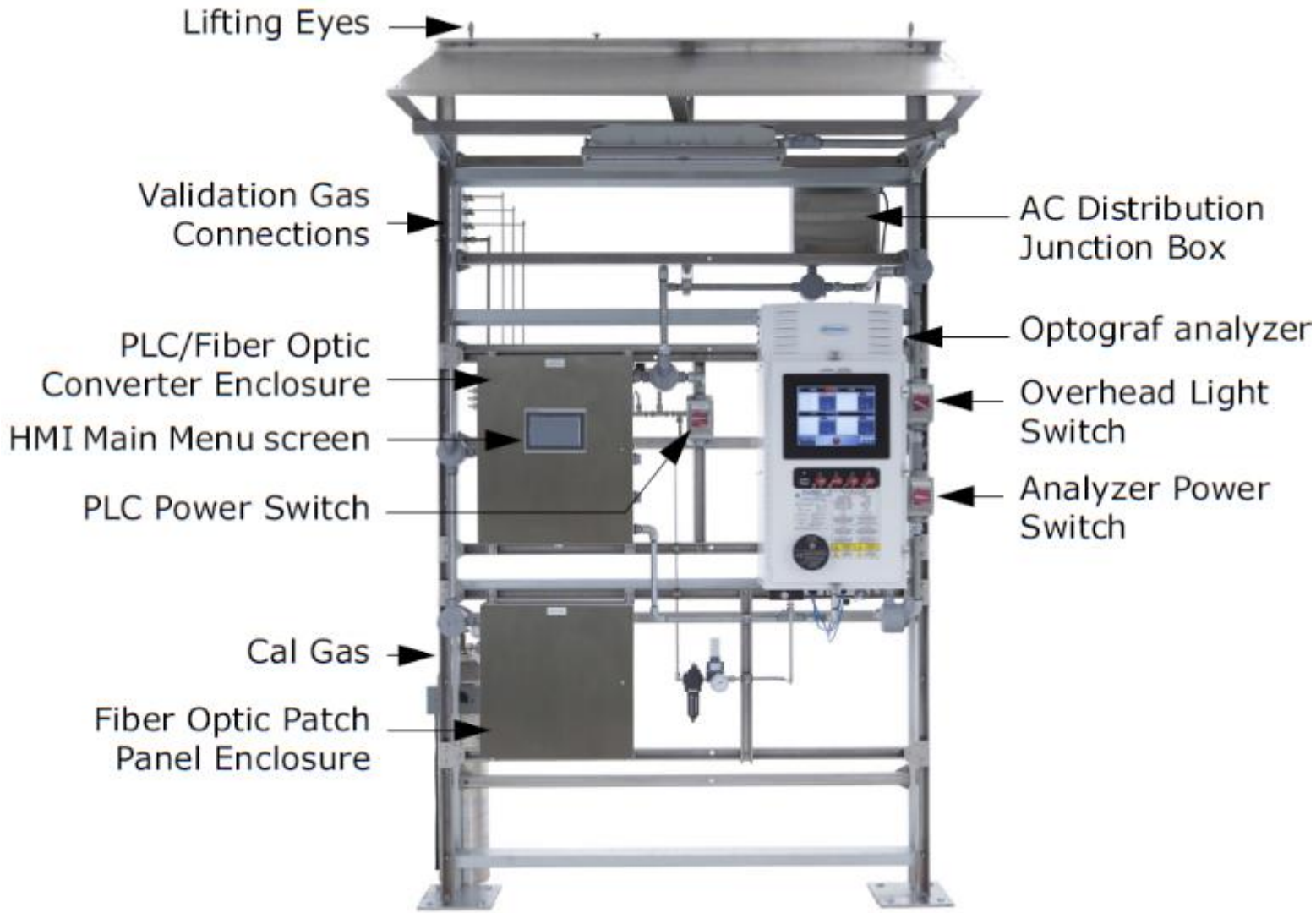
| Processo | Data / Hora | 04/10/2013 01:34 | LABORATÓRIO | 06/10/2013 17:13 | LABORATÓRIO |
|---|---|---|---|---|---|
| | H2 | 0,966 | 0,968 | 0,965 | 0,967 |
| | H2S | 0,006 | 0,008 | 0,005 | 0,003 |
| | CH4 | 0,021 | 0,017 | 0,021 | 0,019 |
| | C2H6 | 0,002 | 0,002 | 0,003 | 0,005 |
| | C3H8 | 0,001 | 0,001 | 0,001 | 0,001 |
| | N2 | 0,001 | 0,001 | 0,001 | 0,001 |
| | iC4H10 | 0,001 | 0,001 | 0,000 | 0,000 |
| | nC4H10 | 0,001 | 0,001 | 0,001 | 0,001 |
| | iC5H12 | 0,000 | 0,000 | 0,001 | 0,001 |
| | nC5H12 | 0,001 | 0,001 | 0,001 | 0,001 |
| | Other | 0,000 | 0,000 | 0,000 | 0,000 |

| Processo | Data / Hora | 08/10/2013 10:37 | LABORATÓRIO | 15/10/2013 12:50 | LABORATÓRIO |
|---|---|---|---|---|---|
| | H2 | 0,965 | 0,962 | 0,967 | 0,963 |
| | H2S | 0,005 | 0,008 | 0,005 | 0,007 |
| | CH4 | 0,024 | 0,022 | 0,019 | 0,021 |
| | C2H6 | 0,003 | 0,003 | 0,004 | 0,003 |
| | C3H8 | 0,000 | 0,001 | 0,000 | 0,001 |
| | N2 | 0,001 | 0,001 | 0,001 | 0,001 |
| | iC4H10 | 0,000 | 0,001 | 0,000 | 0,000 |
| | nC4H10 | 0,001 | 0,001 | 0,001 | 0,001 |
| | iC5H12 | 0,000 | 0,000 | 0,001 | 0,001 |
| | nC5H12 | 0,001 | 0,001 | 0,001 | 0,001 |
| | Other | 0,000 | 0,000 | 0,000 | 0,000 |

- “It is important to note that the level of detection and precision of the Optical chromatography of OPTOGRAF meets levels from 0.1 mol% of concentration.”
- “in my opinion…(we see) the robustness as a greater need.”
- “it is worth noting that the level of detection can be significantly improved when the cell or sensor is installed at higher pressures”

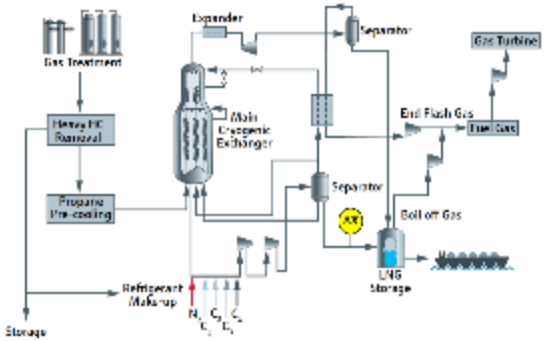
“Due to the robustness of the analytical system demonstrated during the test, we recommend OPTOGRAF instead of chromatographic systems, in and inaccessible places, as well as where the "OPEX" is complex due to the inputs such as Gasses of Drag or Calibration, Columns, Valves and special detectors like TCD or FPD”

# Complete Analyzer Solution – Light Integration With PLC

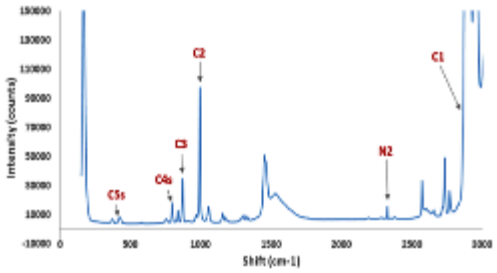


# Key Optograf Analyzer Opportunities in LNG

## Liquefaction Rundown to Storage Tanks



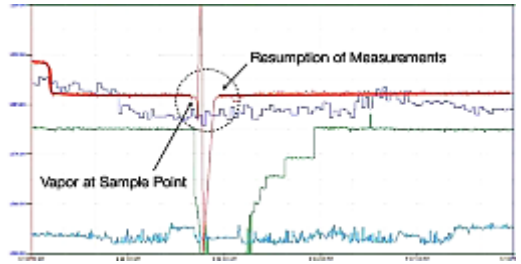

Analysis of LNG BTU for Multiple Ship Loads




**Eliminates Running 'Off Spec' LNG Into Storage Tanks**

## Truck Loading

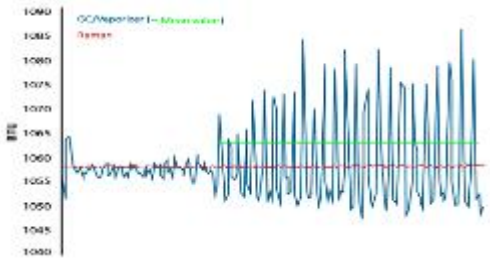
Measurement Stability With Intermittent Flow




**Rapid, Stable Measurement for Quality of LNG Transferred**

## Marine Bunkering

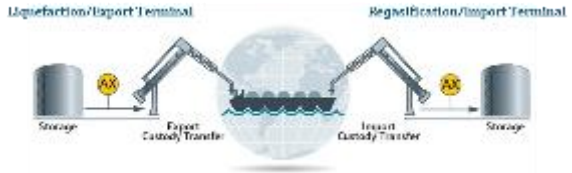
High Precision with Low Maintenance



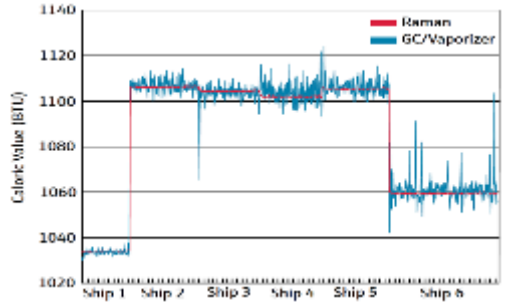

**Requires Virtually No Maintenance or Consumables**

Image Source: https://www.klawlng.com/wp-content/uploads/2015/06/LNG-bunkering.png

## Baseload Import/Export Terminals




Analysis of LNG BTU for Multiple Ship Loads




**~ 20x Lower Uncertainty Can Save $100,000 per shipload**



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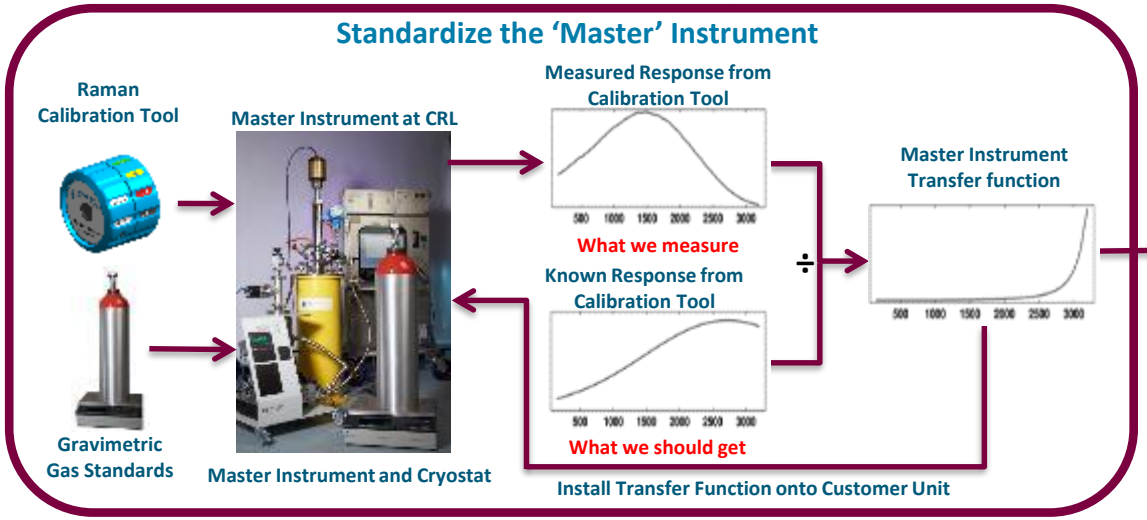
# Calibration and Validation

# Kaiser Raman Optograf Calibration for LNG – Reference Lab Adjustment Option

## At Certified Reference Laboratory (Effectech)

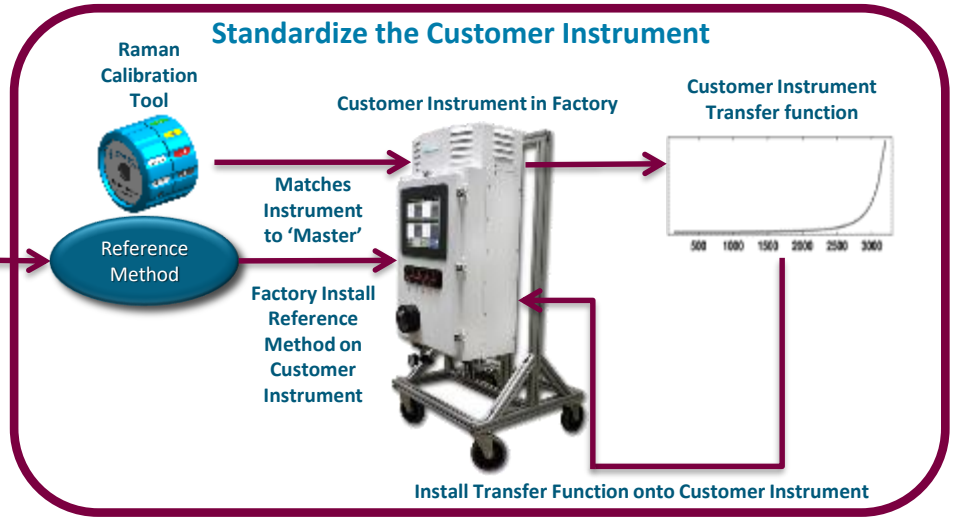
### Standardize the 'Master' Instrument




Response Factors from Gravimetrically Traceable Reference LNG Standards

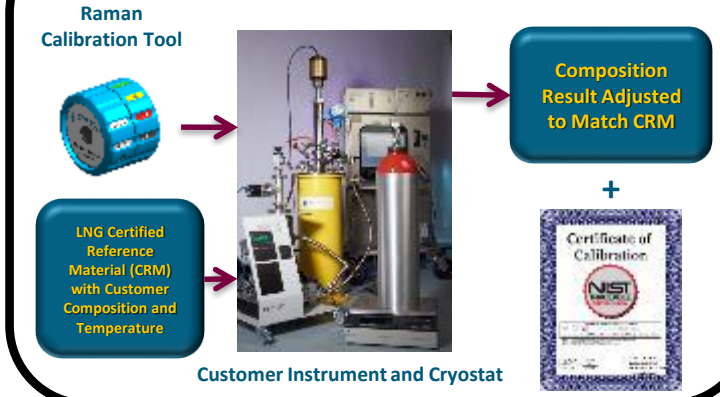
## In Factory During Manufacturing

### Standardize the Customer Instrument



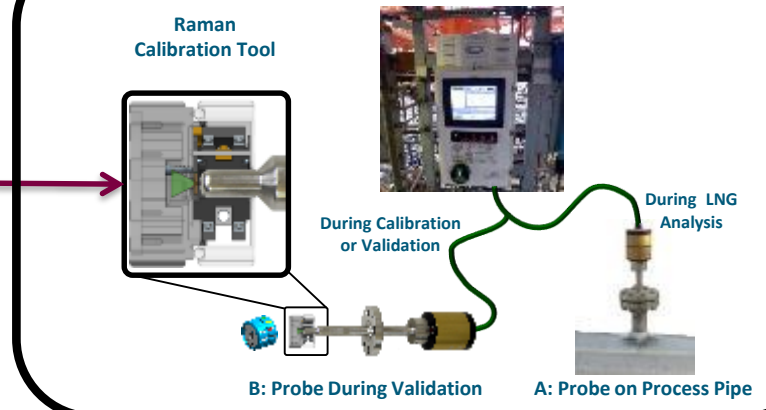

## Customer Unit Calibrated at Reference Laboratory

### Adjust 'Customer' Instrument to CRM




## Field Commissioning of Customer Instrument

### Instrument Adjustment After Installation




### Process Measurements

**BTU + Composition**



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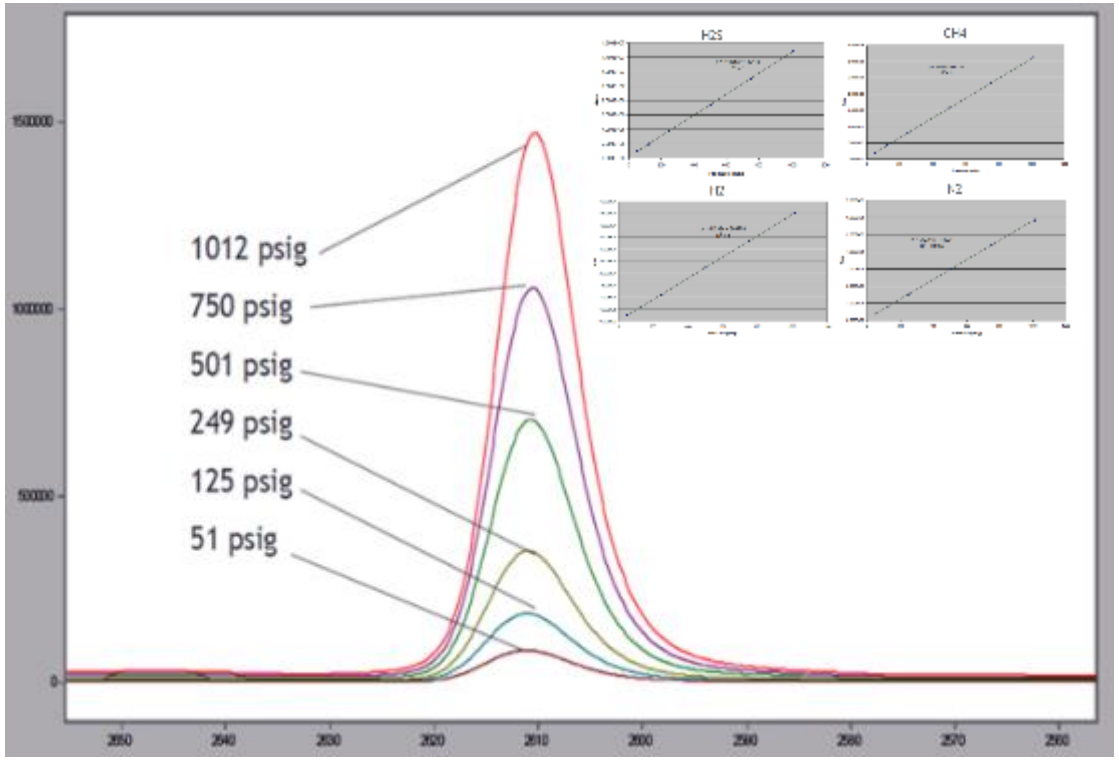
# Raman Spectroscopy – Rules of Thumb

# Why does Fiber Length Matter?

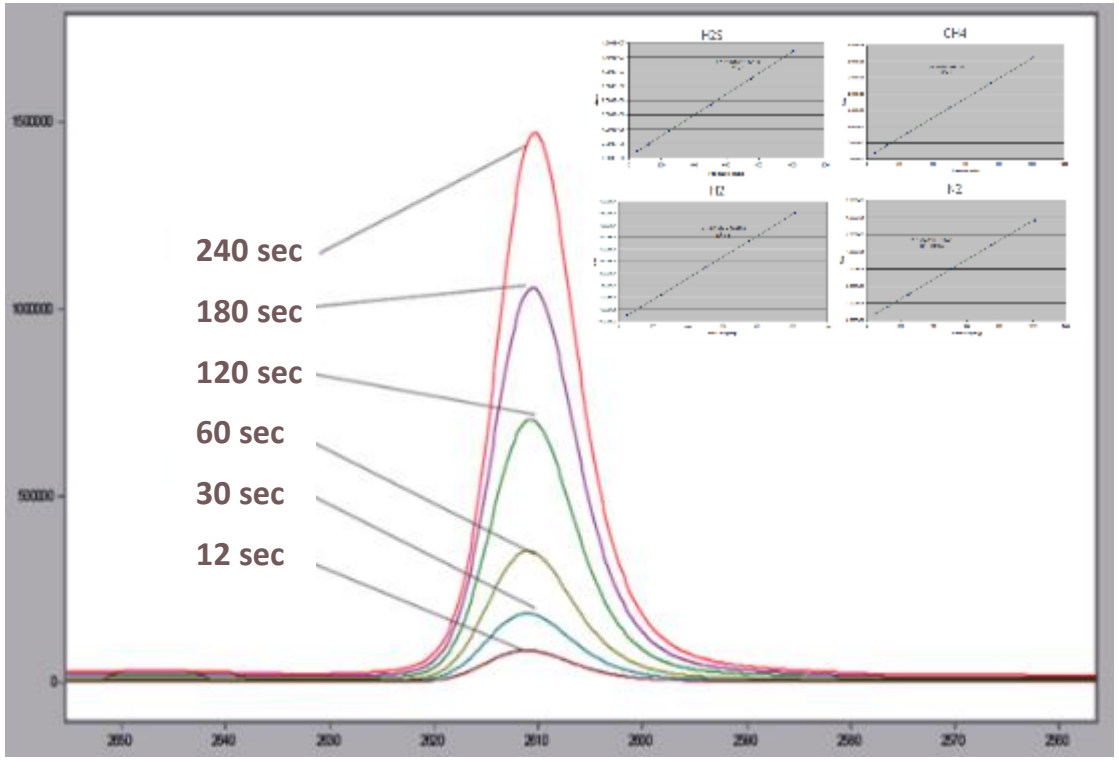

- Light is attenuated as it travels along the optical fiber
- This is non-linear in % transmission
- The attenuation is different for different colors, due to fiber optic material properties
- This means the fiber length affects different chemicals in the gas mixture to different extents
- This effect must be corrected for to ensure accurate composition
- Increased signal loss for a fiber length from 15 m to 100 m is around 50% ‘round trip’

# Why does Sample Pressure Matter?




- Increased pressure increases the density of the gas
- Increased density means more molecules generate Raman signal
- Some peaks may exhibit minor pressure broadening with large pressure differences
- In general, doubling the pressure doubles the Raman signal.
- As a general rule of thumb, increasing the pressure by 4X will improve the Repeatability by 2X.

# Why does Sample Update Time Matter?



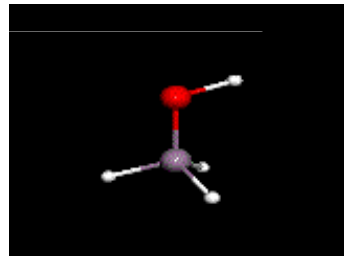

- Sample time has the same effect on signal as pressure
- Increasing the sample time does not, however, generate pressure broadening of peaks
- In general, doubling the sampling time doubles the Raman signal.
- As a general rule of thumb, increasing the sampling time by 4X will improve the Repeatability by 2X.

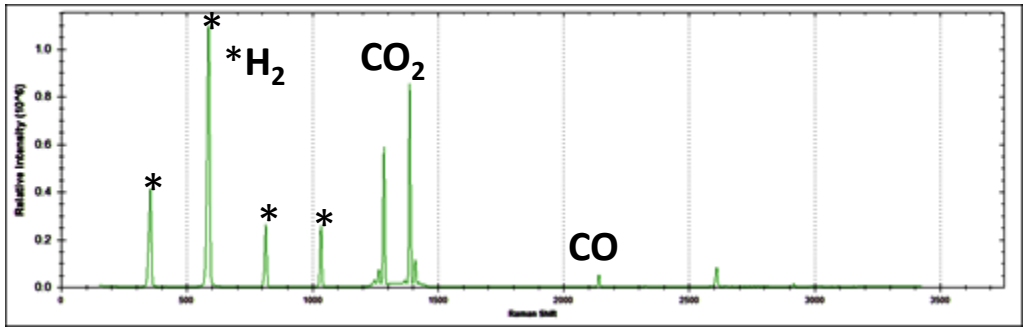
# Does and Don’ts of Raman Technology - Summary

- Detecting of Molecules Yes
- Metals No
- Ions No

- Detection of Gas Yes
- Liquids Yes
- Solids Yes
- Cristal structures Yes

- Concentration measurement Yes
- Fingerprint / Composition detection Yes





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# Questions