

# Raman Spectroscopy in the Ethanol Industry – What Can It Do and Why Should You Care?

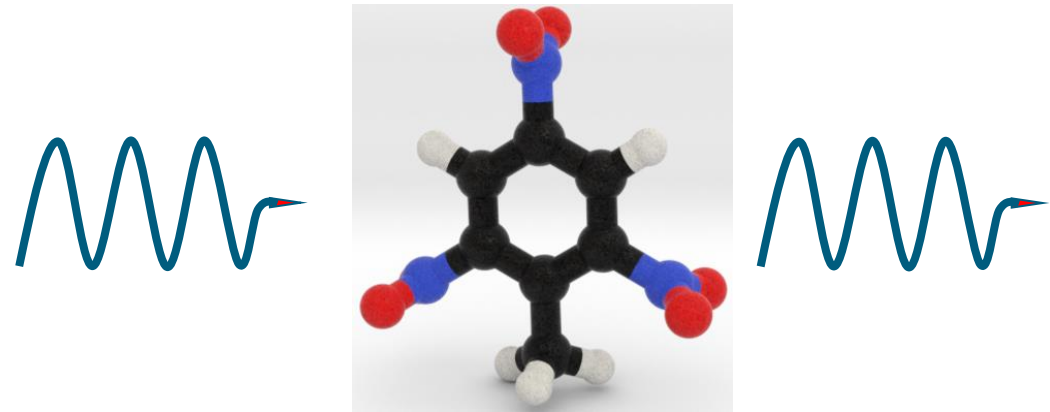
Adam J. Hopkins  
Spectroscopy Product Manager  
Metrohm USA  
October 5, 2021 - FELC



- What is Raman?
- Why use Raman?
- What can Raman do?

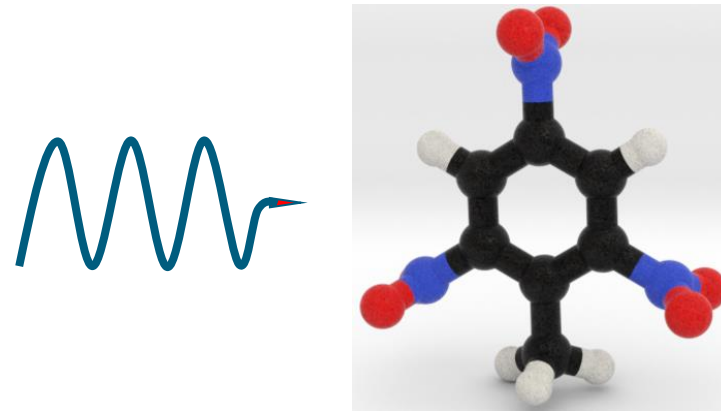
# Light Interacts with Matter

- Transmission



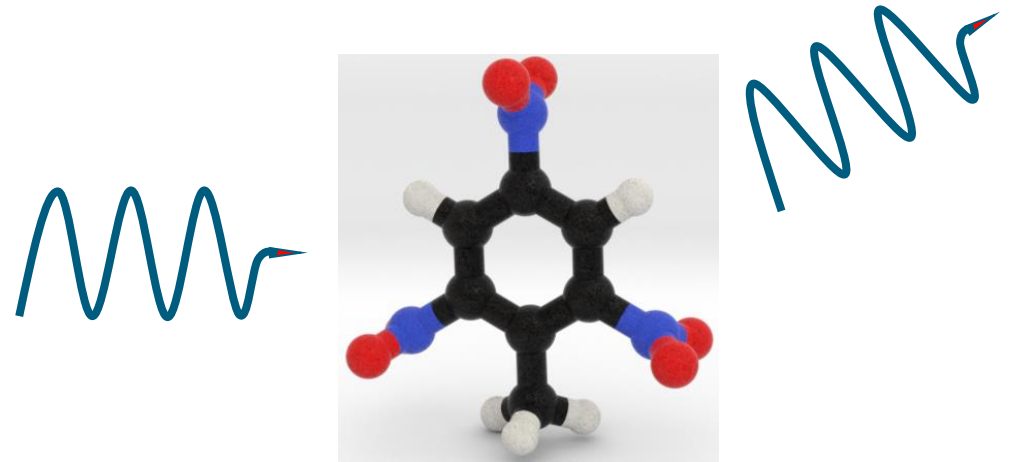
# Light Interacts with Matter

- Transmission
- Absorption
  - UV, vis, IR, NIR



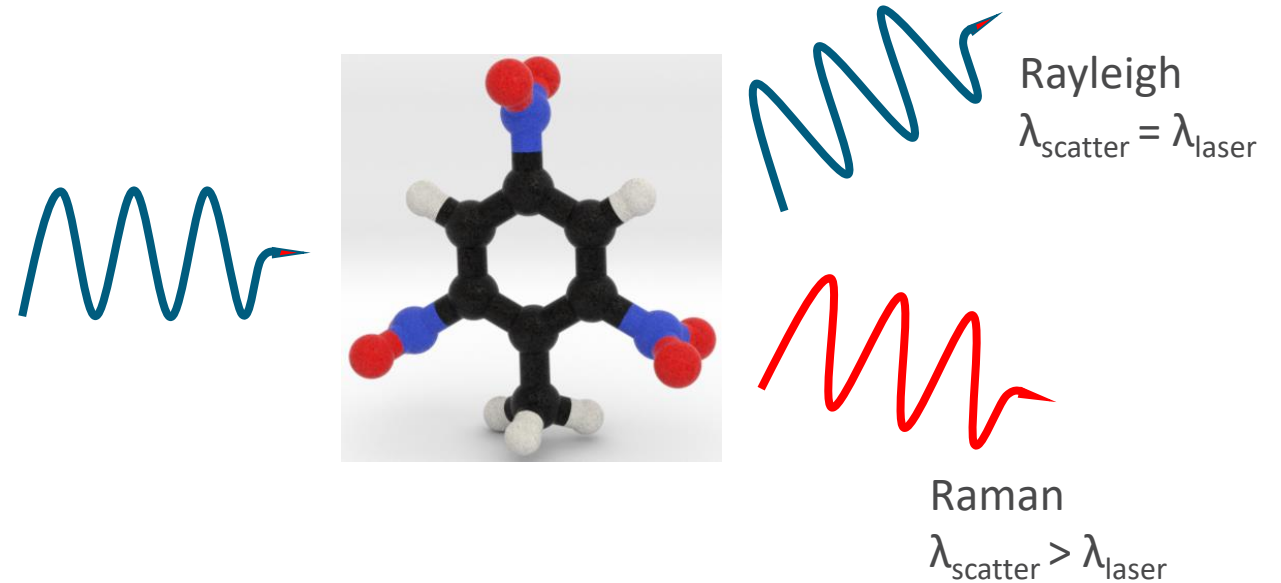
# Light Interacts with Matter

- Transmission
- Absorption
  - UV, vis, IR, NIR
- Elastic scattering (Rayleigh scattering)



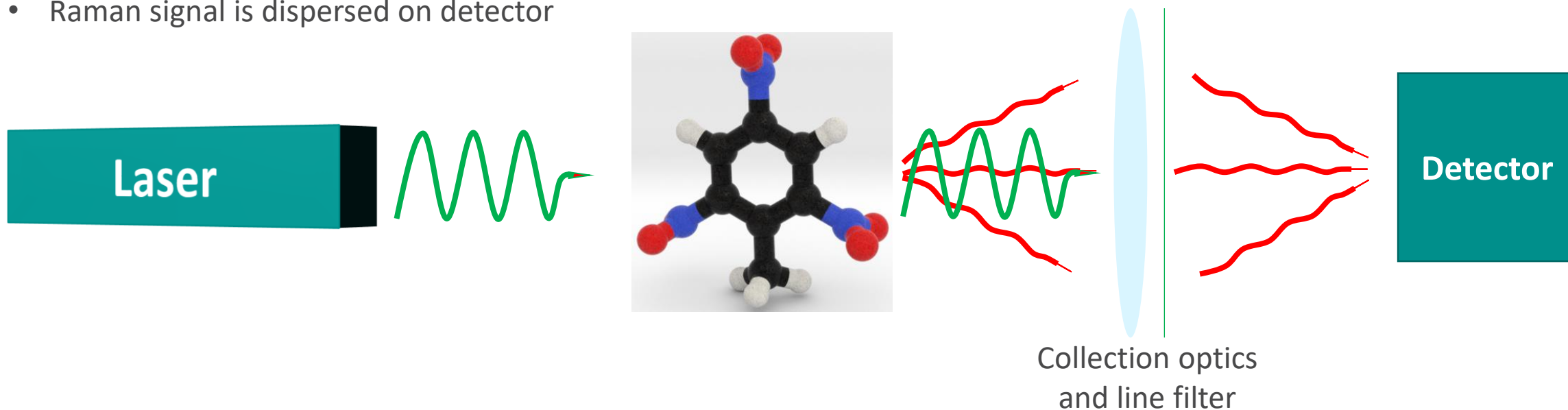
# Light Interacts with Matter

- Transmission
- Absorption
  - UV, vis, IR, NIR
- Elastic scattering (Rayleigh scattering)
- Inelastic scattering (Raman scattering)
  - Vibrational spectrum (molecular fingerprint)



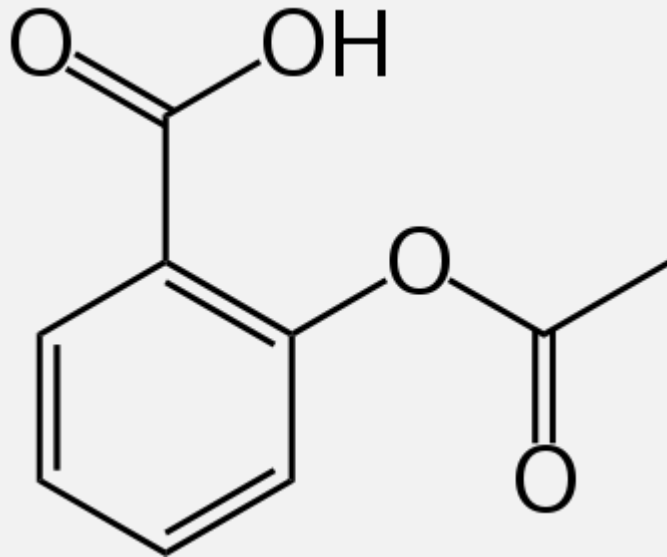
# A Raman Instrument

- Laser sends high intensity light
- 1 out of every 1,000,000 – 1,000,000,000 photons is Raman scattered
- Raman scatters in all directions
- Scattered light is collected and laser light is filtered
- Raman signal is dispersed on detector

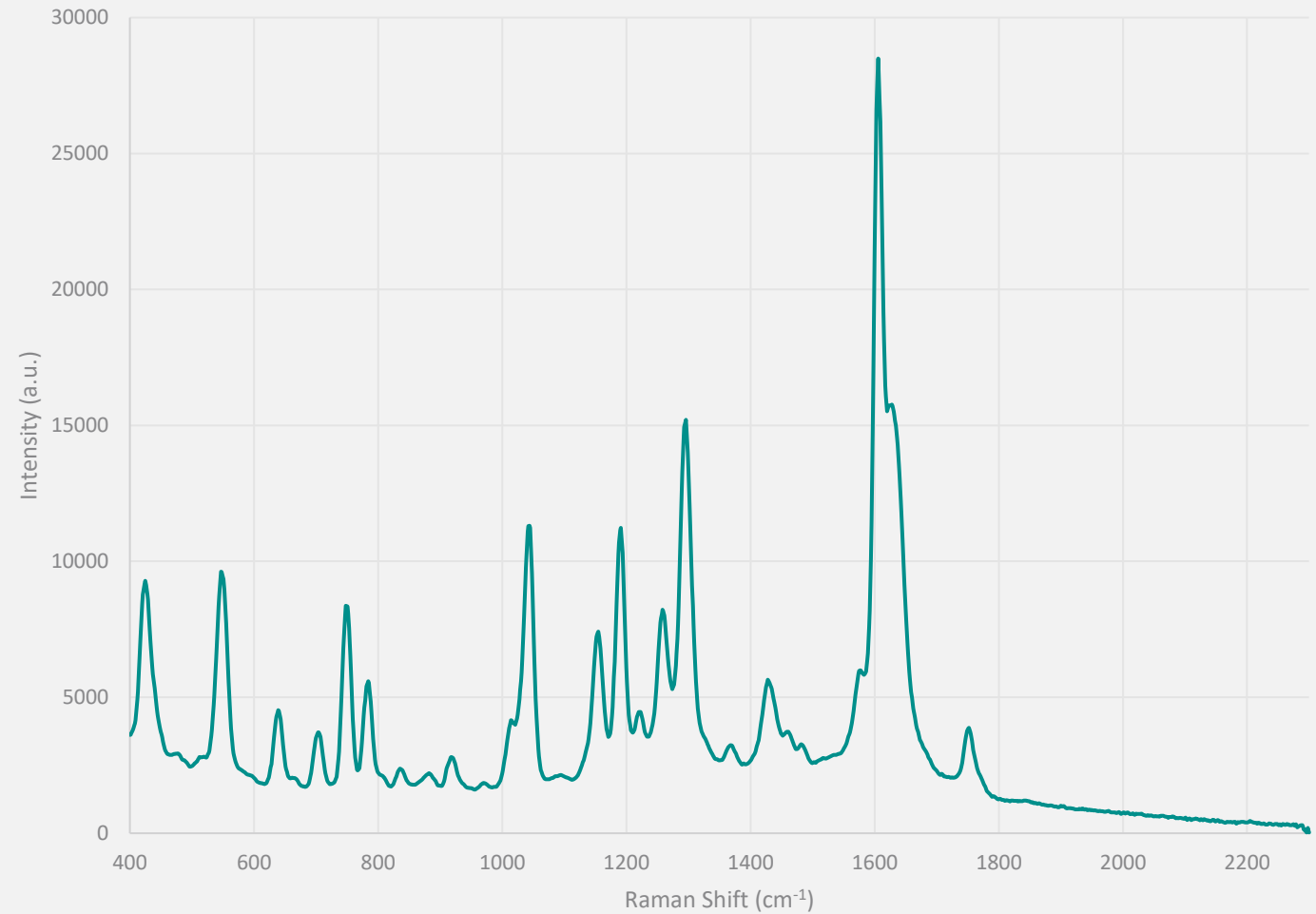


# Information in a Raman Spectrum

- Molecular fingerprint



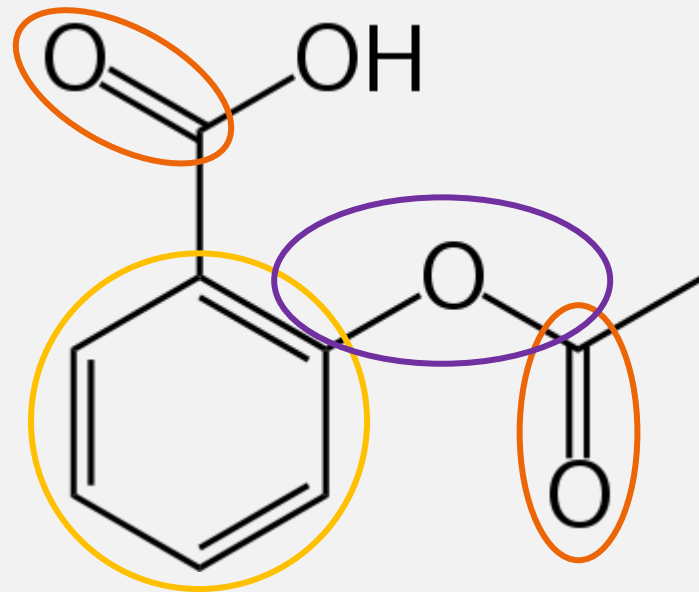
Acetyl salicylic acid (aspirin)



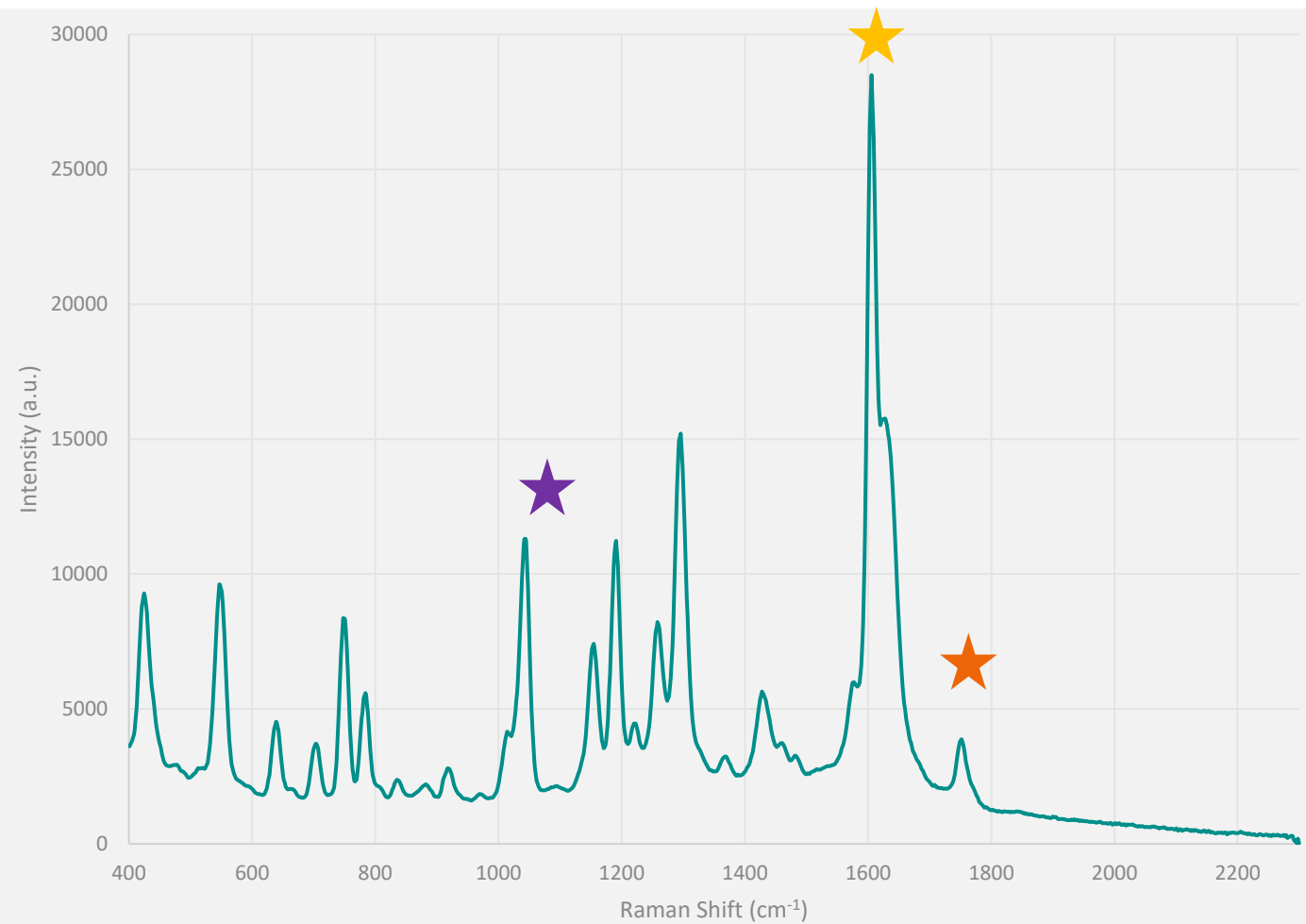


# Information in a Raman Spectrum

- Molecular fingerprint

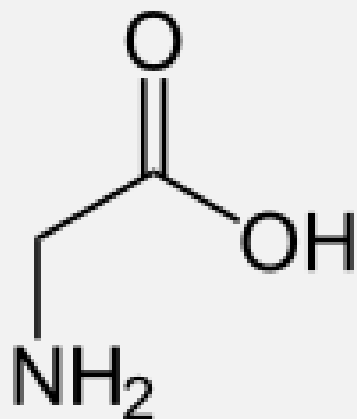


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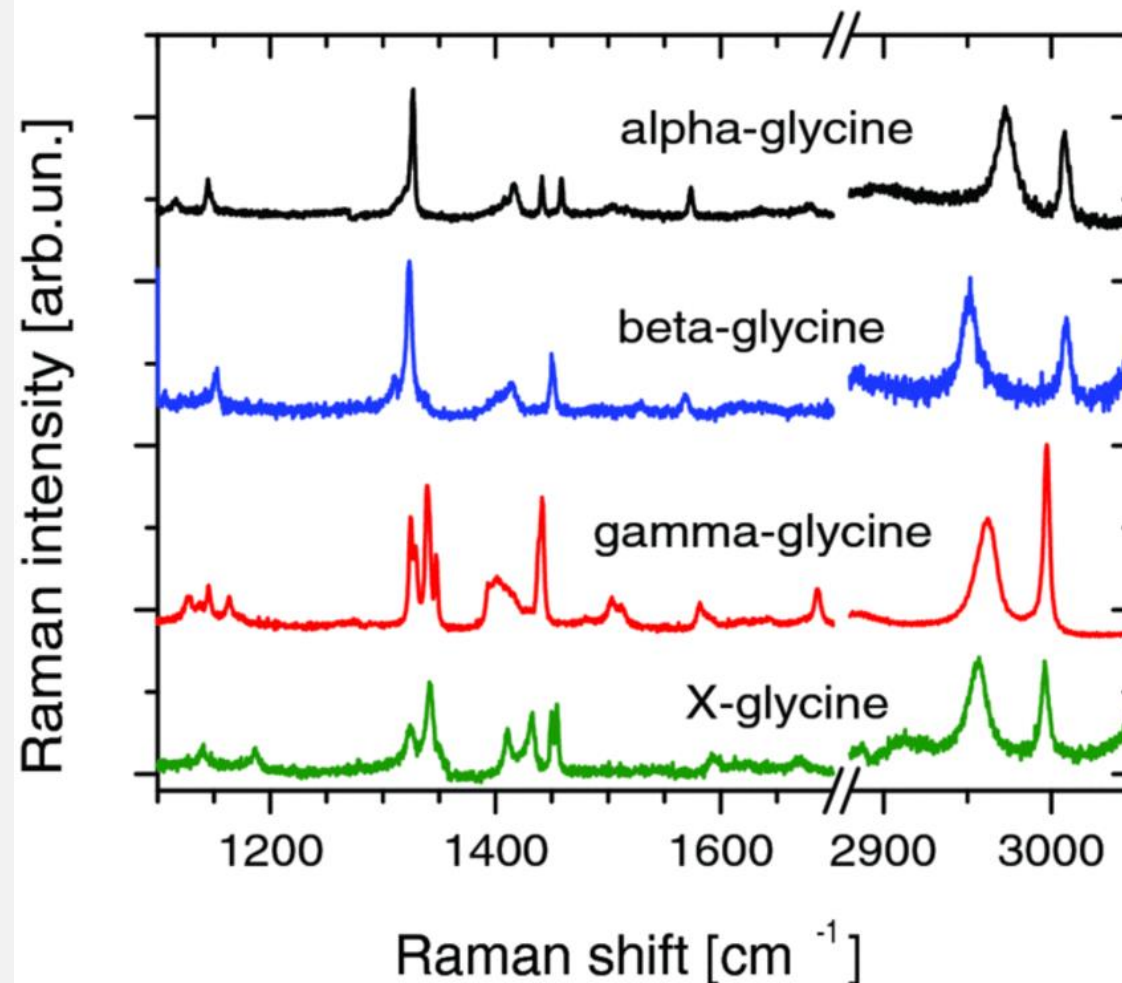


# Information in a Raman Spectrum

- Molecular fingerprint
- Structure
  - Different crystalline structures have different spectra

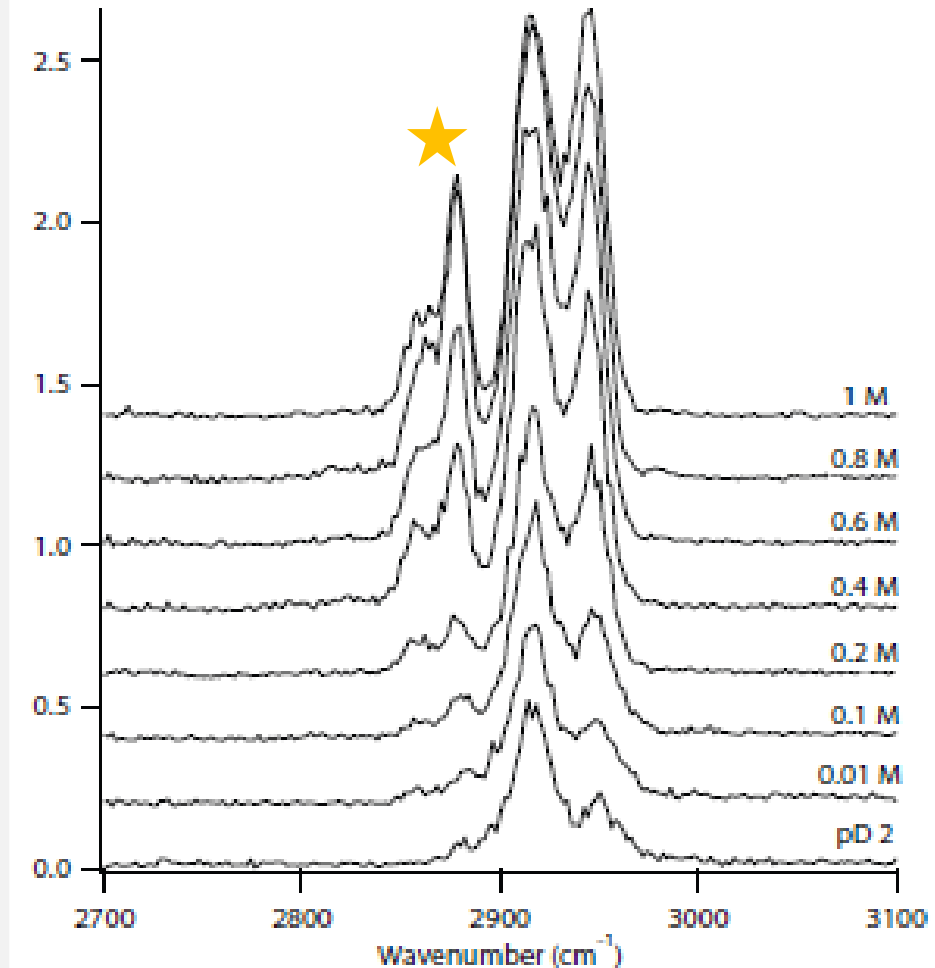


Glycine



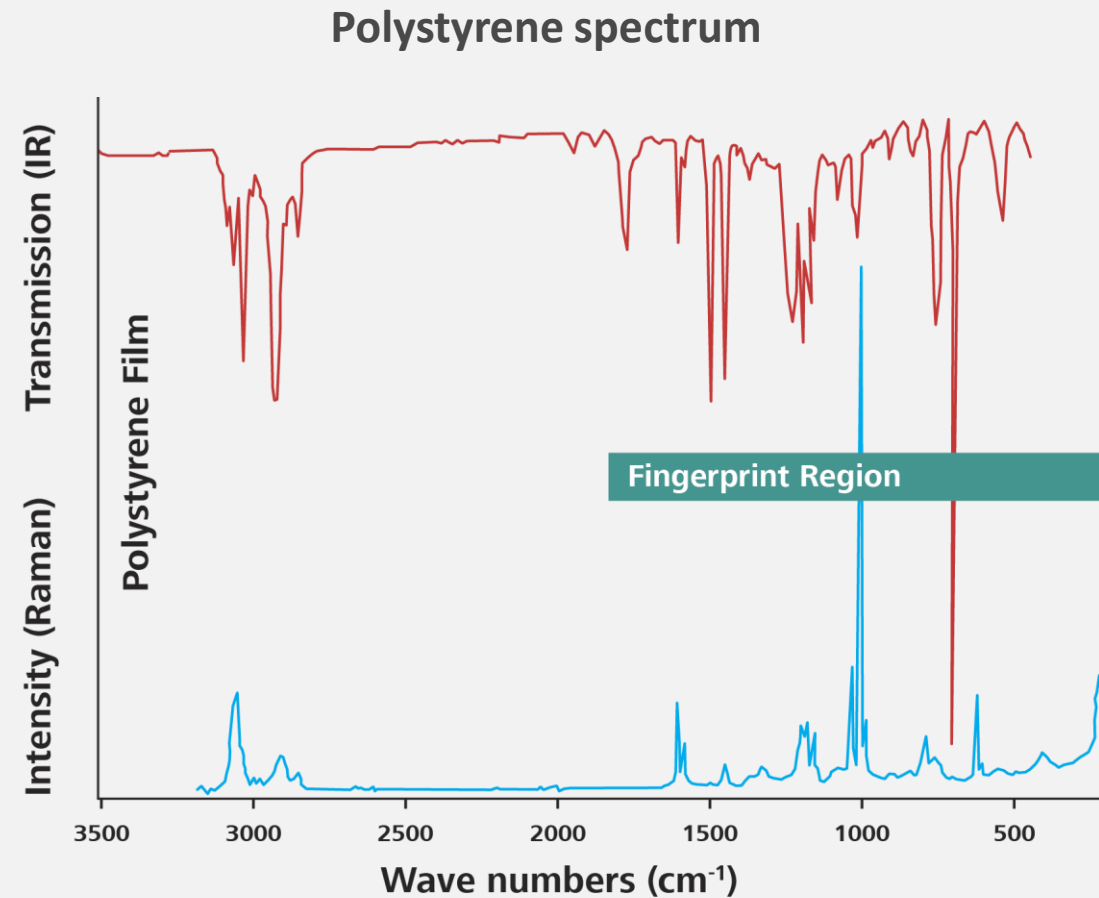
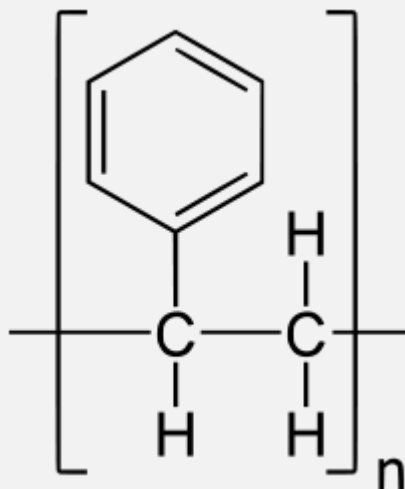
# Information in a Raman Spectrum

- Molecular fingerprint
- Structure
- Quantity
  - All things being equal, fewer molecules = smaller signal



# Infrared vs. Raman Spectroscopy

- Complementary technologies
- Strong IR modes are weak Raman scatterers

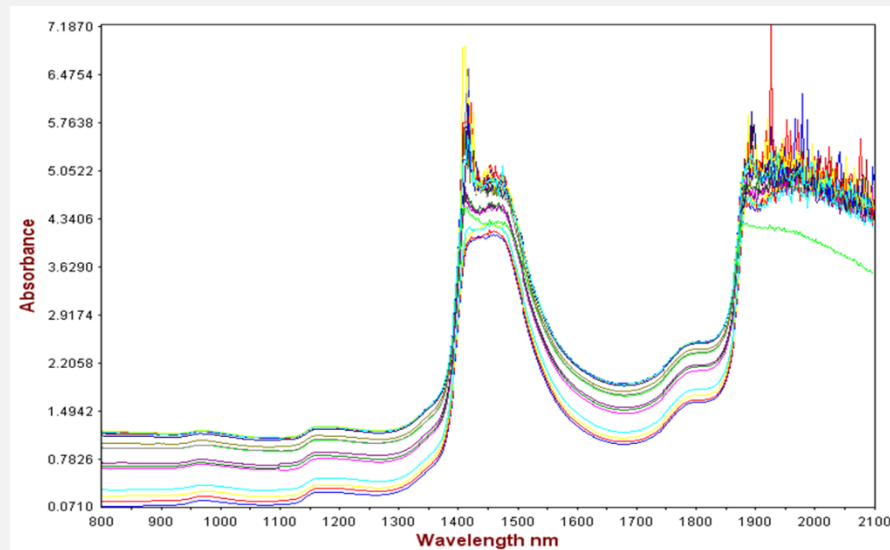




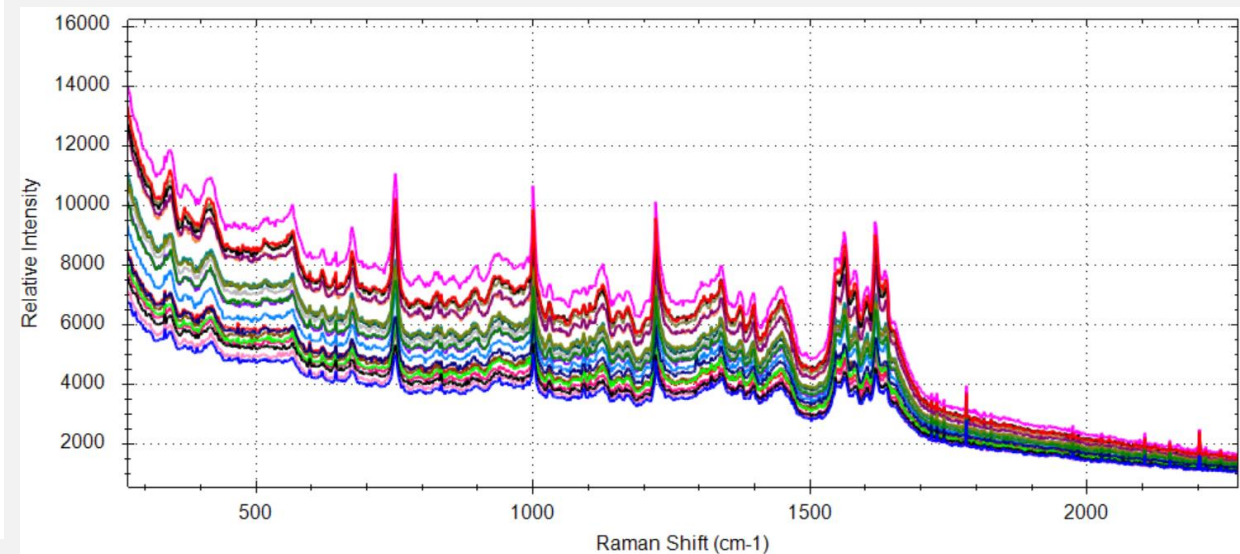
- What is Raman?
- Why use Raman?
- What can Raman do?

# Top Advantages of Raman Spectroscopy

- Insensitive to water – measure bioprocesses and more



**NIR Spectrum in Water**



**Raman Spectrum in Water**

# Top Advantages of Raman Spectroscopy

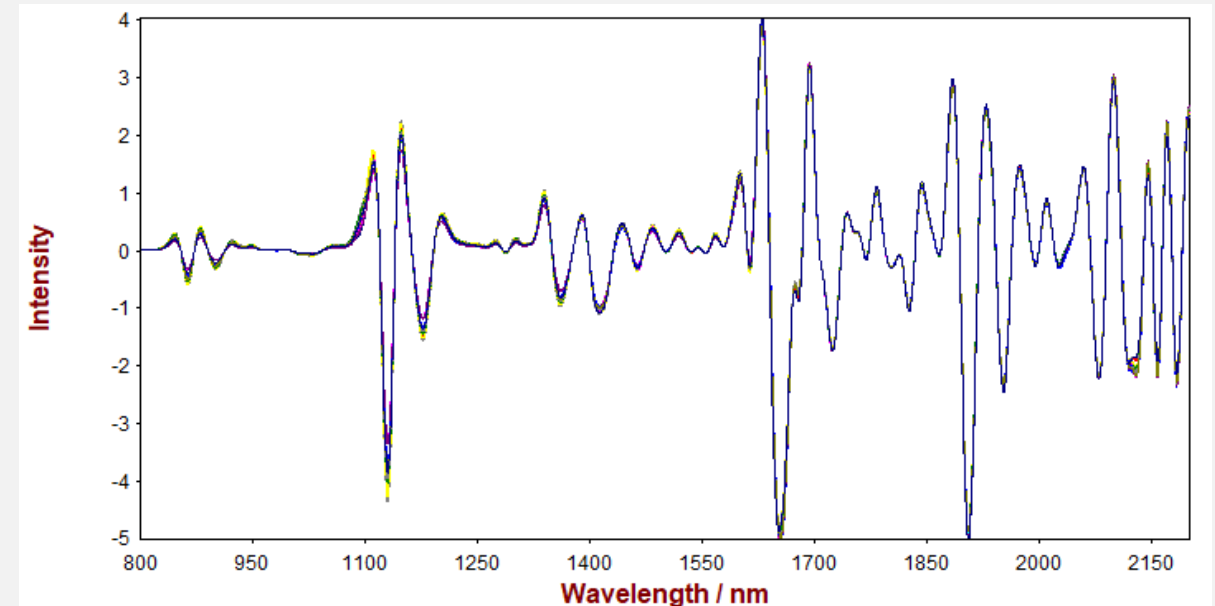
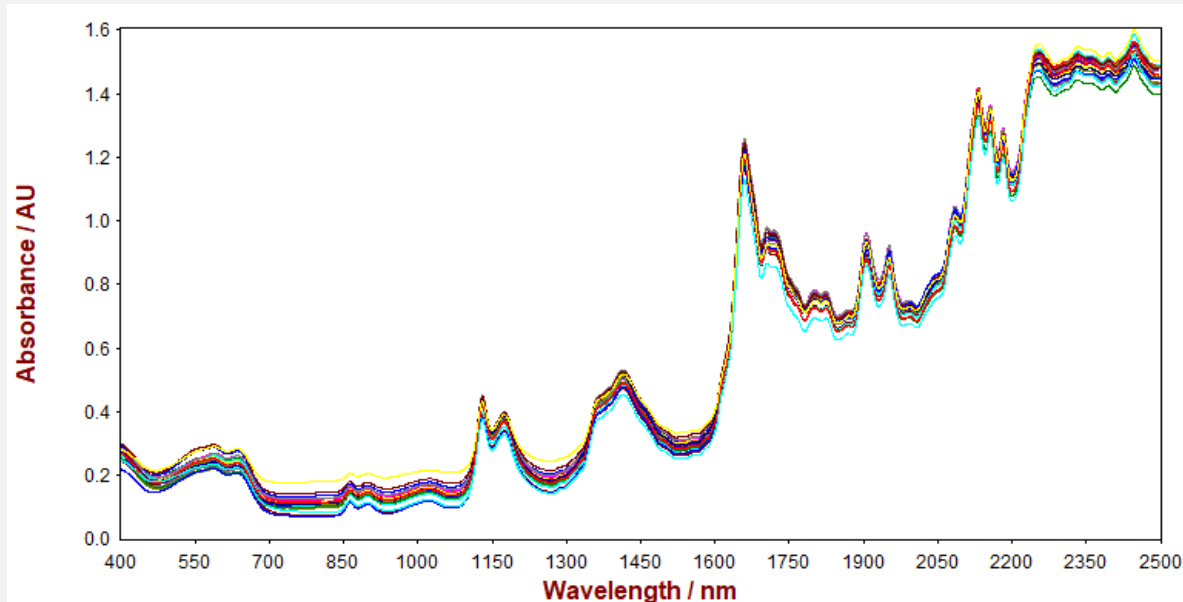
- Insensitive to water – measure bioprocesses and more
- Flexible analysis – measurements where you need them





# Top Advantages of Raman Spectroscopy

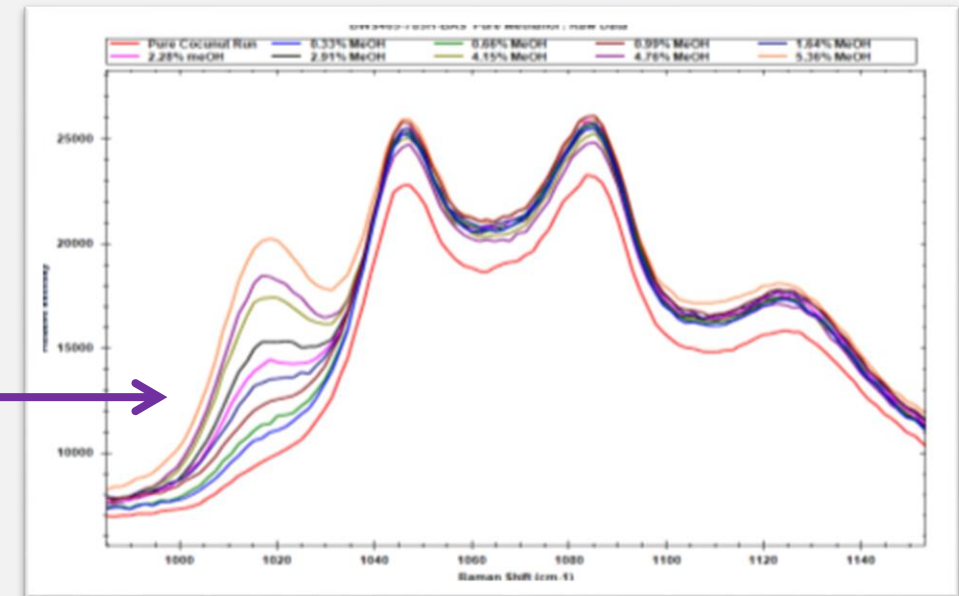
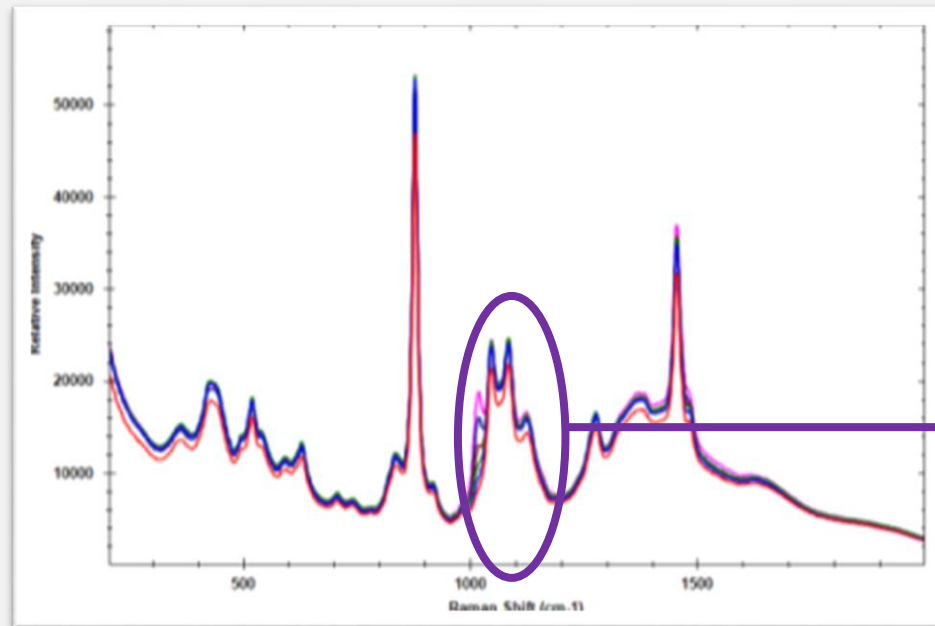
- Insensitive to water – measure bioprocesses and more
- Flexible analysis – measurements where you need them
- Robust methods – spectrometer models less sensitive to change





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# Top Advantages of Raman Spectroscopy

- Insensitive to water – measure bioprocesses and more
- Flexible analysis – measurements where you need them
- Robust methods – models less sensitive to change
- Long lifetime – 5-7 years without source maintenance

# Spectroscopy Applications

- Complementary technologies
- Strong IR modes are weak Raman scatterers

Parameter	Raman	NIR	FTIR
Moisture content	NO	YES	SOMETIMES
Materials in aqueous solutions	YES	SOMETIMES	NO
OH number and acid value	NO	YES	YES
Inorganic materials	YES	NO	YES
Physical parameters	NO	YES	SOMETIMES
Chemical bond/structure	YES	NO	YES
Through container analysis	YES	NO	NO
Organic materials	YES	YES	YES

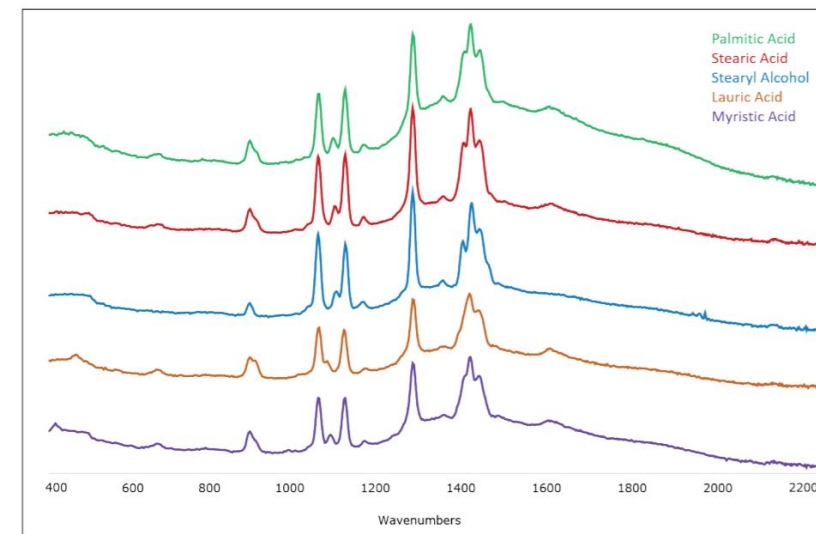


- What is Raman?
- Why use Raman?
- What can Raman do?

# Material Identification

Table of Results for Verification of Edible Oils

Sample	Training Set (# Samples)	African Palm (43)	Avocado (50)	Canola (60)	Coconut (42)	Corn (60)	EL Olive (60)	EV Olive (52)	Grapeseed (60)	OV Coconut (31)	Peanut (60)	Prem. EV Olive (60)	Pure Olive (52)	Pure Palm (30)	Refined Sesame (60)	Sunflower (60)	Walnut (60)
African Palm	P	#		#									#	#			
Avocado		P						#			#	#					
Canola			P													#	
Coconut				P					#								
Corn				#	P	#									#		#
Extra Light Olive				#	#	P				#					#		
Extra Virgin Olive		#					P	#			#						
Grapeseed		#						P				#					
Org Virgin Coconut				#					P								
Peanut				#	#	#				P					#		
P. Extra Virgin Olive		#						#			P						
Pure Olive		#		#				#				P					
Pure Palm	#			#								#	P				
Refined Sesame				#	#	#				#					P		
Sunflower			#	#		#										P	
Walnut			#	#	#												P



- Edible oils from different sources contain different fatty acids / ratios of fatty acids
- Give rise to variations in Raman spectral signatures
- Metrohm White Paper WP-035EN – “Facile Verification of Edible Oils with Raman Spectroscopy”

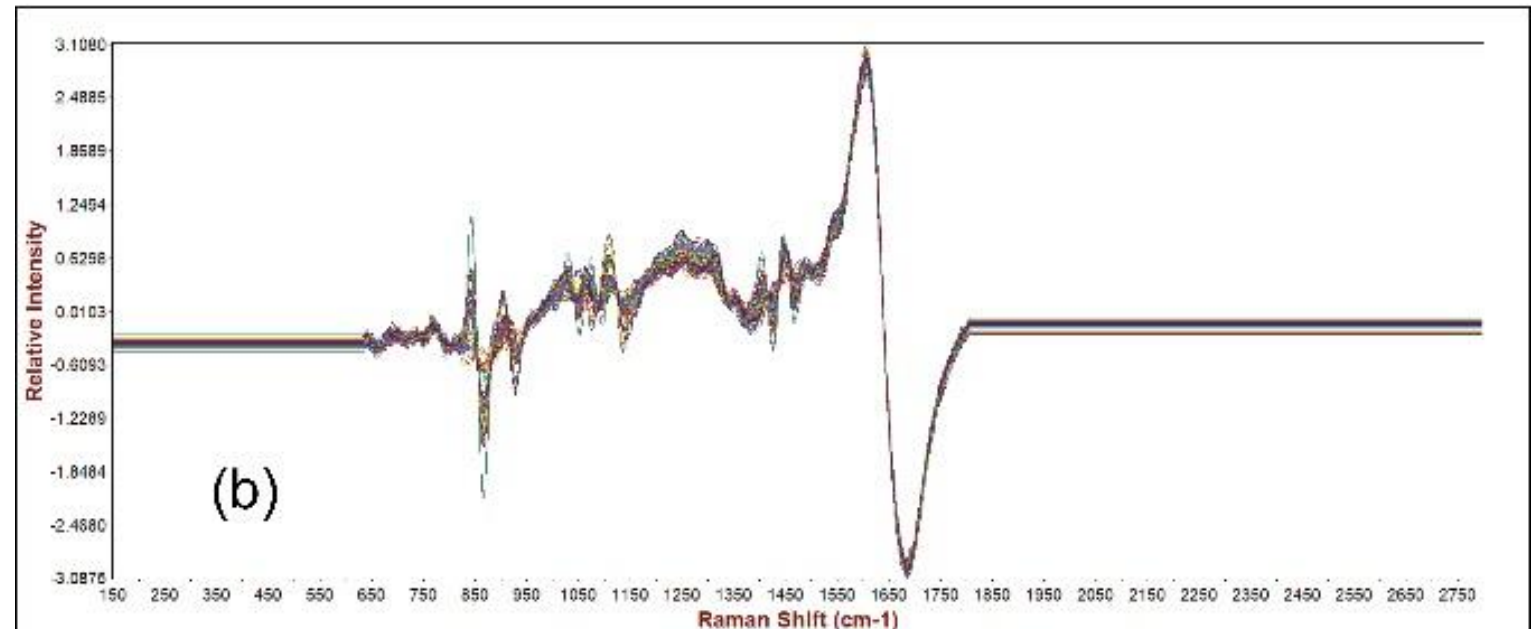
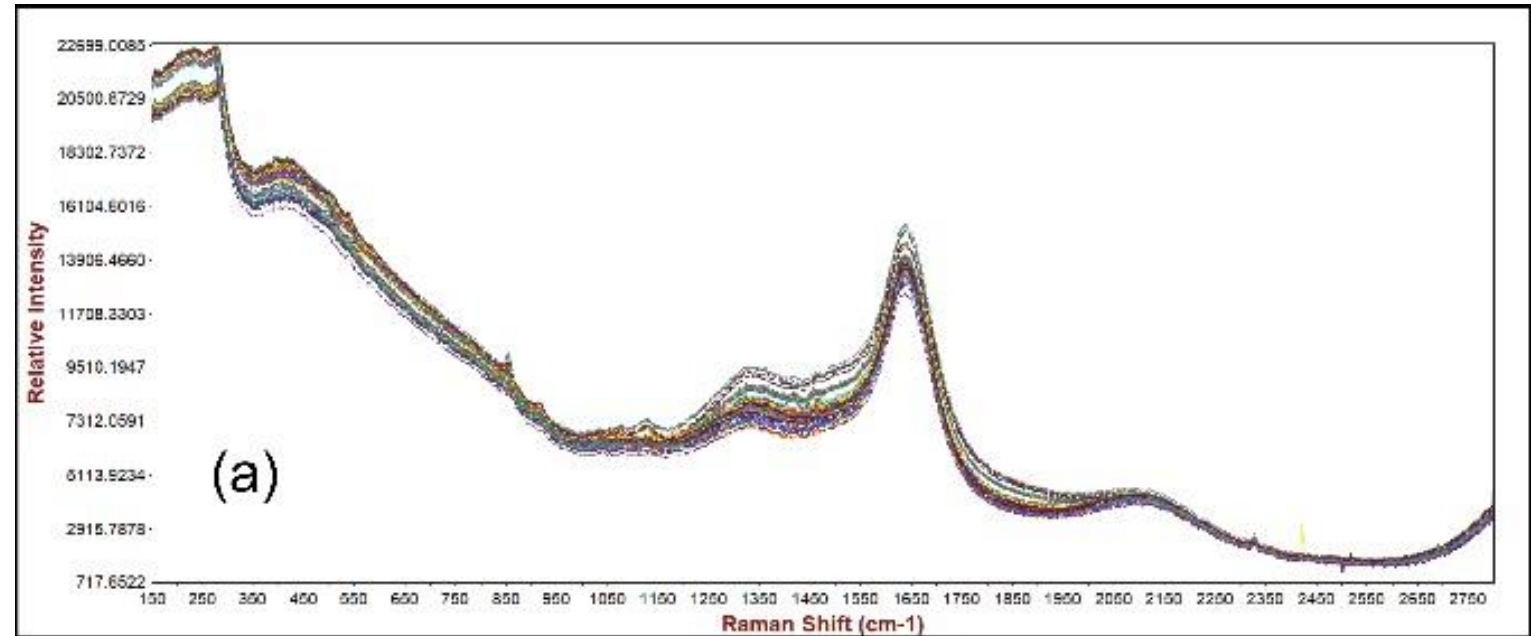
# Cell Growth Monitoring

Measurement frequency – 10 min

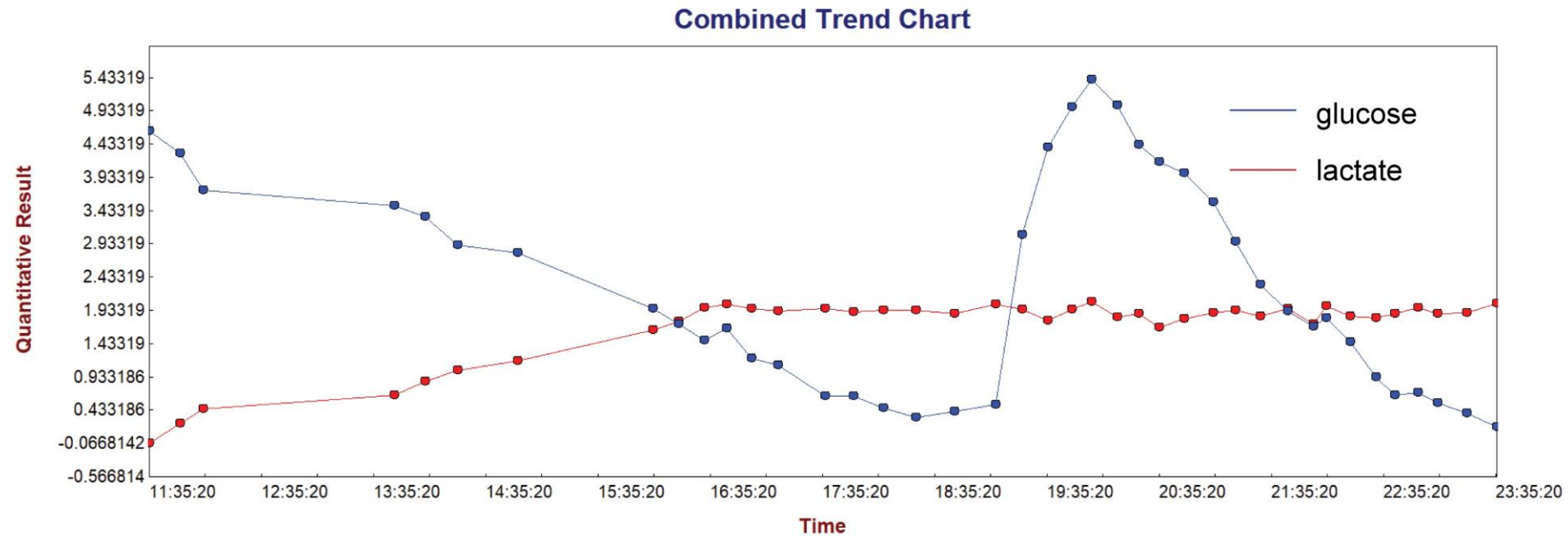
Measurement time – 30s

Parameters of interest:

- Glucose
- Lactate

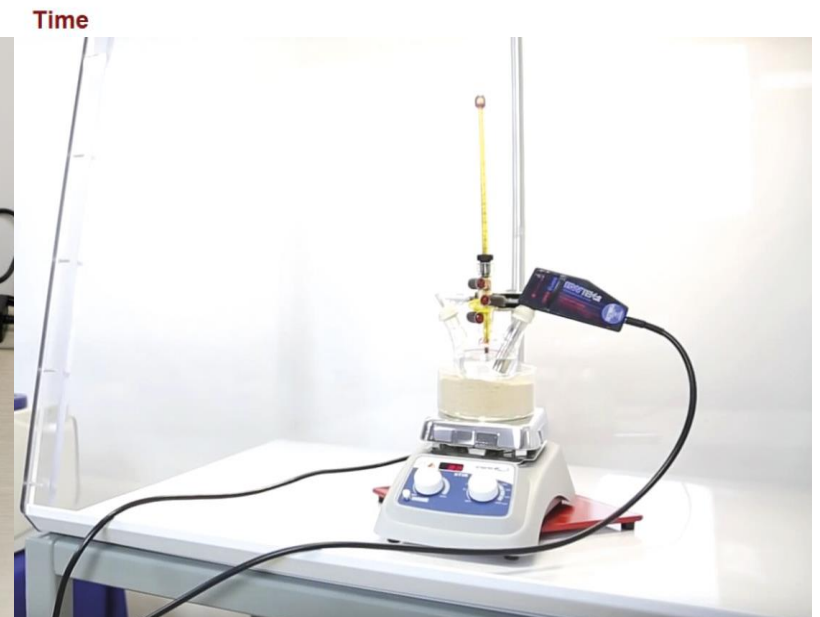


# Cell Growth Monitoring

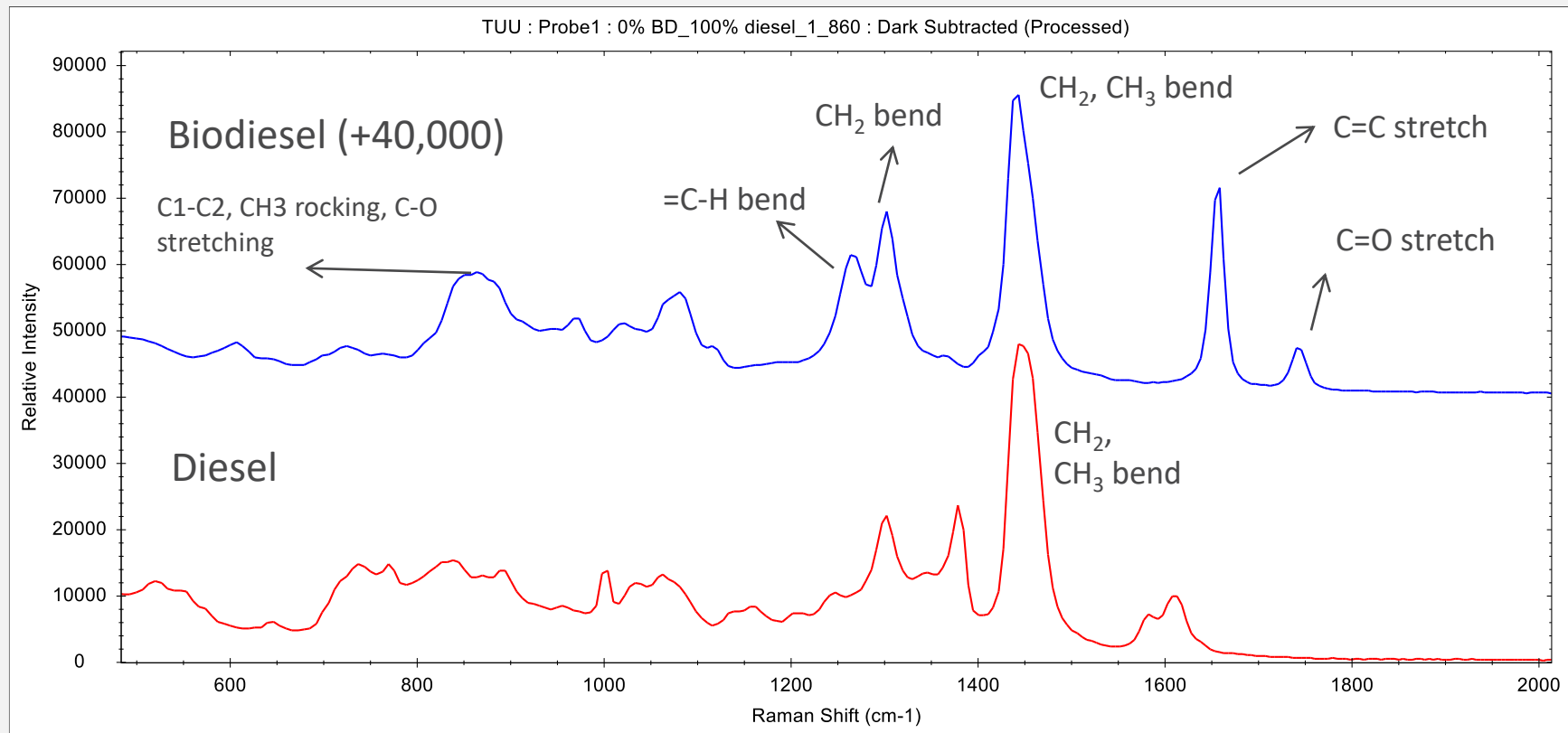


Monitor health indicators such as lactate in real time

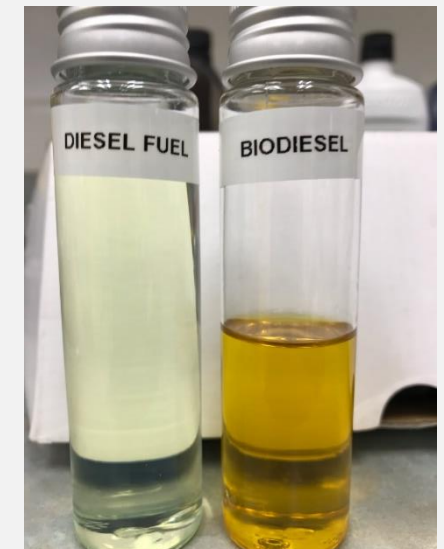
Limit  $\sim 0.1$  g/L



# Biodiesel Blending

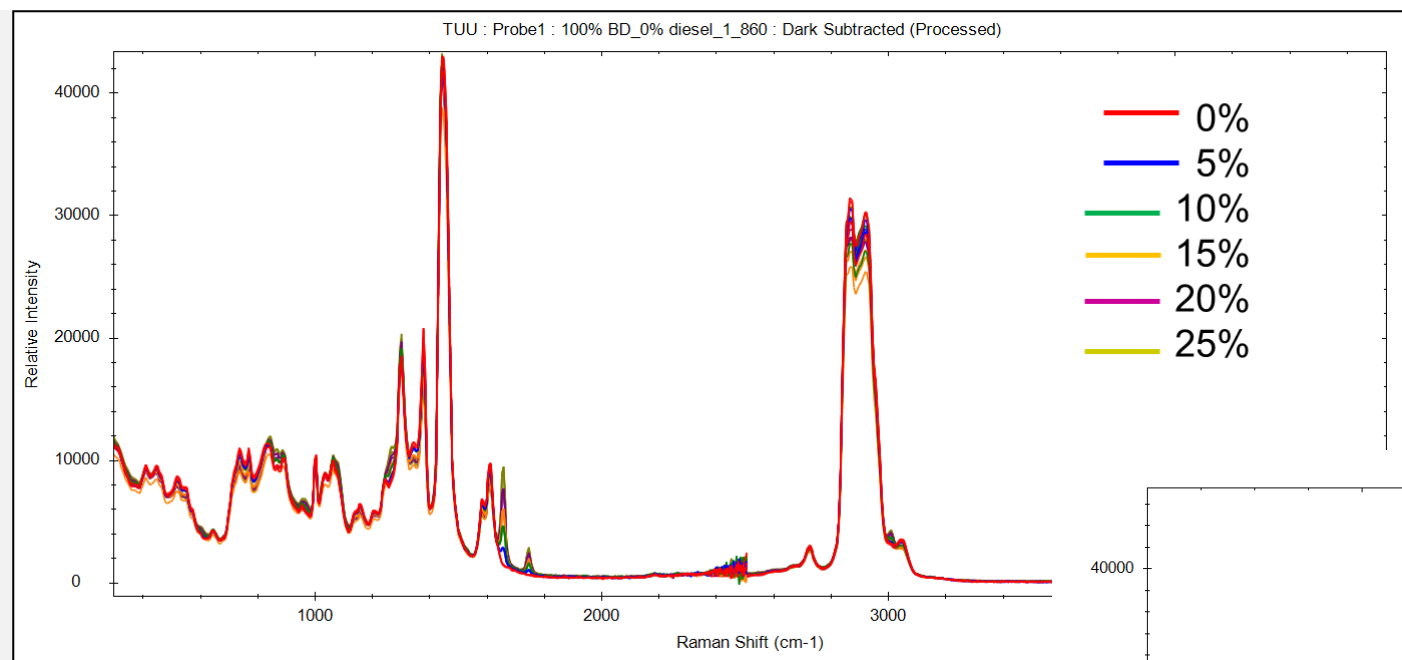


- Diesel acquired locally
- Biodiesel standard from Sigma Aldrich (CoA available)



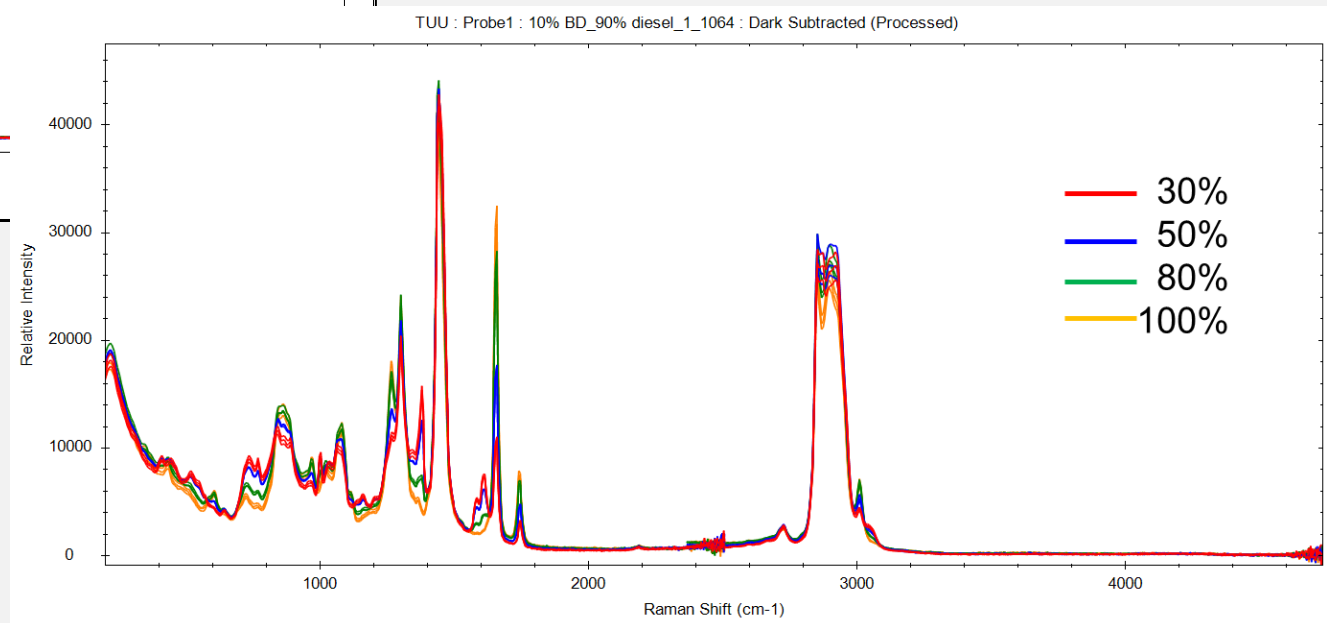


# Biodiesel Blending



Model predicts concentration with  
0.55% error

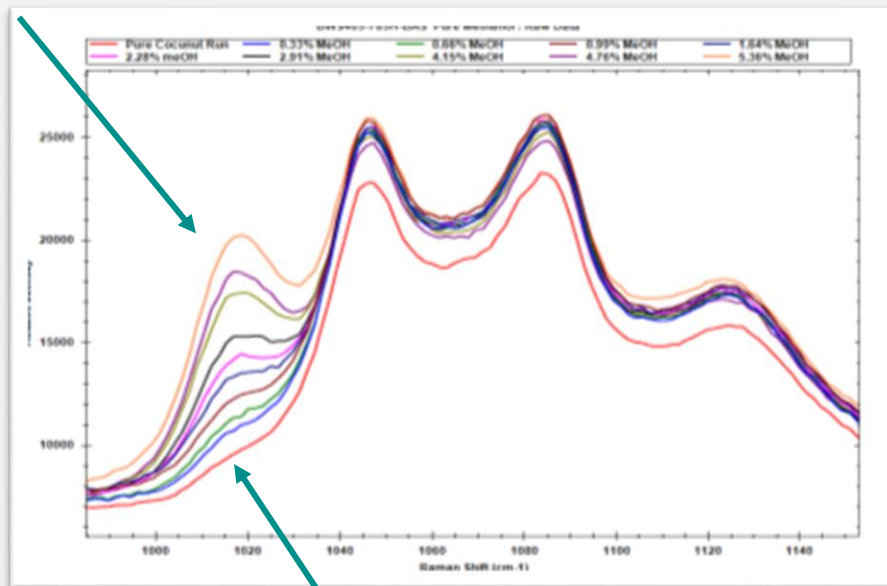
Diesel → Biodiesel



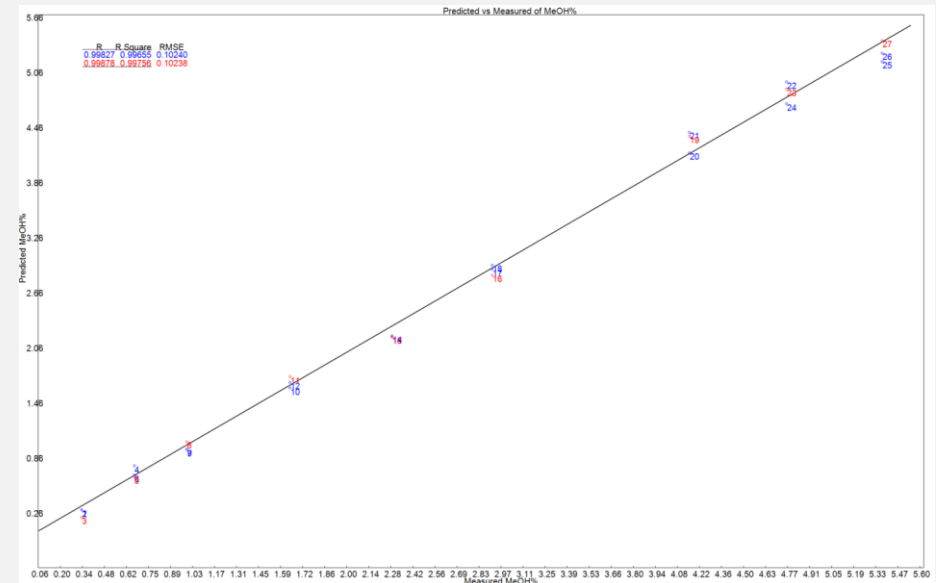
# Methanol Contamination Detection & Quantification

- Identify unique spectral signatures of contaminants
- Quantify contamination level

5.47% MeOH

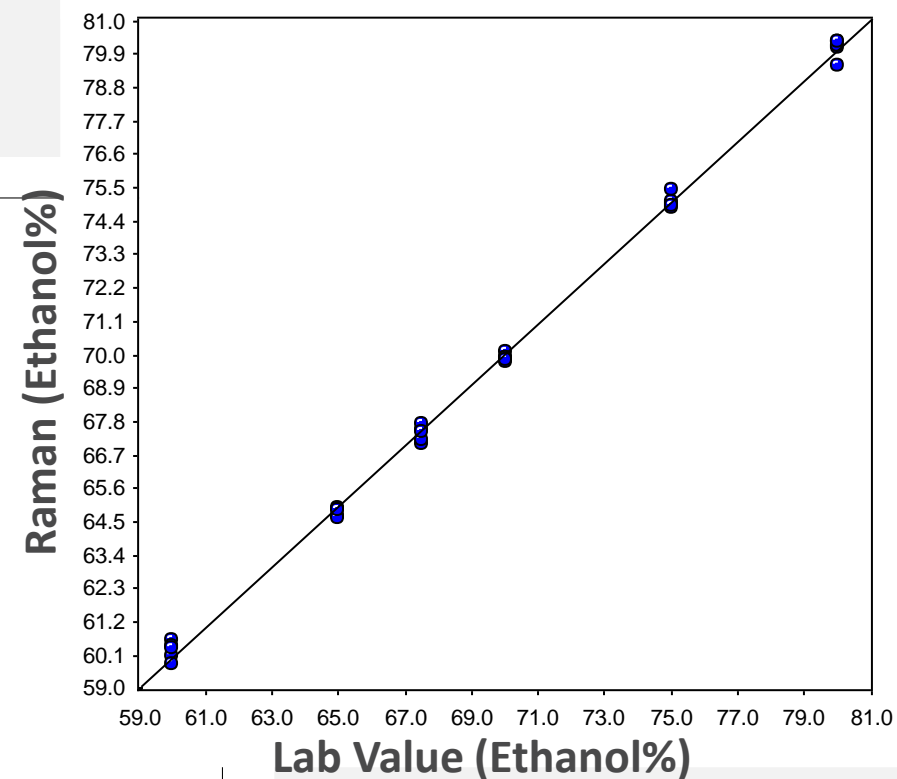
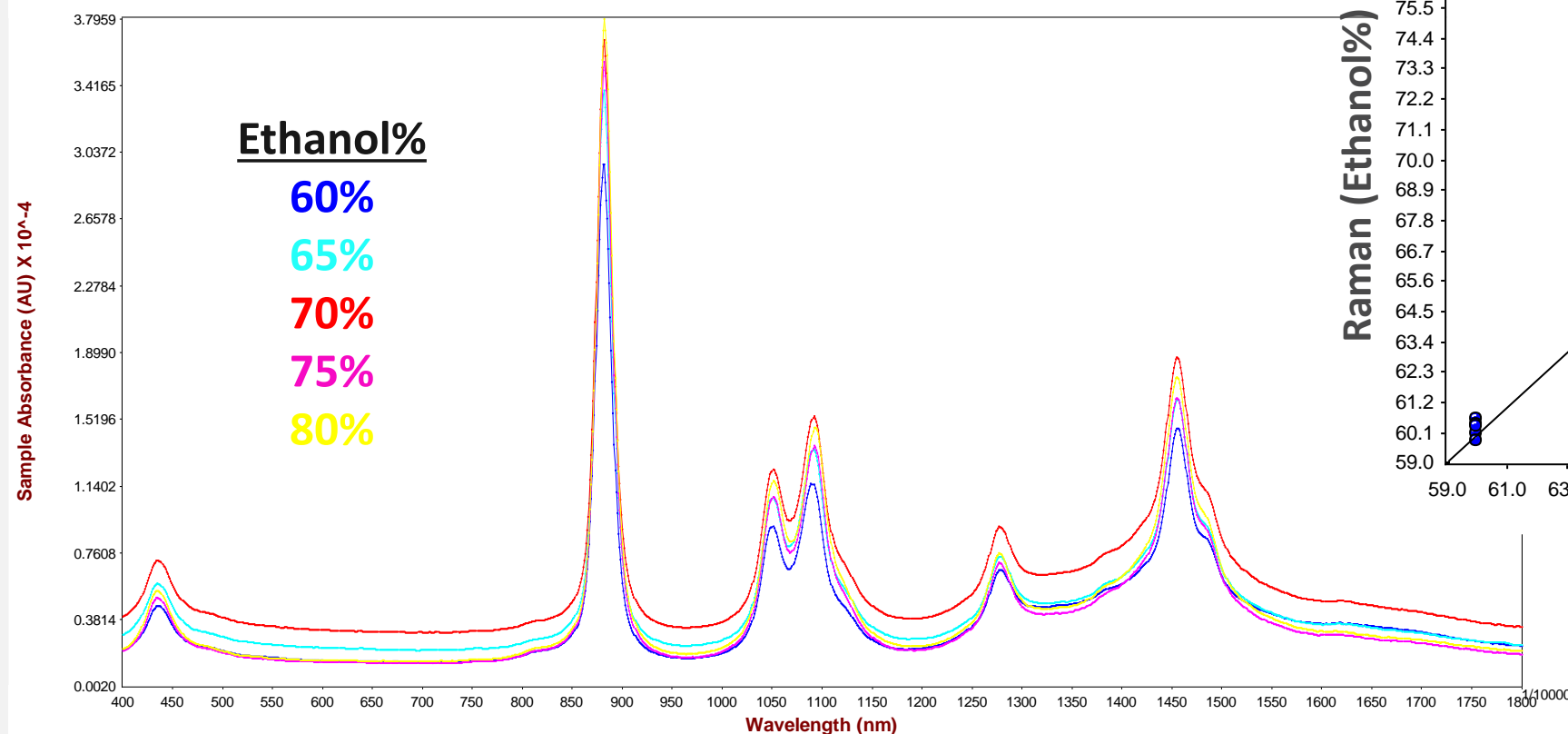


0.34% MeOH

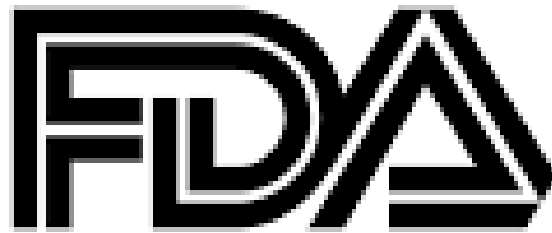


# Hand Sanitizer Production

Hand sanitizer must be at least 60% EtOH or iPrOH to be effective



# Regulatory Recognition



ASTM INTERNATIONAL



Visit the Metrohm booth  
on the exhibition floor

A large, solid yellow circle that serves as a background for the text "Questions?".

Questions?