# Raman Applications in Polymer Industry

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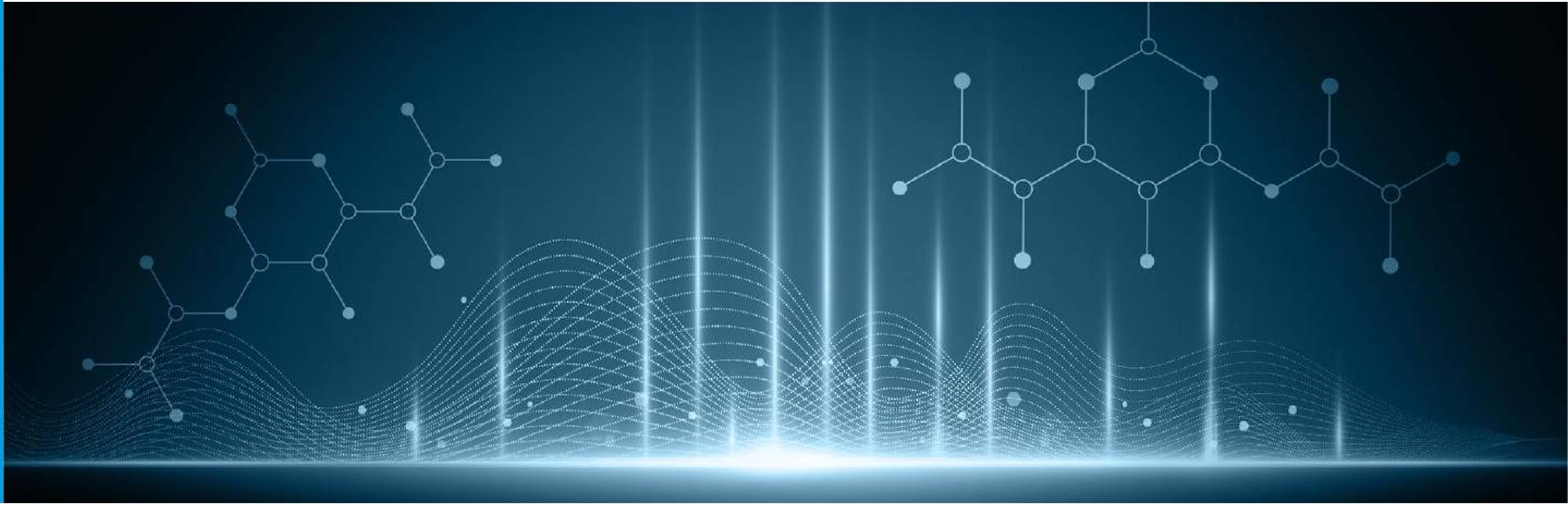
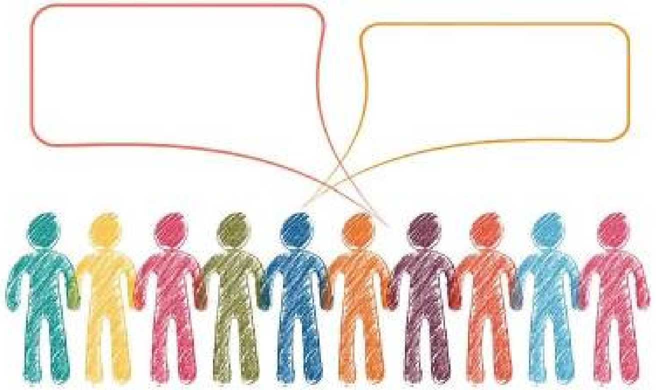


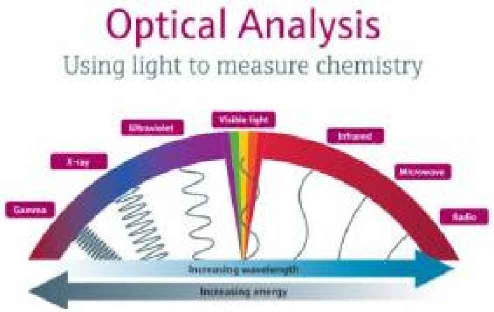
# Agenda

- Who is Endress + Hauser & Optical Analysis?
- Where is Inline Raman used?
- How does it work?
- What do we offer?
- Examples of  Raman applications

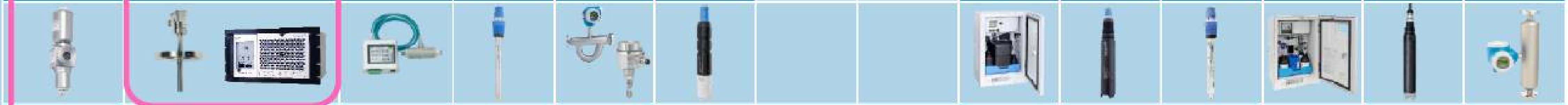
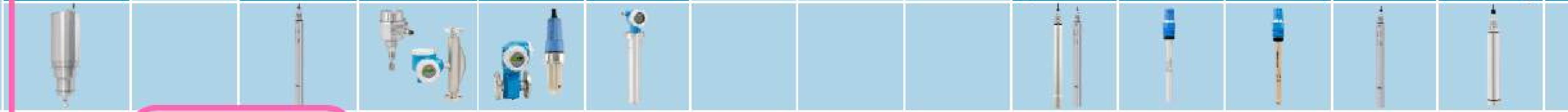


# Who Is Endress+Hauser Optical Analysis ?

- **Kaiser Optical Systems Inc.** and **spectra sensors** joined the Endress + Hauser Family in 2014
- Since 1990s, Kaiser has been a major supplier to the Raman community
- Founded in 1979, developing state-of-the art **holographic technology**
- Global production centre based in Ann Arbor, MI, USA for spectroscopic products
- Optical Analysis support groups in Europe and Asia Pacific
- We are Global - having offices or representation in Americas, Europe, and Asia
- A team of Raman and Process Automation experts!

# Analysis - Window into process

| | Color | Composition | Concentration direct | Concentration calculated | Conductivity | Density | Disinfection[1] | Impurity[2] | Moisture $H_2O$ | Metal[3] Nutrient[4] | Oxygen (Dissolved) | pH ORP | Sum[5] parameter | Turbidity | Viscosity |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Gases | | Raman | | Ultrasonic | | MEMS | | TDLAS | TDLAS | | Quench Fluorescen. | | | | |
|  | | | | | | | | | | | | | | | |
| Liquids | Photometer | Raman | | Ultrasonic | Conductive | Resonance | Amperomet. | | | Colorimetric | Amperomet. | Glass | Colorimetric | Absorption | Torque |
|  | | | | | | | | | | | | | | | |
| Liquids | Spectrometer | | Spectrometer | Resonance | Inductive | Radiometric | | | | Photo/ Spectrometer | Quench Fluorescen. | ISFET | Spectro-meter | Back-Scattering | |
|  | | | | | | | | | | | | | | | |
| Solids | | Raman | | | | Radiometric | | | TDR | | | | | | |
|  | | | | | | | | | | | | | | | |

[1] Chlorine (free, total) ▪ Chlorine dioxide ▪ Bromine ▪ Ozone [2] $NH_3$-$CO_2$ ▪ $C_2H_2$-$H_2S$ [3] Chromate ▪ Iron ▪ Aluminum ▪ Hardness ▪ Silica ▪ Sodium [4] Ammonium ▪ Nitrate ▪ Nitrite ▪ Phosphate ▪ Total P ▪ Total N [5] TOC ▪ SAC ▪ COD

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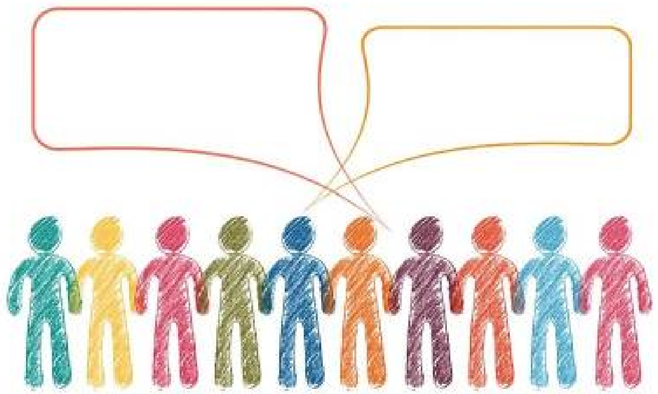

# Raman Applications

Life Sciences

Chemicals

Food& Beverage


Oil & Gas

# Raman in the Chemical Industry

### Polymer precursors and derivatives

- Acetylene ($C_2H_2$) in acetylene converter
- Feed streams and moisture on cracker
- Low-density polyethylene (LDPL)
- Linear low-density polyethylene (LLDPE)
- High-density polyethylene (HDPE)
- Polypropylene (PP)
- Polyvinyl chloride (PVC)
- Polystyrene (PS)

### Hydrocarbon analysis

- Benzene, toluene, xylenes, ethylbenzene
- Cyclohexane
- Butadiene
- $C_4$ hydrocarbons
- Cumene
- Styrene
- Acrylonitrile

Polymers

Specialty chemicals and catalysts

Solvents, paints, & coatings

Inorganics & diatomic molecules

Agrochemicals & hazardous materials

Synthetic Rubber

# Raman Applications in Oil & Gas

- Hydrocarbon processing
- Hydrogen production/purity
- HyCO production
- Methanol production
- Ammonia production
- Hydrogen recycle
- Gas turbine fuel feed
- Synthetic natural gas/ IGCC power plants
- LNG
  - Baseload custody transfer
  - Rundown to storage tanks
  - Mixed refrigerant optimization
  - Bunkering
  - Truck loading
  - Wobbe Index, Calorific Value, composition

- PIONA
- CDU rundown
- Isomerization unit
- Catalytic reforming
- Catalytic cracking
- Hydrotreating
- Sulfur recovery unit
- Naphtha cracking
- Final product blending

# Raman applications in Life Sciences

## Bio-Pharmaceutical (Large Molecules)

- Bioprocess monitoring and control
- PAT/QbD applications
- Cell culture
- Fermentation
- Downstream operations
- cGLP/cGMP

## Chem-API (Small Molecules)

- Reaction chemistry
- Yield crystallization
- Polymorph
- Blending
- Drying and other drug product unit operations
- Granulations, tablets, and capsules

…and more!

# Raman applications in F&B

## Edible oils (lab, process)

- Edible oil manufacturing
- Oils or fats in food and beverages

## Plant-based proteins (lab, process)

- Fermentation monitoring
- Protein R&D

## Dairy (lab, process)

- Dairy solids processing
- Macro + micronutrients

## Alternative proteins (lab, process)

- Cell-based meats
- Fungi, algae, or air-based proteins

## Alcohol / Spirits

- Fermentation






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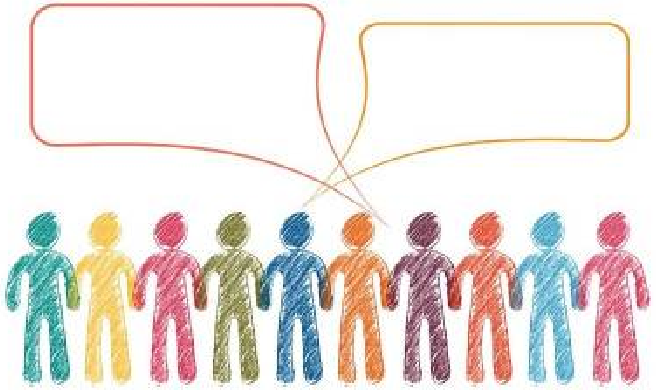
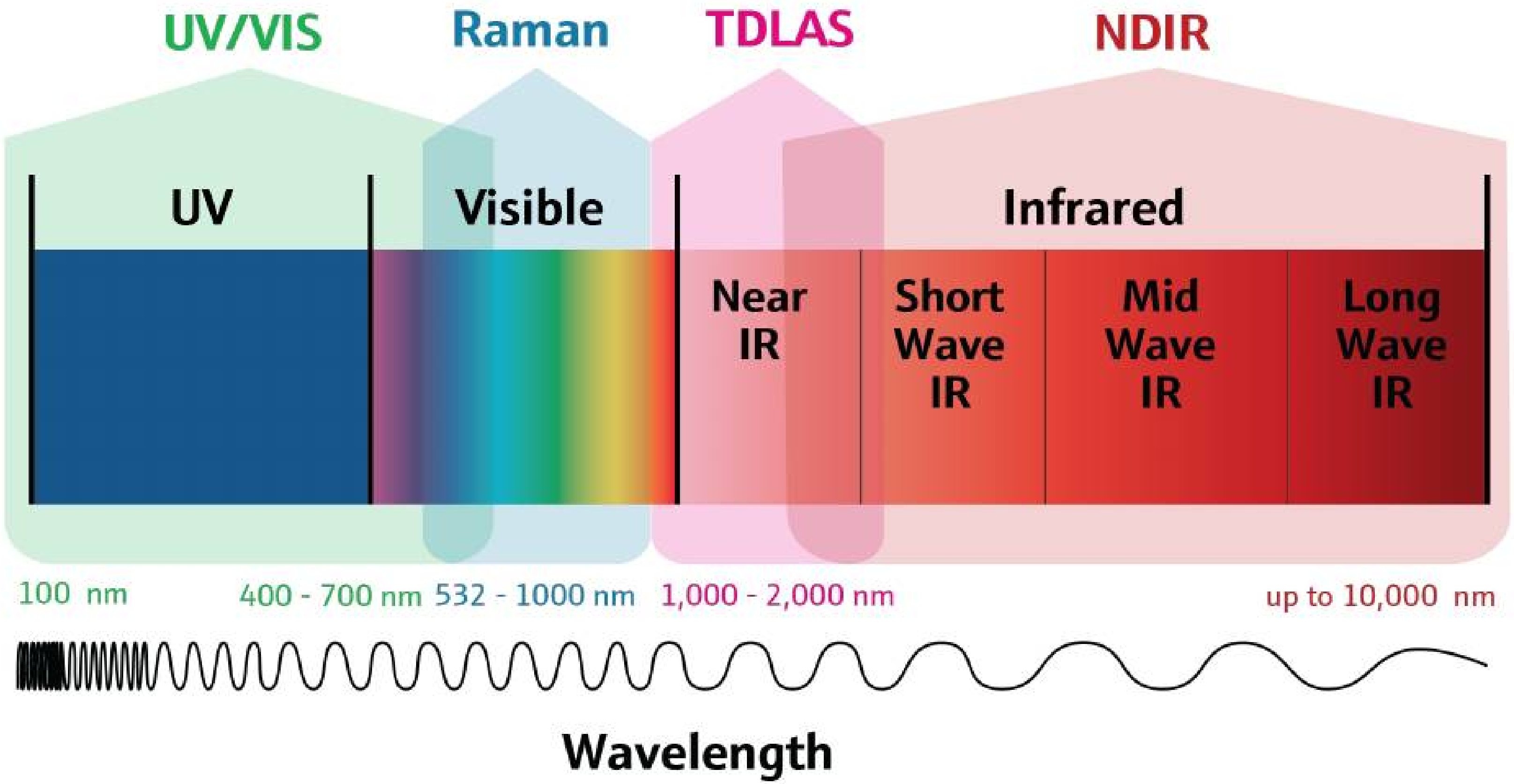


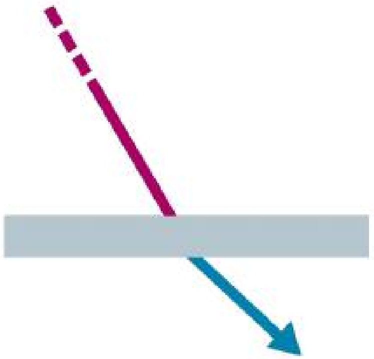
# Analysis methods using different light wavelengths




Raman spectroscopy can use UV or visible or near-infrared light to measure chemistry in solids, liquids, or gases.

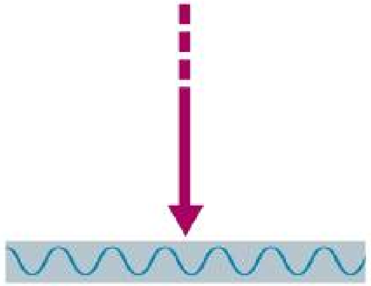
# What happens when light interacts with matter?

**Refraction**



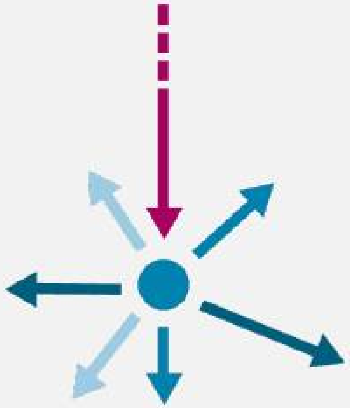
Refractive Index (RI)

**Absorption**



UV/VIS, NIR, TDLAS

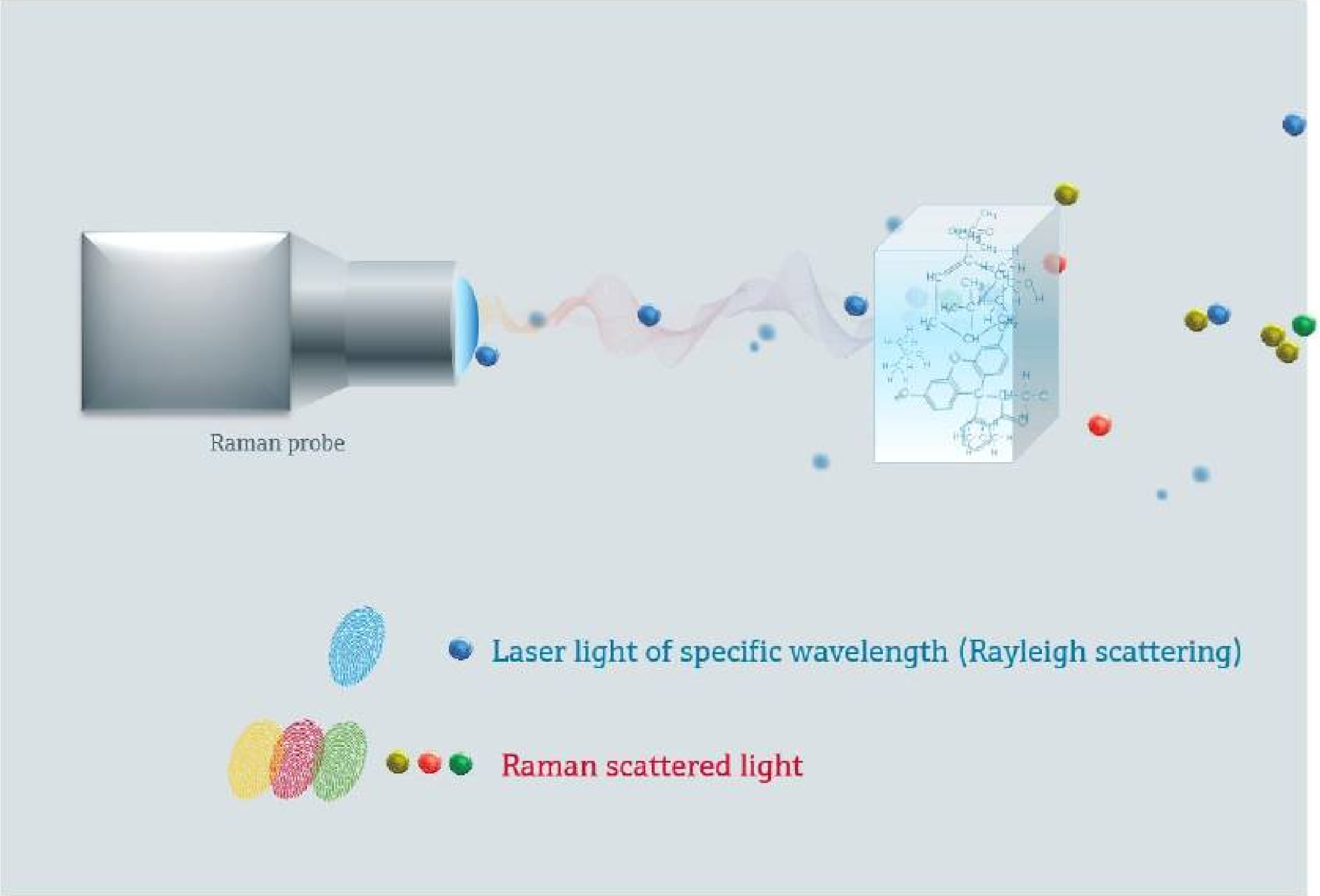
**Scattering**



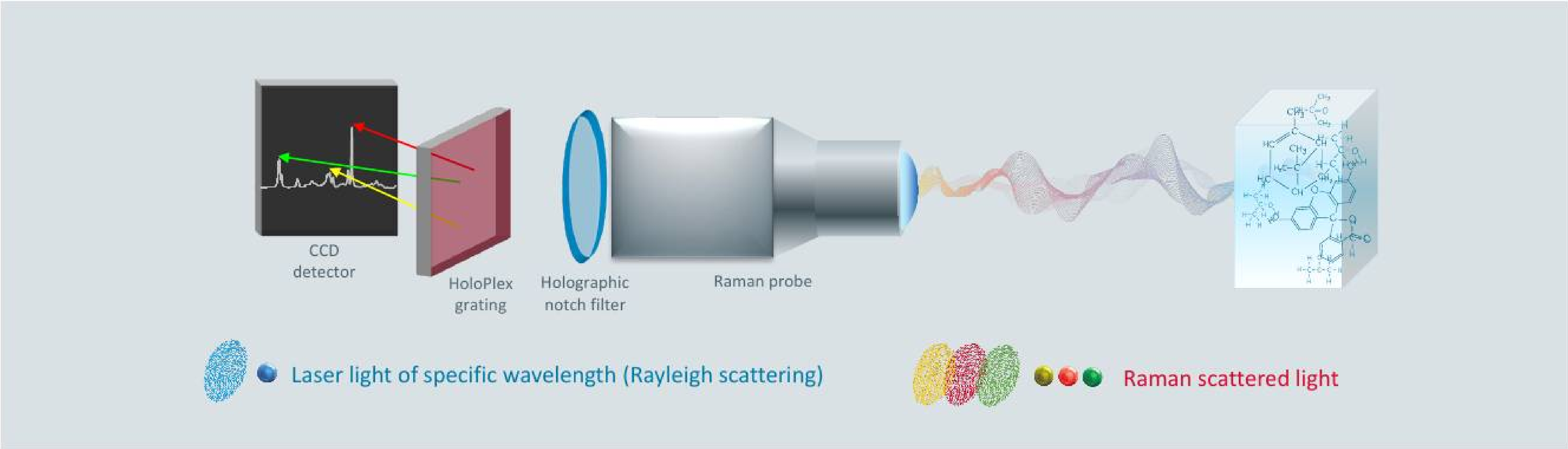
Raman spectroscopy

# Principle of Raman

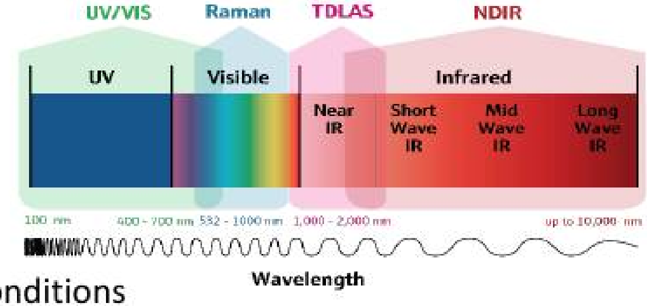
- Laser light **of specific wavelength** interacts with molecules which causes scattering
- **1 out of $10^8$** photons is frequency-shifted due to specific energy transfer (Raman shift)
- Result: **specific photons** allow **identification** and **quantification** of materials (solvent, products, substrate)



# Our Patented Raman analyzer Technology




- Laser light of specific wavelength interacts with molecules which causes **scattering**
- **1 out of $10^8$ photons** is frequency-shifted due to specific energy transfer (Raman shift)
- Result: specific photons allow **identification** and **quantification** of materials
- Patented designs with **over 40 years of experience**
- Specially designed Holographic Notch Filter, HoloPlex Grating for superior performance regardless of conditions
- Controlled Laser Modules ensure stable **consistent emission**



# Comparing NIR , FT-IR and Raman Spectroscopy

**NIR**

- Absorption
- Overtones
- No sample preparation
- Fiber optics OK
- Unresolved information
- Convenient Sampling
- C-H, N-H, O-H
- Water a problem
- No diatomic response

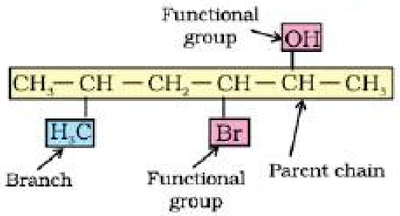
**FT-IR**

- Absorption
- Fundamental information
- Sample preparation
- Process measurements less flexible (no long fiber optics)
- High spectral density
- Organics
- Water a problem
- No diatomic response

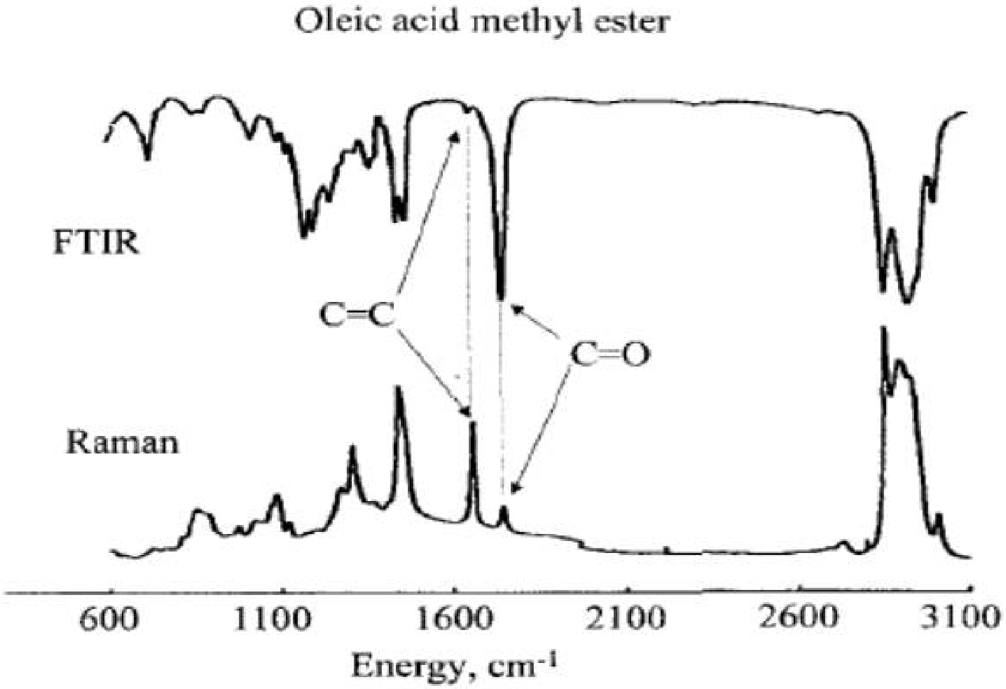
**Raman**

- Emission
- Fundamental information
- No sample preparation
- Fiber optics OK
- High spectral density
- Convenient sampling
- Organics and inorganics
- Water not an issue
- Strong diatomic response

**Color key:**
Green = positive aspects
Red = negative aspects



# Raman and mid-IR (FT-IR) spectra

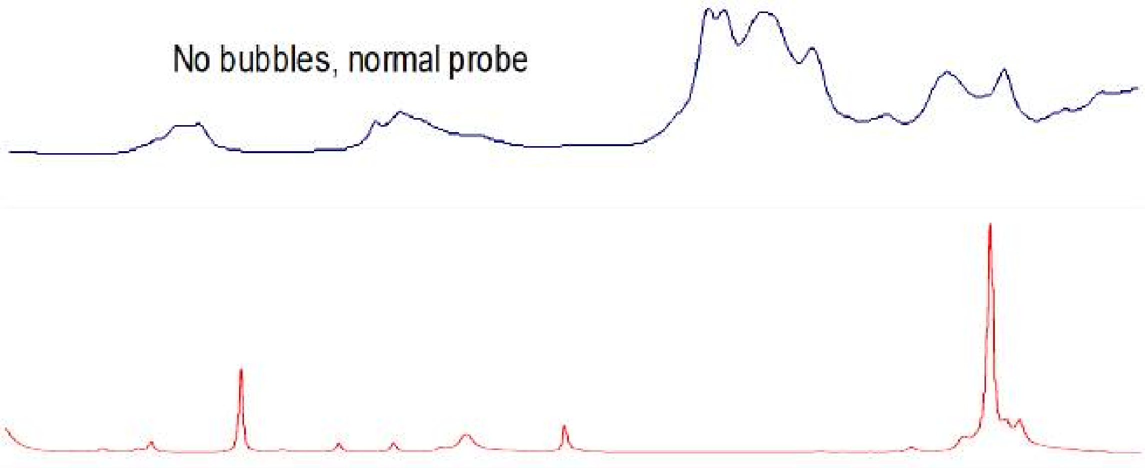



- Raman is complementary to mid-IR, general rule of thumb – bands strong in the mid-IR are weak in Raman, and if weak in mid-IR are strong in Raman
- Raman spectra tend to be much less affected by water and it is usually easier to implement/sample than mid-IR

# Raman and Near Infra Red (NIR) spectra

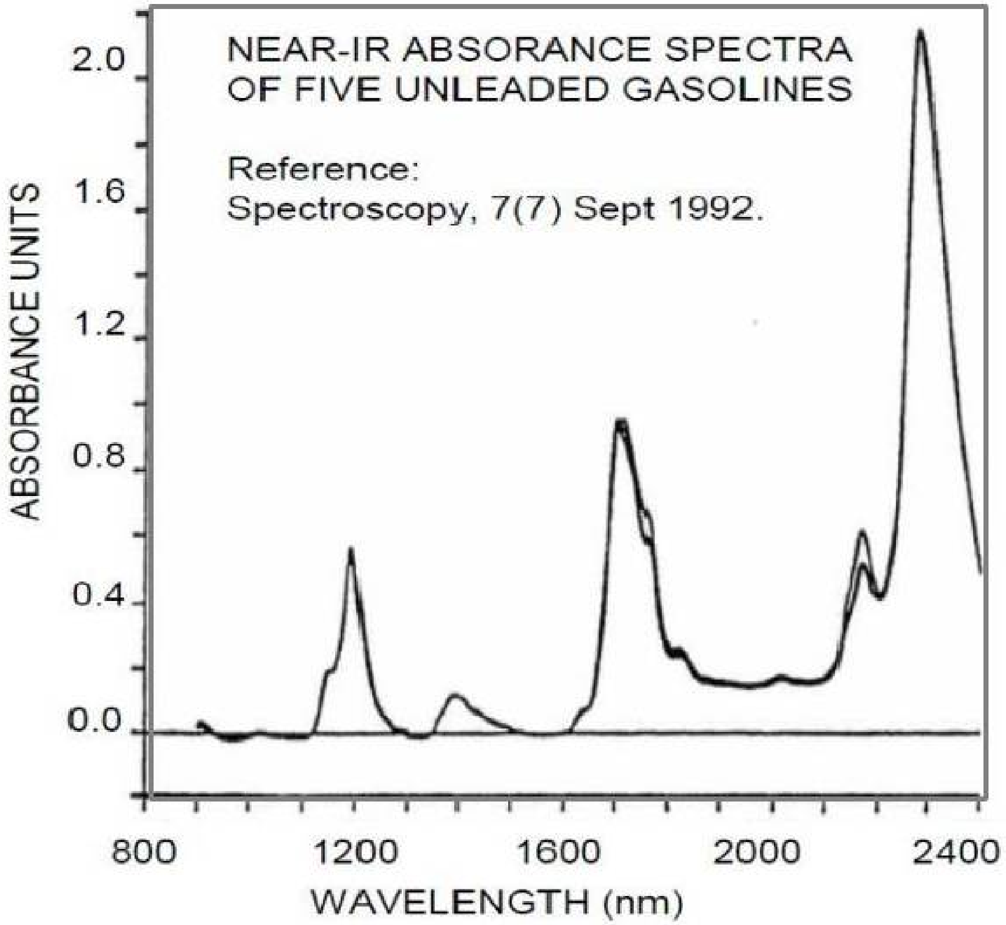
Acetone -- NIR

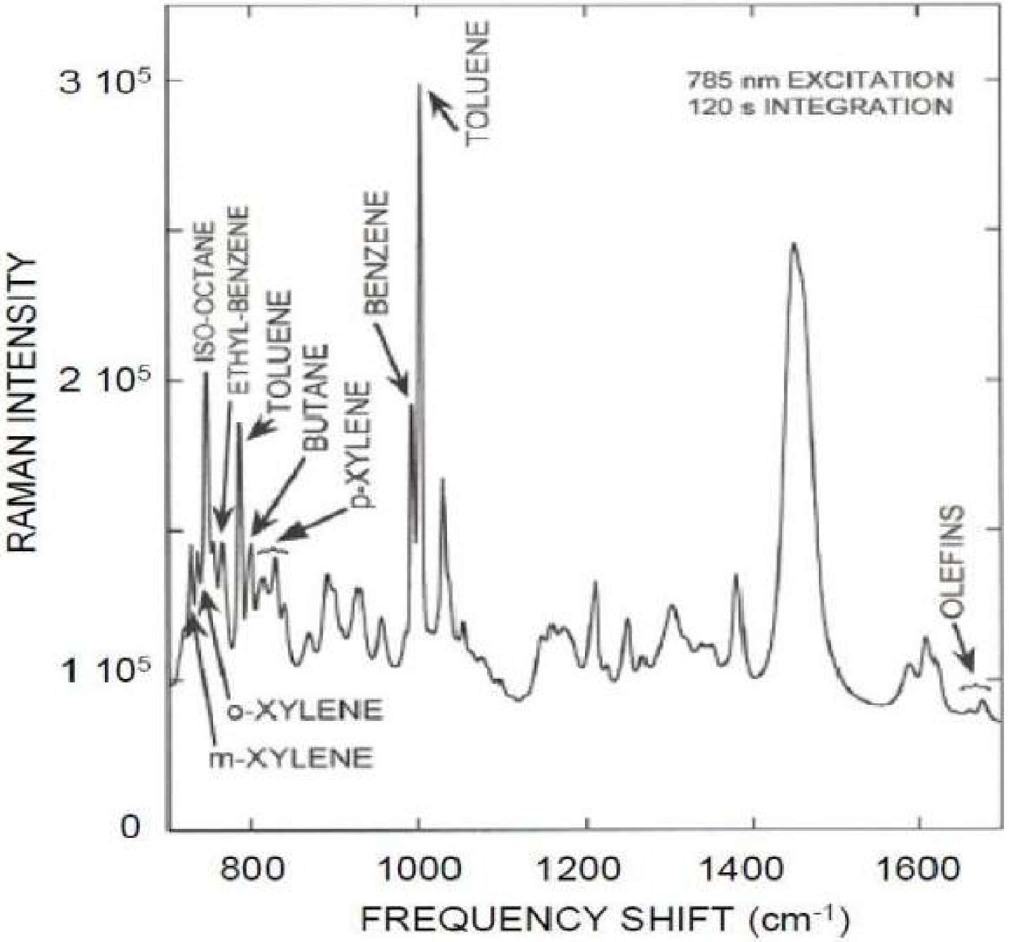
Acetone -- Raman




- Raman spectrum is much simpler than NIR
- Quantitation via simple peak area methods possible with Raman
- NIR quantitation usually needs chemometrics as spectrum consists of broad overlapping and redundant peaks

# Gasoline: NIR vs. Raman



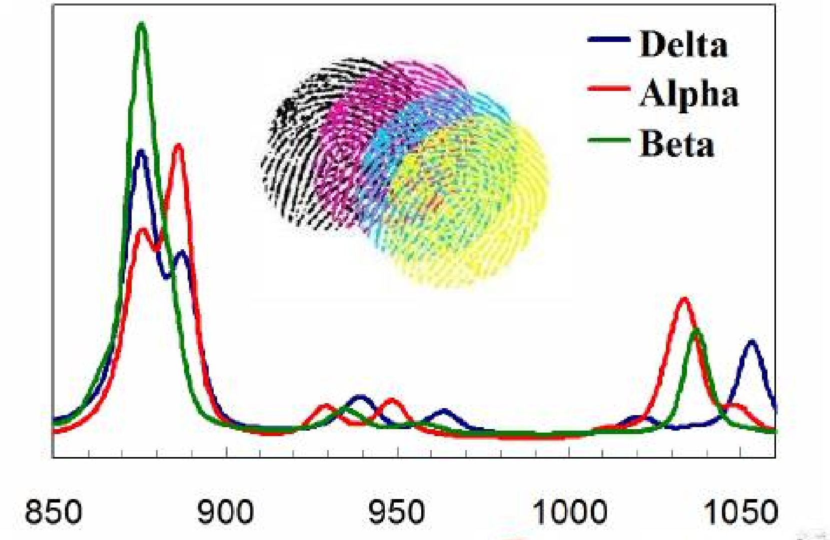



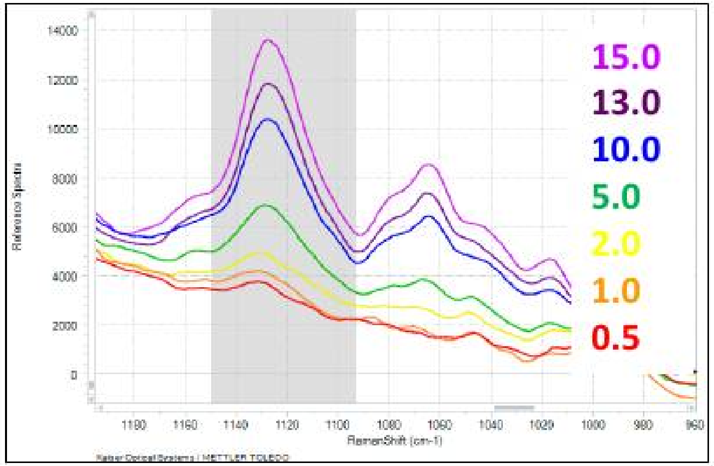
# Raman Spectra & Our Business

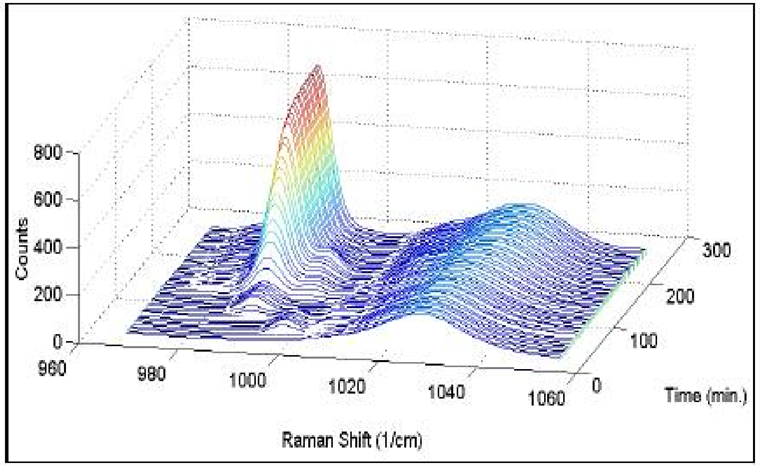
What?

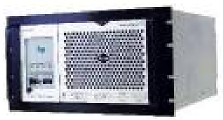
**How much?**

**Has it changed?**



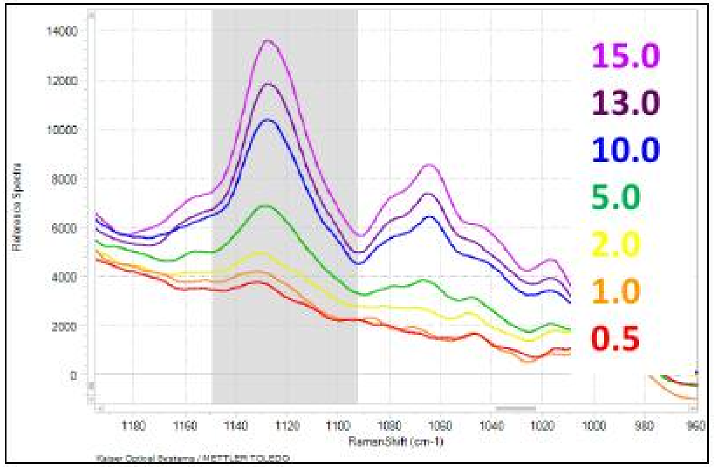



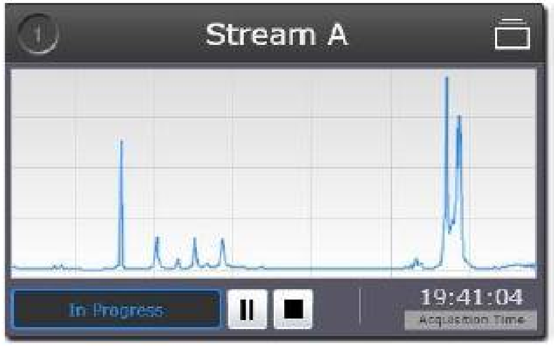



# Quantification

How much?

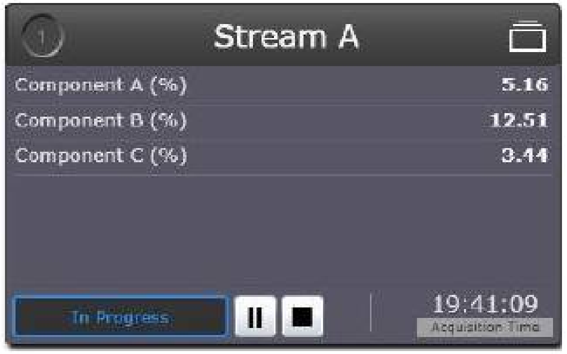



## 1. Inline Raman Spectra




Quantify

Calibrate

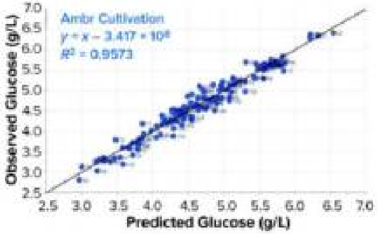


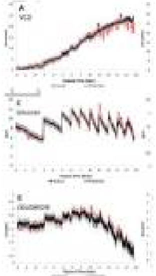

## 2. Current offline measurements:

HPLC, GC, Titration, Nova, XRD, SEM, more….

**To reduce or eliminate sampling with inline Raman implementation*

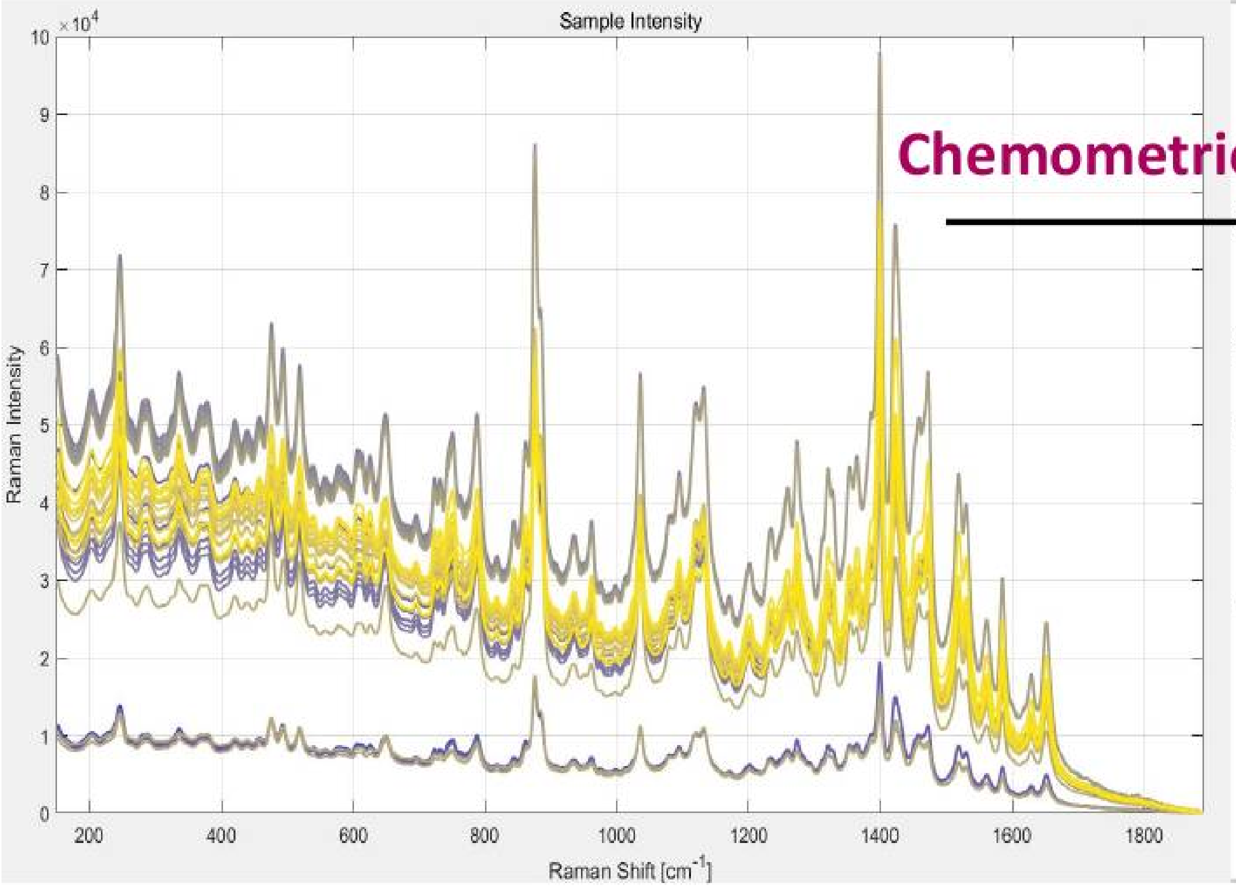
## 3. Modelling / Chemometrics



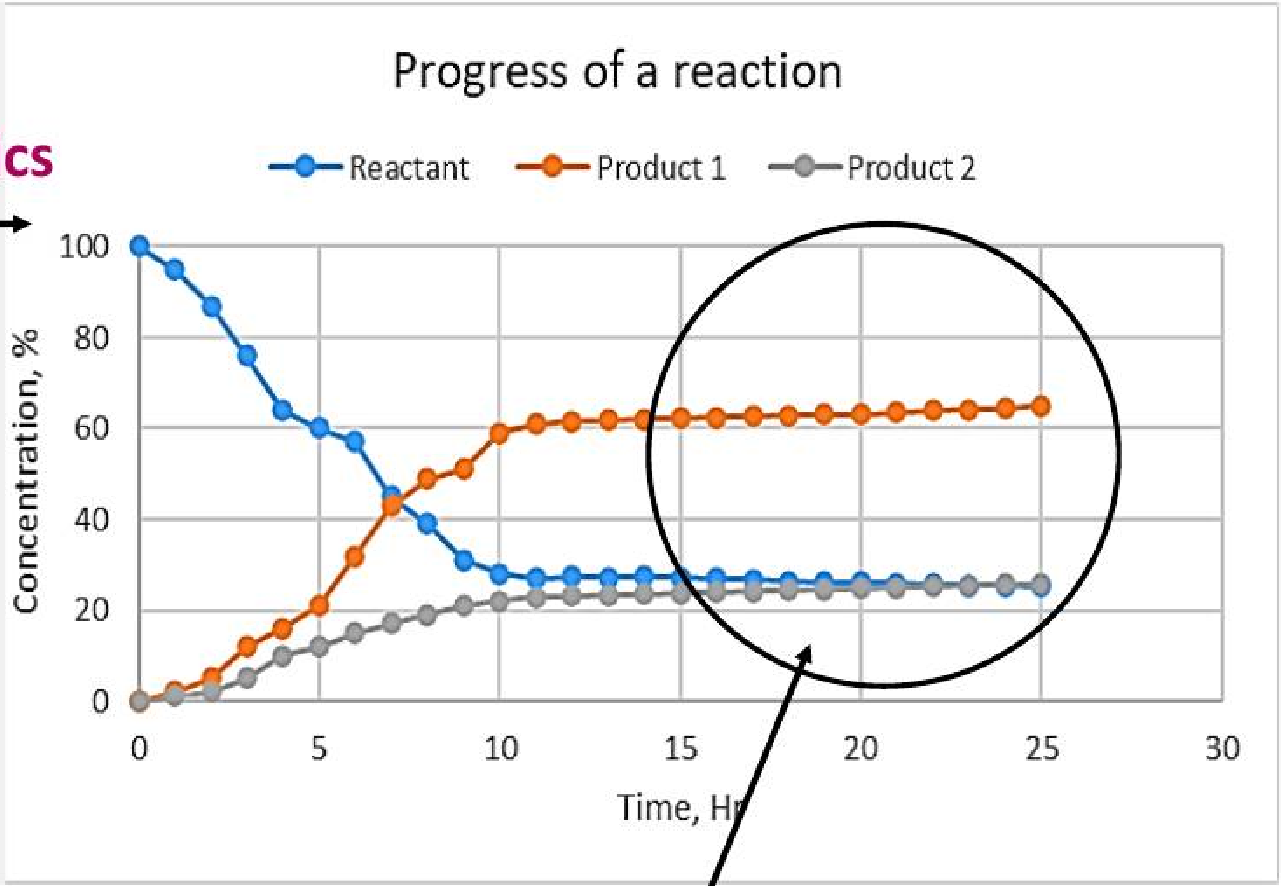
## Reaction Monitoring

**Has it changed?**




Chemometrics

**Real-time model predictions**




In the process, this stage is to be monitored

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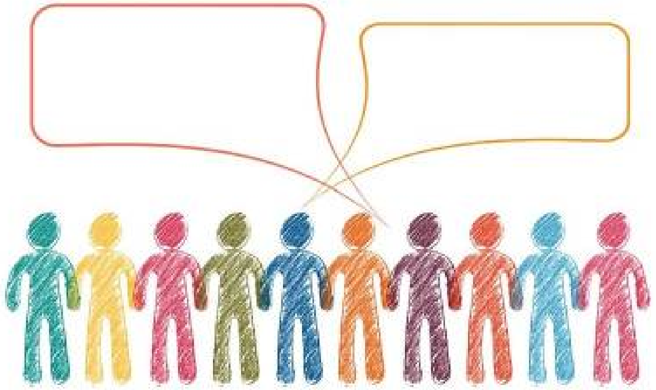
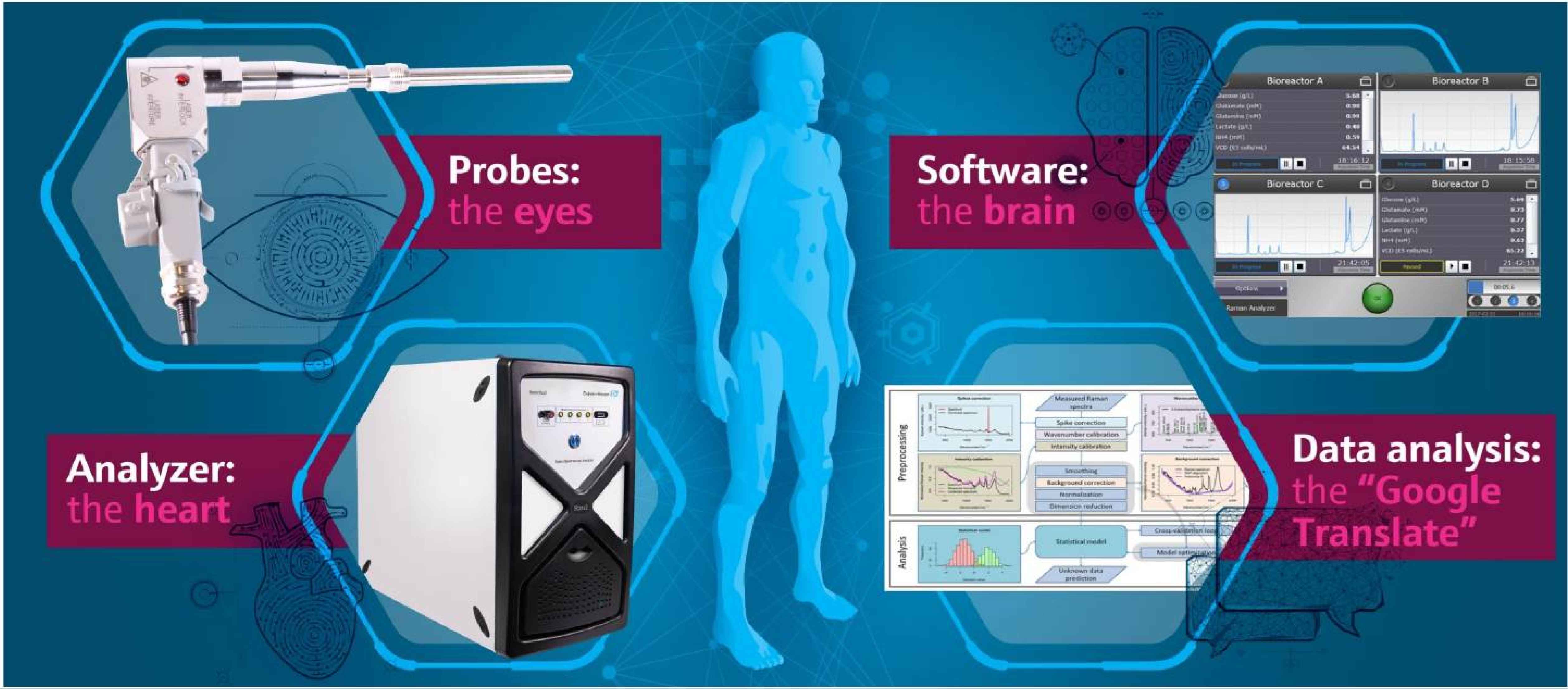


# Components of our Raman analyzer systems



# Raman analyzers-“*the heart*”

- ✓ *Solid, Liquid or Gas (532nm, 785nm, 1000nm)*
- ✓ *Benchtop, Mobile Cart, Cabinet rack mounted, etc*
- ✓ *1-channel, 4-channel*
- ✓ *General Purpose, Hazardous*
- ✓ *….*

## Raman Rxn2 analyzer

- Liquids, solids, or gases / lab to process analysis

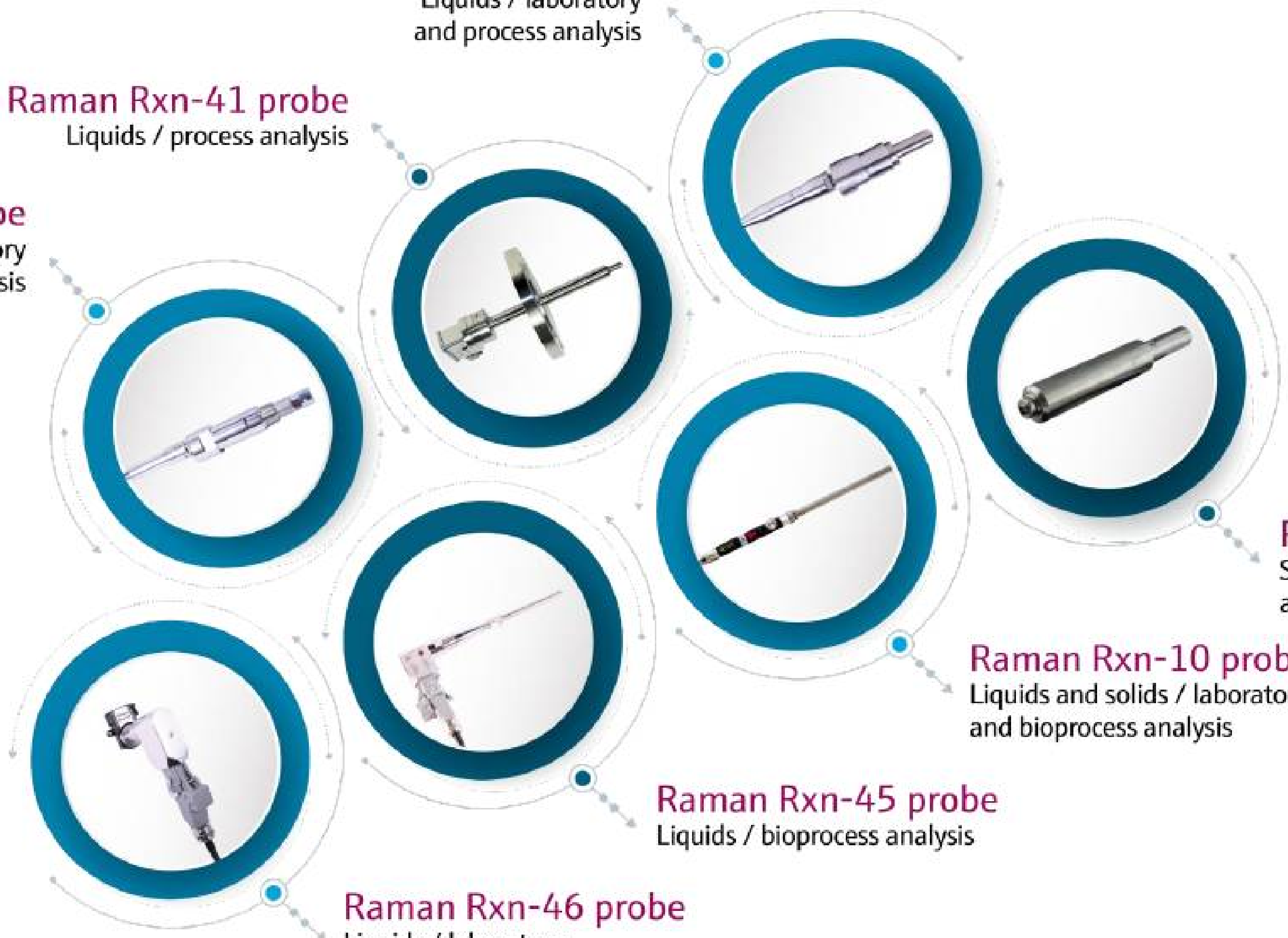
## Raman Rxn4 analyzer

- Liquids, solids, or gases / process analysis

## Raman Rxn5 analyzer

- Gas-phase / solutions-based / process analysis

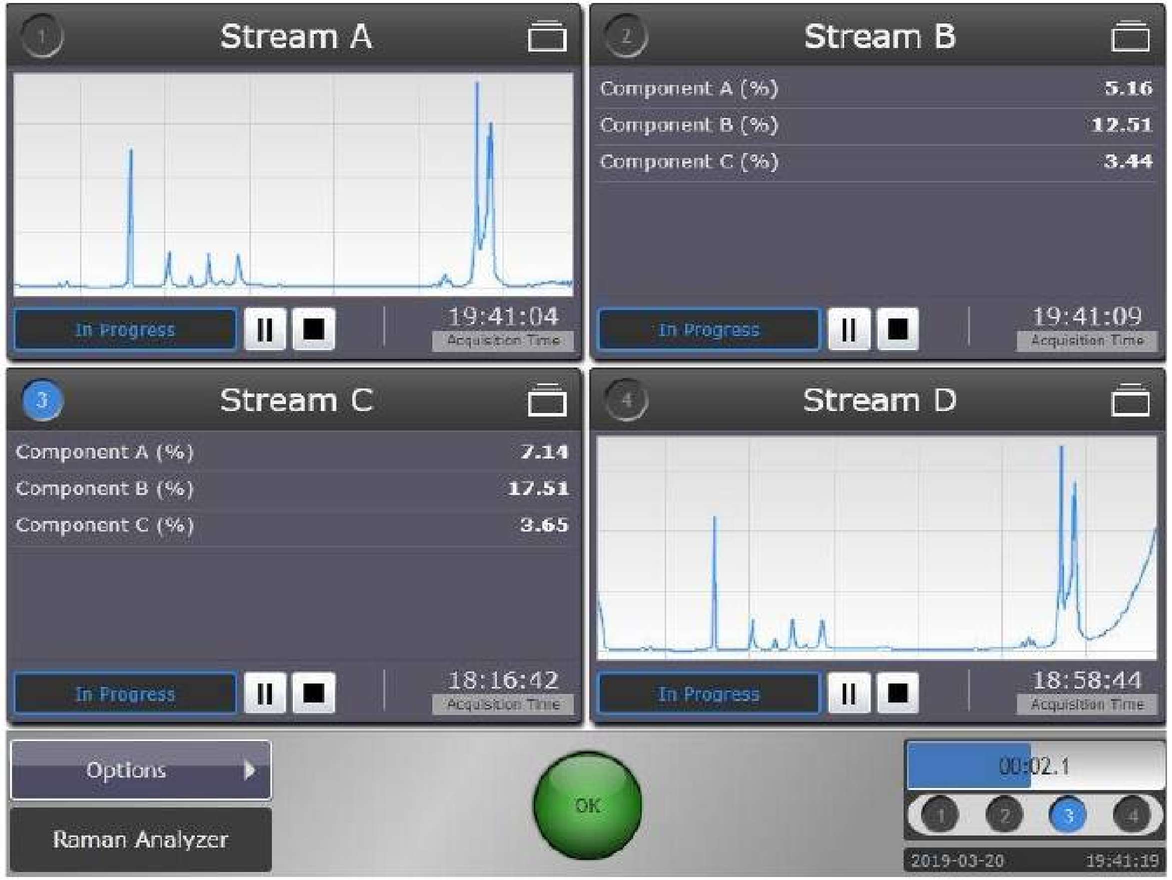
# Raman probes-*"the eyes"*




- ✓ *Temperature*
- ✓ *Pressure*
- ✓ *Material compatibility*
- ✓ *Contact, Non-contact*
- ✓ *Process Connection*
- ✓ *Length of probe*
- ✓ *Solid, Liquid, Gas state*
- ✓ ...

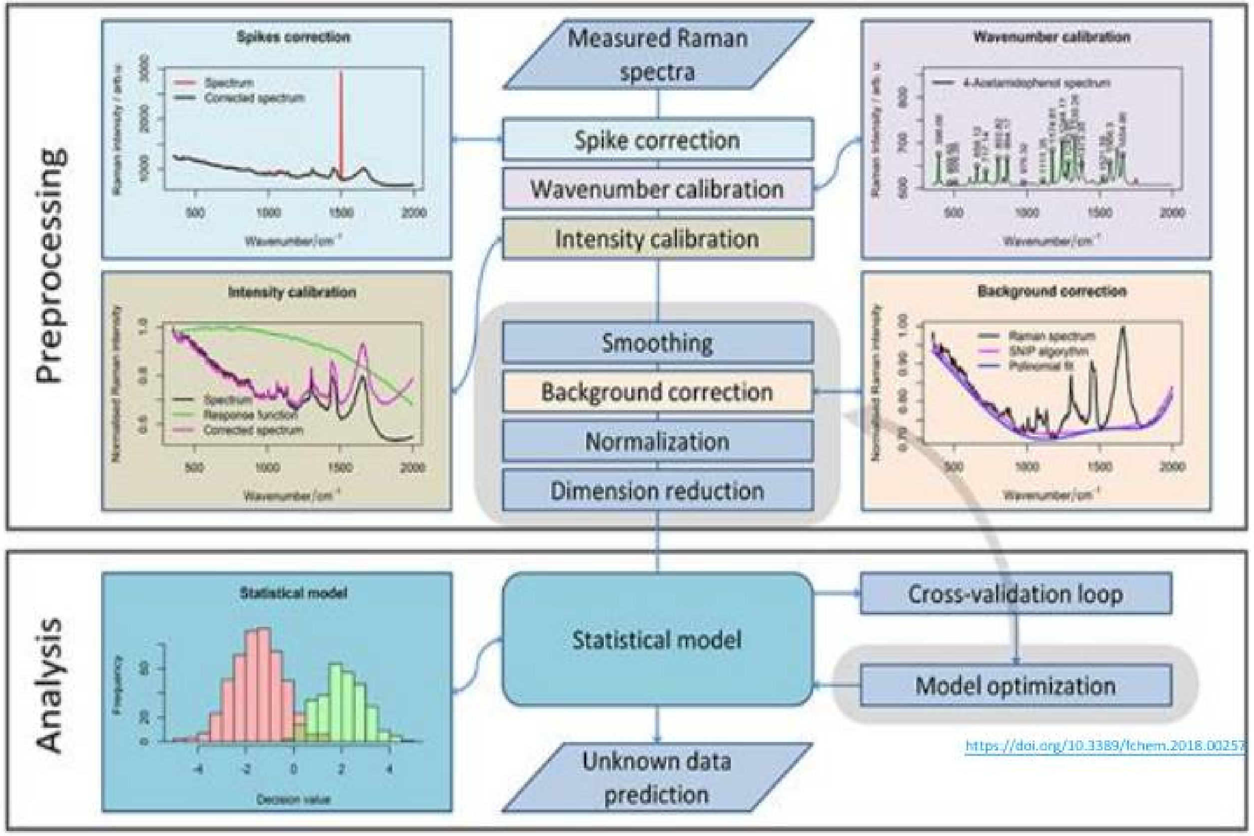
# Raman RunTime embedded software-*"the brain"*

- Embedded controller with easy-to-use touch screen or remote interface
- Streamlined calibration and verification
- Multiple collection modes: continuous, periodic, manual
- Embodies IIoT/Industry 4.0 strategy



# Data analysis-*"Google translate"*

- Real-time model predictions
- Multiple embedded univariate and multivariate (MVA) predictor options
  - SIMCA (Sartorius)
  - **PEAXACT (S-PACT)**
  - GRAMS IQ (ThermoFisher)
  - Solo predictor
  - Unscrambler engine
  - Built-in LNG method






Endress+Hauser

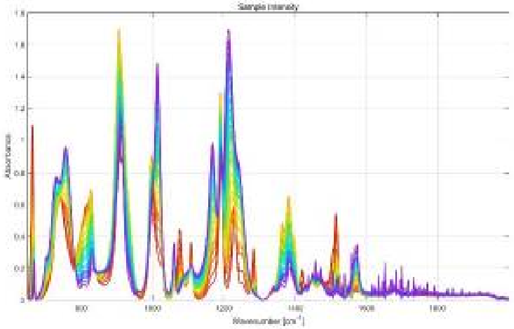
# Data Analysis and Automation-Illustration

**Analysis results serve as input for process monitoring and control**

**Chemistry, Biology, Physics, Medicine etc.**

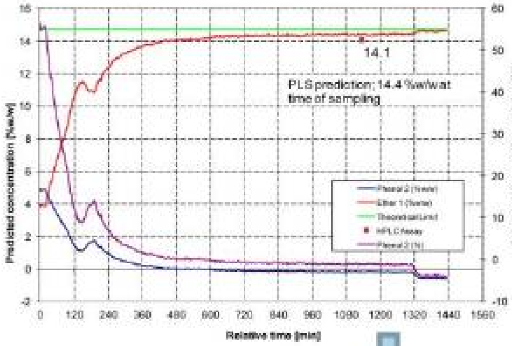
*Data Collection*

**Data**



*Prediction*

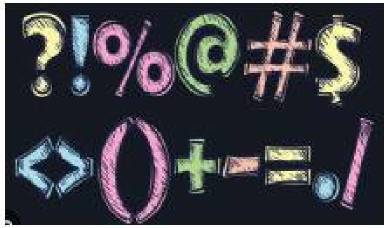
**Information, Trends Conclusion, Results**



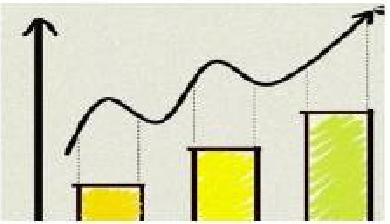

Measurement (Runtime)

*Correlation*
*Calibration*
*Validation*

**Mathematical Tools**



**Statistics**



**Computation**

UNIFIED ARCHITECTURE

Modbus TCP

Automation

Analysis (Software)

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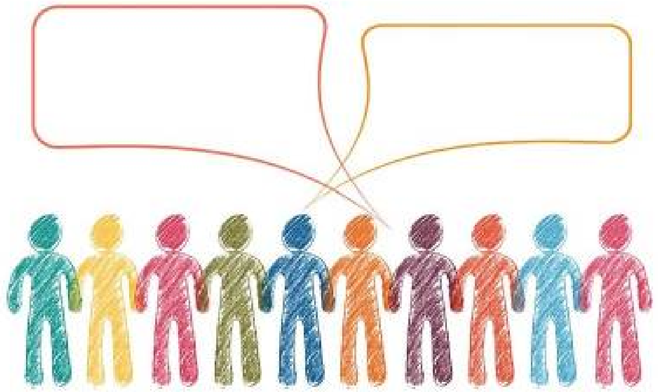
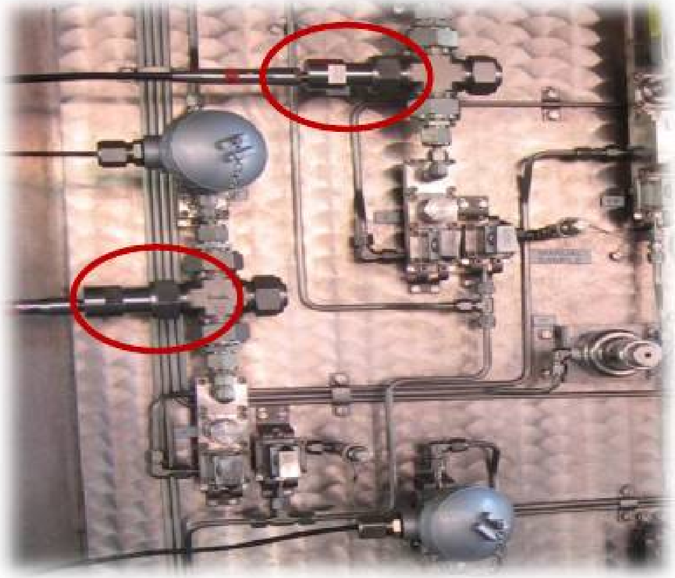
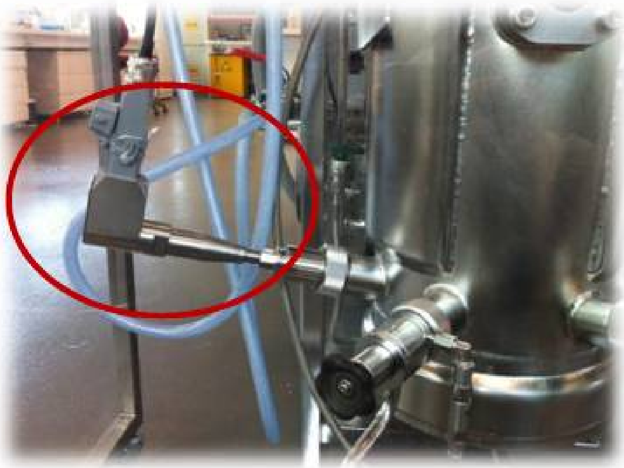


# Today: Raman is everywhere, especially process

# Raman Probe Installations



# Chemicals – Lab to Process Stages

**Our Value to You: Cross-Scale & Model Transferability**

**Process Development**

**cGMP Manufacturing**

# Value of Raman technology in the Chemical industry

## Why Raman spectroscopy vs other measurement technologies?

- The ability to measure the purity of feed streams, **monitor reaction progress**, **detect end-points of reactions**, and determine the **quality of the end products**
- **Reduced personnel risk exposure** in the field and improved plant/environmental safety
- Better **overall process performance**, **reduced giveaway**, and higher profitability
- Higher nameplate capacity and **accelerated product release**

## Why our Raman analyzer systems?

- Unparalleled in-line process measurement accuracy, precision and reliability
- 24/7 unattended monitoring
- Process customization capabilities
- Calibration transferability from laboratory to process systems
- Hazardous area certifications

# Chemical Industry – Major Players using our Raman

- **Arkema** – On-line Process Monitoring
- **Akzo Nobel** – On-line Process Monitoring
- **Chevron Philips Chemical** – Polyethylene Polymerization Advanced Dual Loop License
- **Huntsman** –Process Monitoring of Titanium Dioxide
- **Kuraray** –Polymer Process Monitoring and Optimization, Distillation Monitoring
- **Rhodia** – Process Monitoring, Reaction Safety, Crystallization

ARKEMA

AkzoNobel

Chevron Phillips CHEMICAL

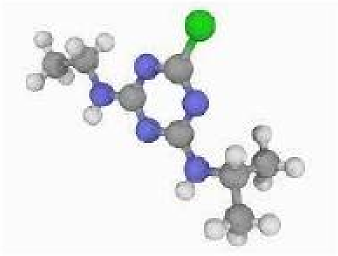
HUNTSMAN
Enriching lives through innovation

Rhodia
Member of the Solvay group

kuraray

# Chemical Industry – Major Players using our Raman

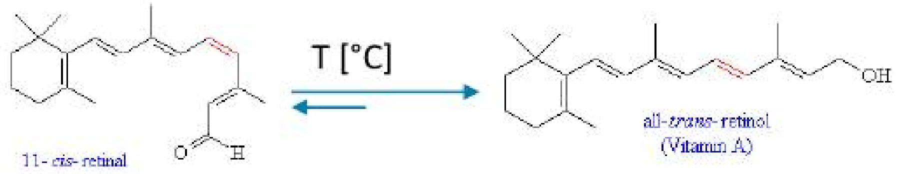
- **Evonik** – R&D and pilot – diverse organic reactions for process development & understanding
  - Plan: Worldwide role out of applications with technical and application support from Evonik Germany
- **BASF** –Polymerization, Process Monitoring and Optimization, PAT, ATEX (diverse organic reactions)
- **Bayer** – Process Monitoring and Optimization, PAT
- **Arlanxeo/Lanxess** – Production Polymer (Synthetic Rubber / Elastomers)

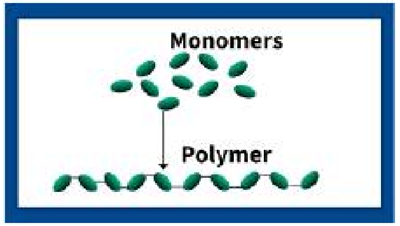


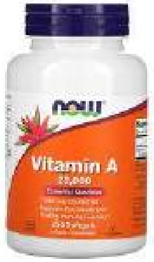


# Chemical Industry – Major Players using our Raman

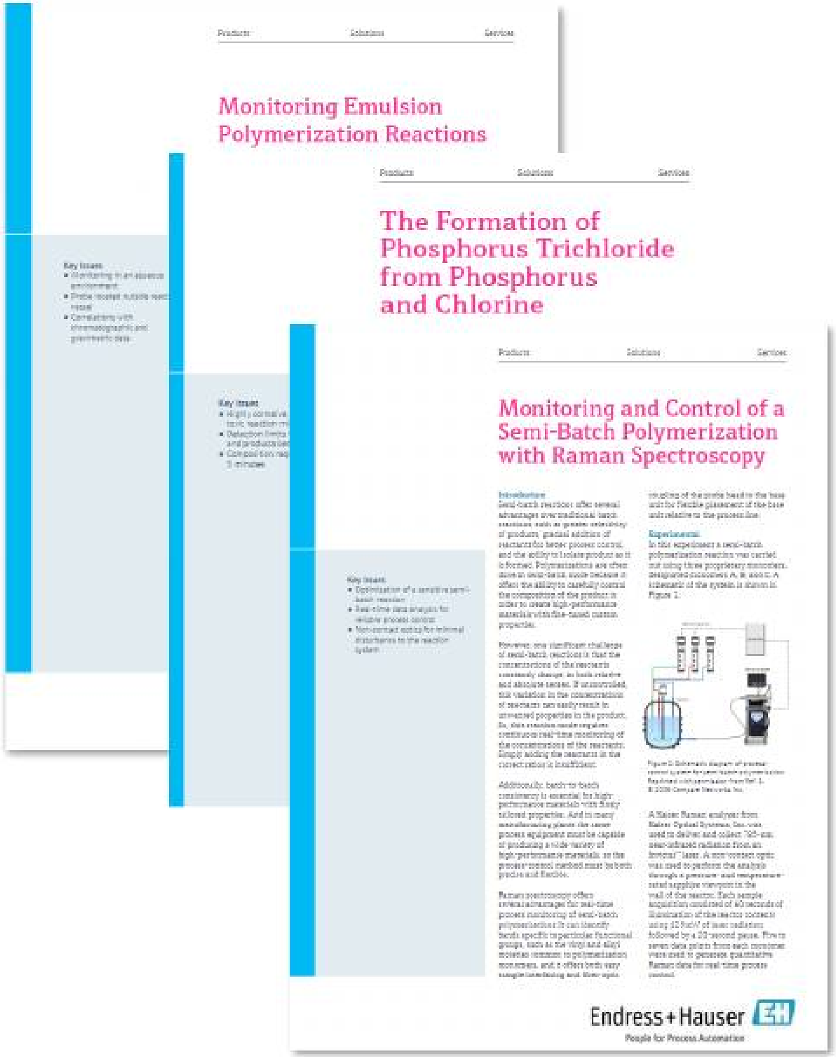
- **Trinseo** – Polymers (Synthetic Rubber / Elastomers)
- **DOW** –Process Monitoring and Polymer Process Optimization (Styrene and Synthetic Rubber)
- **DSM** –Vitamin production, Divers
  - Vit B2 production with C=C formation
  - Cis trans isomerization for Vit A (Retinol)
  - Decaffeination – $CH_2CL_2$ extraction




# Learn more – available application notes for the Chemical Industry




- The production of methyl chlorosilanes
- Monitoring the rutile/anatase ratio in $TiO_2$ production
- Monitoring $CaCO_3$ polymorph formation in the presence of polymeric additives
- Raman spectroscopy to support REACH registration of gases
- Tandem Raman and IR spectroscopies for monitoring of soil gases in $CO_2$ sequestration
- Rapid monitoring of antisolvent addition crystallization and dehydration
- Off-line and on-line Raman spectroscopy of API-containing extruded films
- Raman-based endpoint detection of a heterogeneous etherification reaction
- Monitoring emulsion polymerization reactions
- Microstructural analysis of polybutadienes
- In-line monitoring of ethylene vinyl acetate copolymer with Raman spectroscopy
- Investigation of surface-catalyzed NO decomposition

# Potential Polymer Applications

- **Composition during polymerization**
  - In the reactor
  - Feed streams and recycle streams
  - Purification
- **Composition of finished plastic**
  - Relative amounts of homo-polymers in co-polymers and blends
  - Additives
  - Unreacted monomer
- **Morphology before, during, and after processing (extrusion, film or fiber drawing)**
  - Crystallinity
  - Orientation

- **Properties correlated to molecular composition and structure**
- **Some other Notable Polymer Apps**
  - Control of Styrene and Food Grade Acetates
  - Monitoring of coatings on various pellets
  - Installed in biodegradable polymer Fermentations

# Crystallinity and density of PET

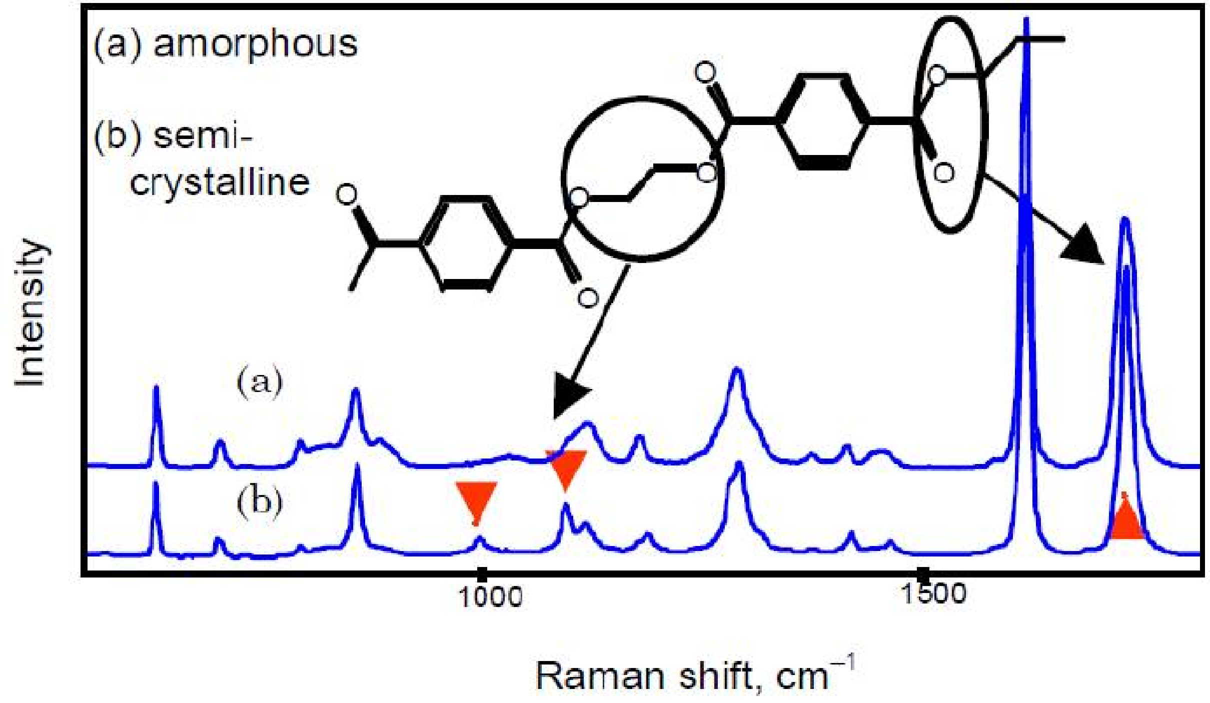
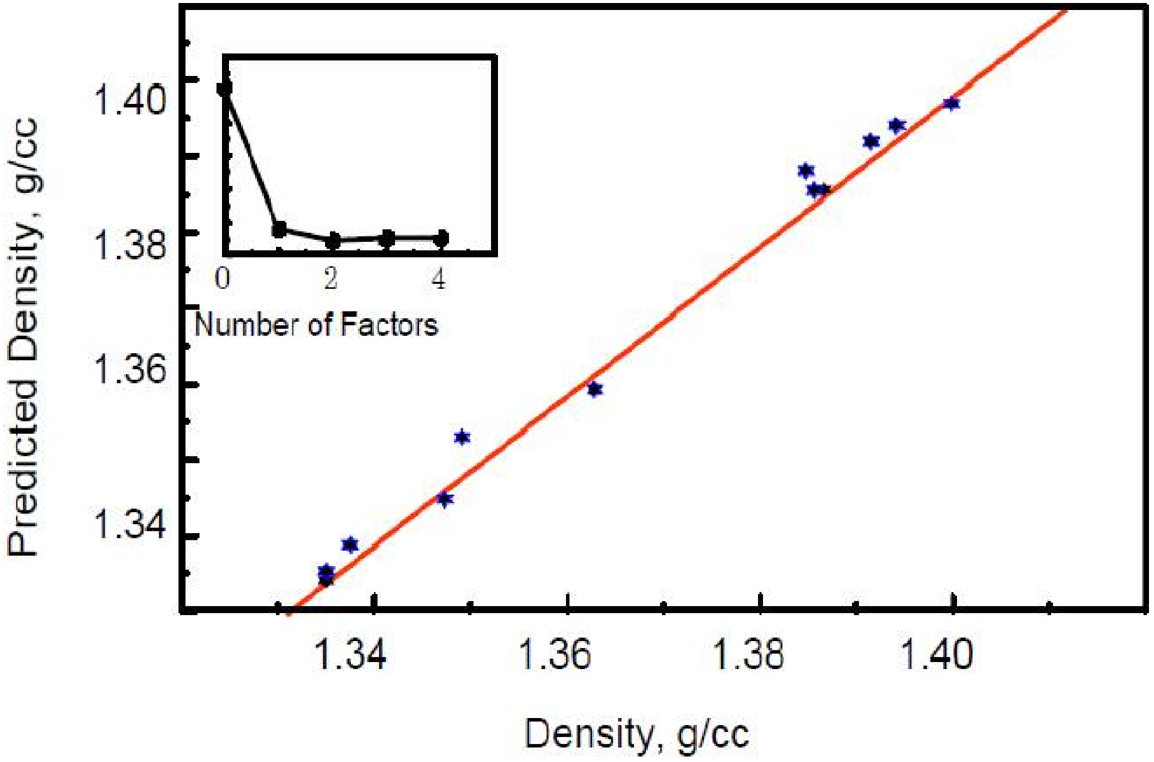
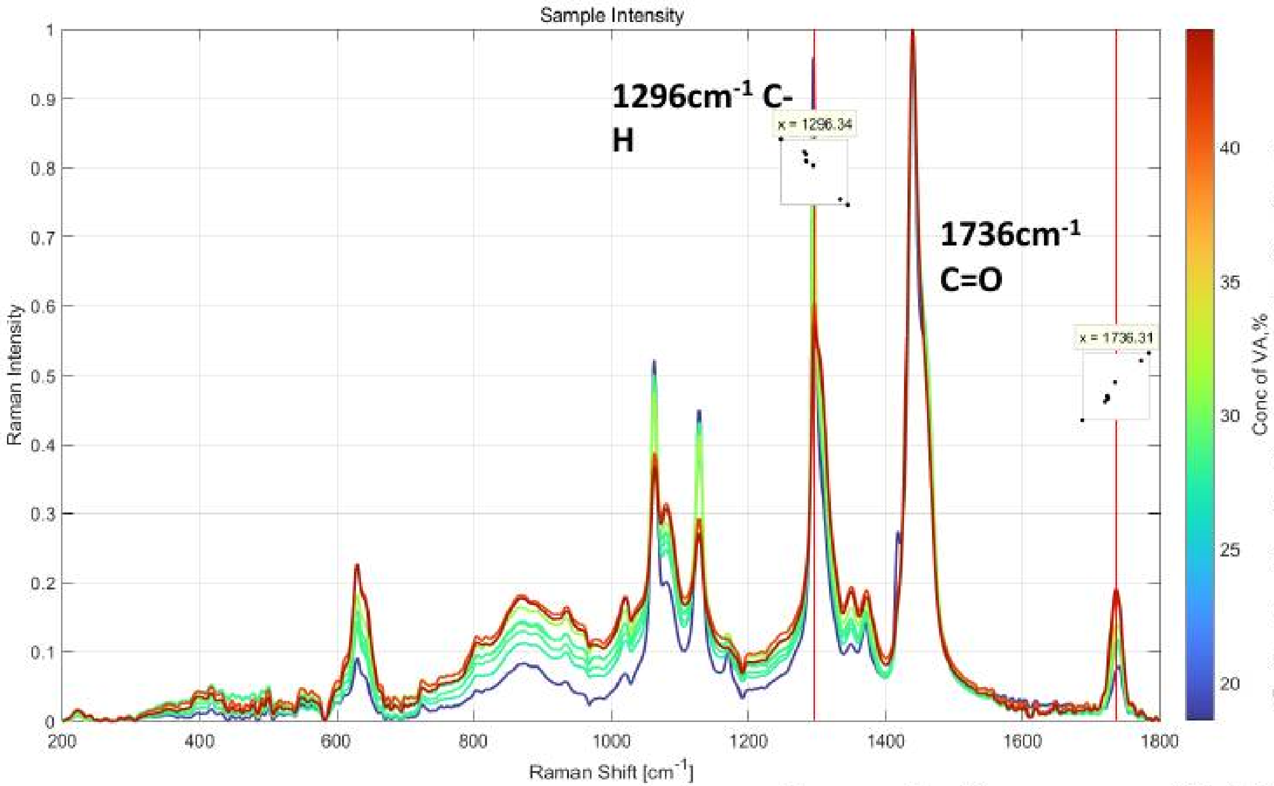


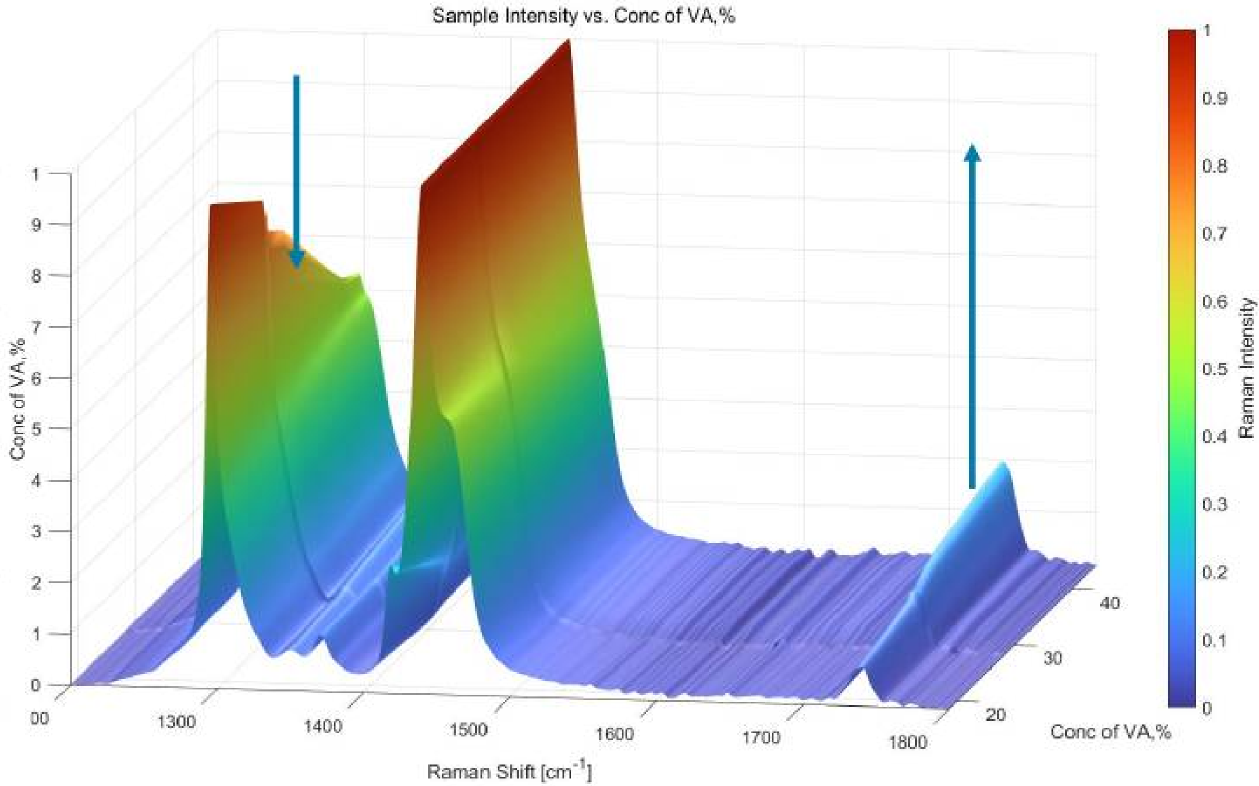

**Figure 1.** Raman spectra of (a) amorphous and (b) semi-crystalline PET films. The red arrows indicate those bands that are sensitive to conformation (1000 and 1096 $cm^{-1}$) and crystallinity (1730 $cm^{-1}$).




The average of these Raman-measured densities was 1.350 g $cm^{-3}$, which is in good agreement with the bulk density value of 1.349 g $cm^{-3}$ measured with a density gradient column.

# Data Prediction in vinyl acetate(VA) and polymer samples



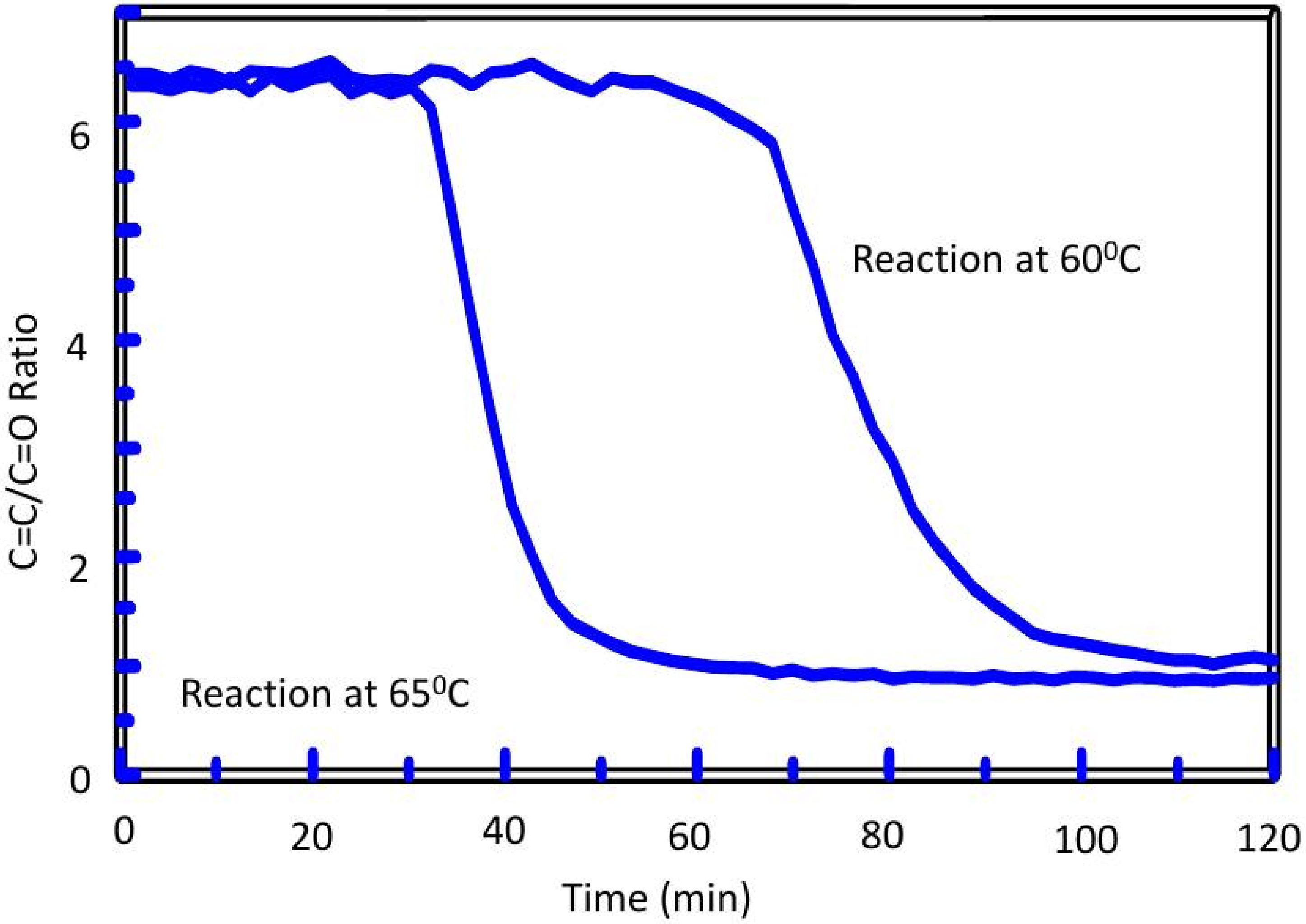




Concentration range= 18-44%

$R^2$ = 0.9944

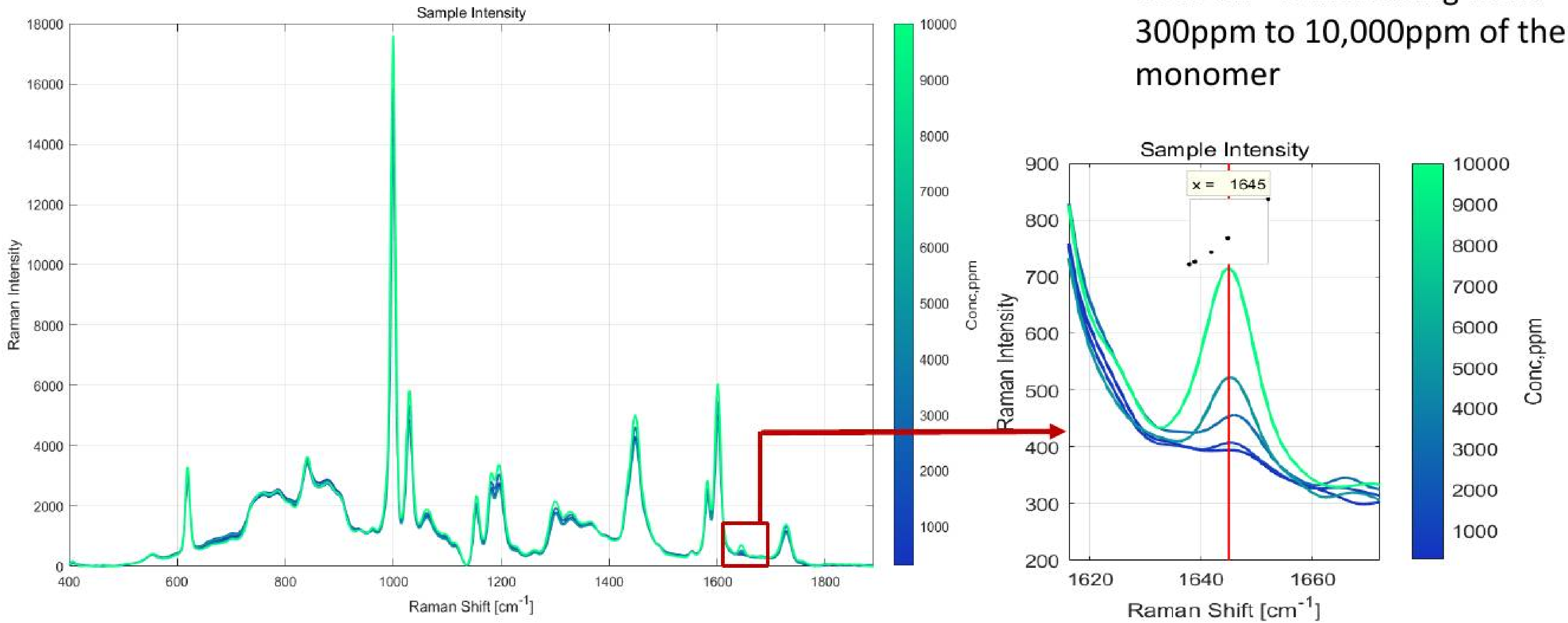
RMSECV = 0.77 %

# Vinyl Acetate Polymerization Kinetics



# Styrene acrylic emulsion with different concentrations of VAM

Symmetric C=O stretch Peak at 1645cm$^{-1}$ is increasing from 300ppm to 10,000ppm of the monomer



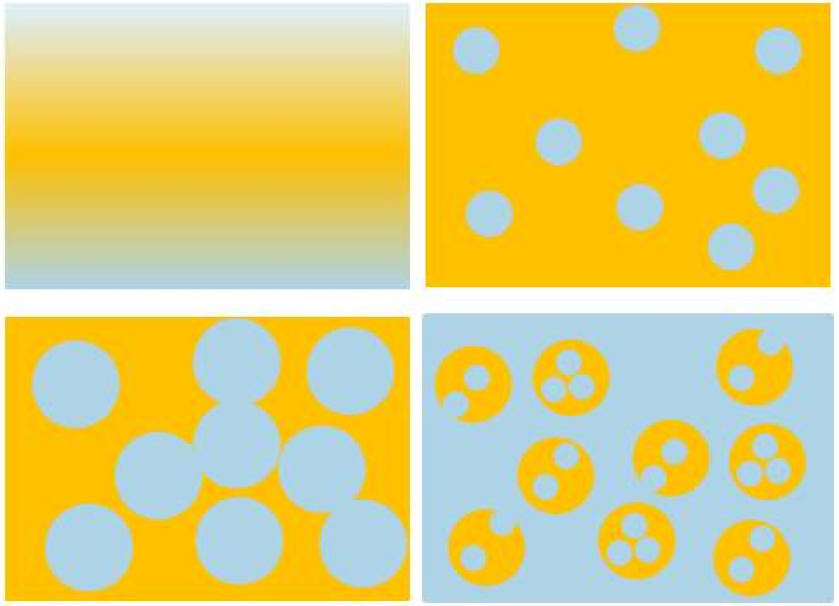
# Monitoring of a High-Impact Polystyrene Process

- High impact polystyrene (HIPS) widely used
- Uses of HIPS
  - Food processing
  - Graphics and printing
  - Toys
  - Gasoline tanks

- Mechanical properties highly dependent upon synthesis conditions

- Challenge: predicting mechanical properties of HIPS during synthesis

- Solution: Raman spectroscopy with dual sampling probes immersion and non-contact



High impact polystyrene formation: From miscible phases to heterogeneous biphasic polymer with "salami morphology"

Polystyrene (PS)
Polybutadiene (PD)

Ref: Nadège Brun et al, Chemical Engineering & Technology 37, no. 2 (February 2014): 275–282.

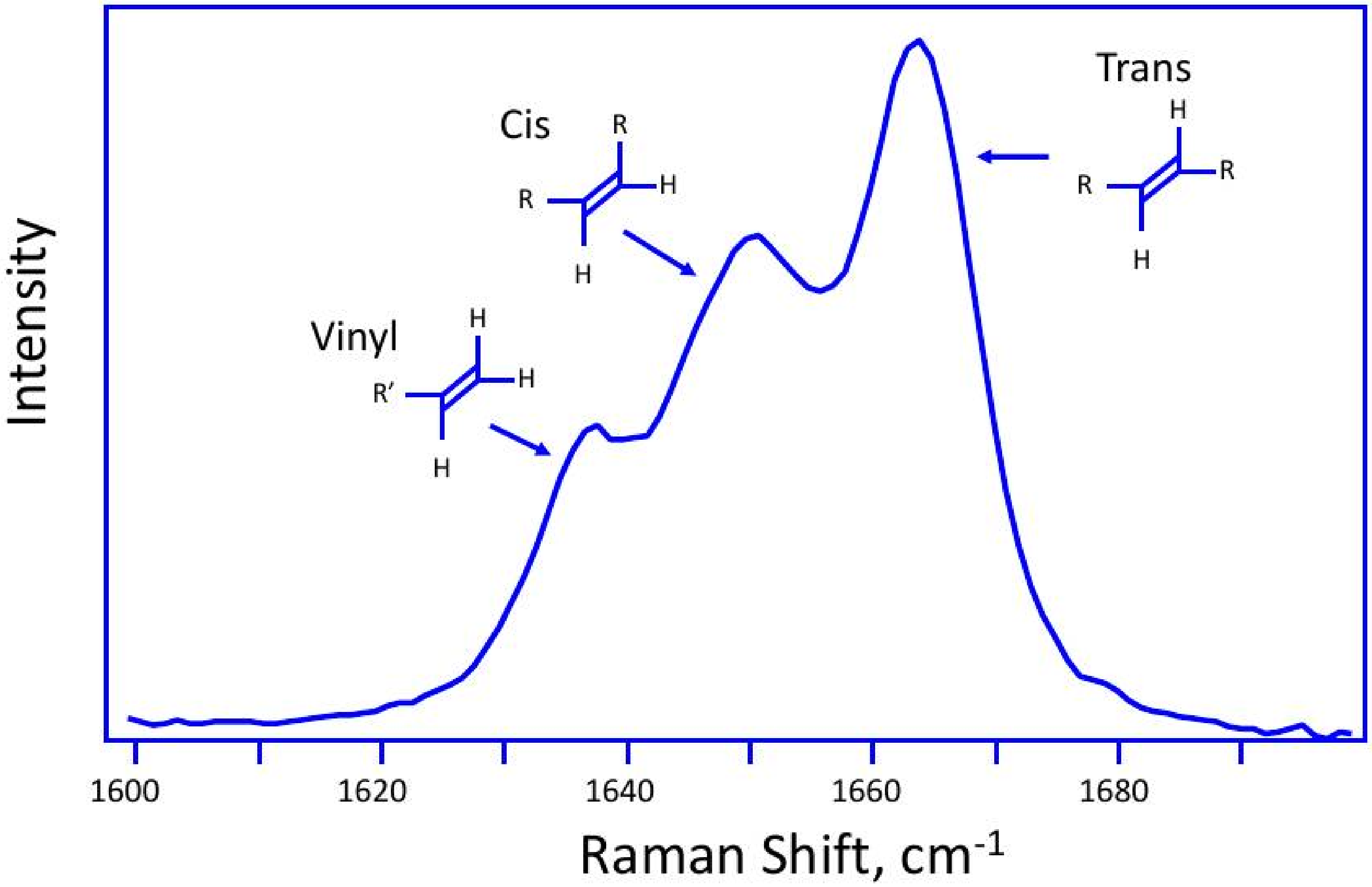
# Vinyl Polymerization

$CH_2=CXY \longrightarrow -CH_2-CXY-CH_2-CXY-$

| X | Y | Monomer | Polymer | Other Name |
|---|---|---|---|---|
| H | H | Ethylene | Polyethylene | PE |
| H | $CH_3$ | Propylene | Polypropylene | PP |
| H | Cl | Vinyl Chloride | Poly(vinyl chloride) | PVC |
| H | CN | Acrylonitrile | Polyacrylonitrile | Orion |
| H | $C_6H_5$ | Styrene | Poystyrene | PS |
| $CH_3$ | $COOCH_3$ | Methyl methacrylate | Poly(methyl methacrylate) | Plexiglas, Lucite |

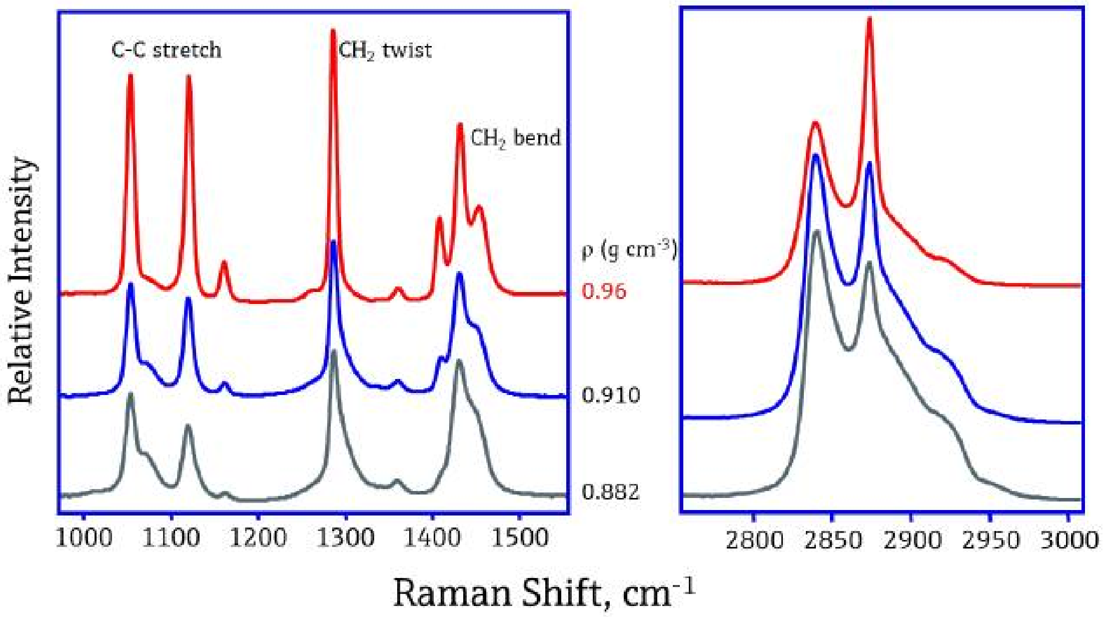
Raman analyzers are **very sensitive to vinyl group concentration and substitution.**

# Polybutadiene Microstructure Analysis

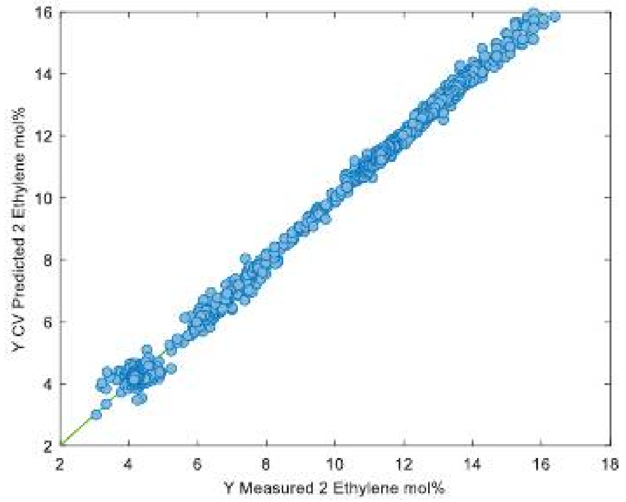


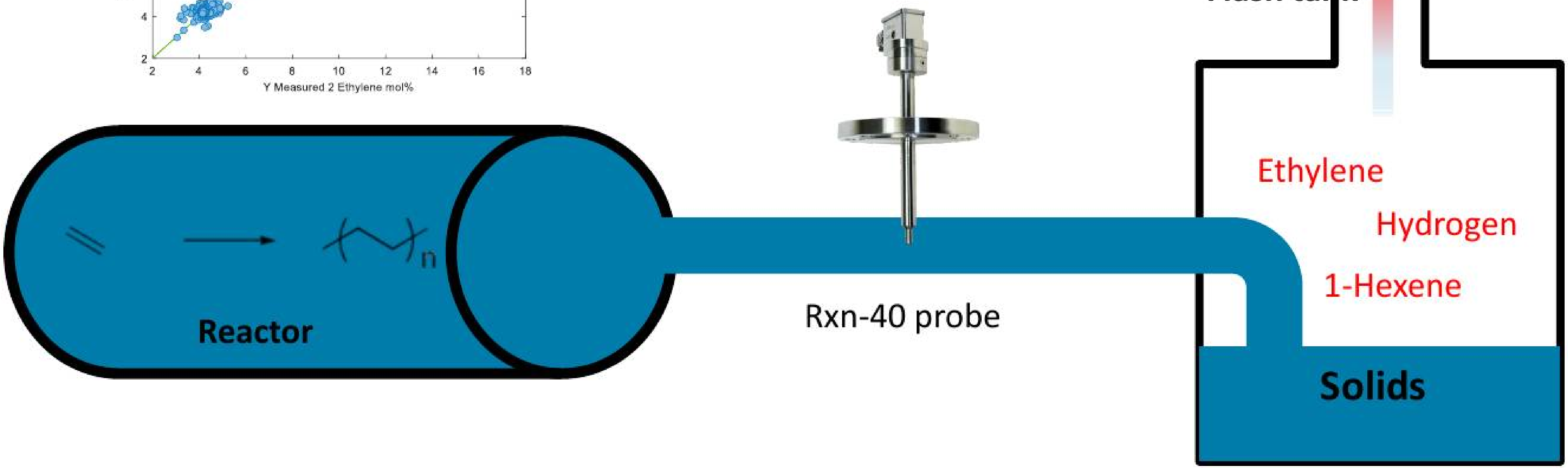
# Polyethylene, PE

- High-density polyethylene, HDPE:  density range 0.955 to 0.970 g/cc, greater strength, less creep less gas permeable than LDPE
- Low-density polyethylene, LDPE, density range 0.920 to 0.935 g/cc, more flexible, better clarity than HDPE
- Raman applications
  - Crystallinity determination
  - Density determination
  - Orientation of high-modulus fibers in extruders, and films
  - Additive monitoring



# Polyethylene polymerization



# Key highlights

- Provide quicker answers than other testing techniques (i.e. wet chemistry and chromatography)
- Predict concentrations of components in complex matrices even in the presence of heavy interference by other components
- Do not require frequent recalibration
- Accuracy, precision, robustness, and reproducibility of results
- Prediction ranges provide good indication of process outcome
- Lab analysis ensures compliance, online analysis drives optimization.

# Raman in Polymer Applications-Key features

## Advantages

- No sample preparation
- Non-destructive analysis
- Suitable for aqueous and colored samples
- Can analyze solids, films, fibers, and melts
- Fiber-optic probes enable in-line measurements
- Fast analysis with real-time monitoring capability

## Common Parameters Monitored

- Monomer concentration
- Degree of cure
- Crystallinity
- Blend composition
- Additive concentration
- Polymer degradation
- Molecular orientation

# What we are working on today and tomorrow

- **Automate** plants safely, efficiently and sustainably
- Integrate smart field devices securely
- Digitalize field devices and analyzers
- **Make laboratory techniques suitable for processes**
- Replace human senses with new sensor technology
- Reduce complexity in plants
- **Enable data-driven decisions**
- Make work in the process industry attractive and meaningful


thank you
danke
謝謝
ngiyabonga
teşekkür ederim
gracias
спасибо
dank je
tapadh leat
bedankt
dziękuję
obrigado
sukriya
kop khun krap
go raibh maith agat
mochchakkeram
merci
terima kasih
grazie
arigatō
dakujem
takk
taiku
мерси
sagolun
hvala
mauruuru
감사합니다
ありがとう
ευχαριστώ
Баярлалаа
рахмат
blagodaram
dhanyavadagalu
shukriya
trugarez
хвала
asante
mahalo
kiitos
dankie
enkosi
sobodi
dekuji
mesi
tack
barka
mersi
paldies
misaotra
mamnun
chnorakaloutioun
gracies
sulpay
diolch
xiexie
tanemirt
rahmet
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akun