Mid-Infrared Spectroscopy

Theory and Applications for Fuel Analysis

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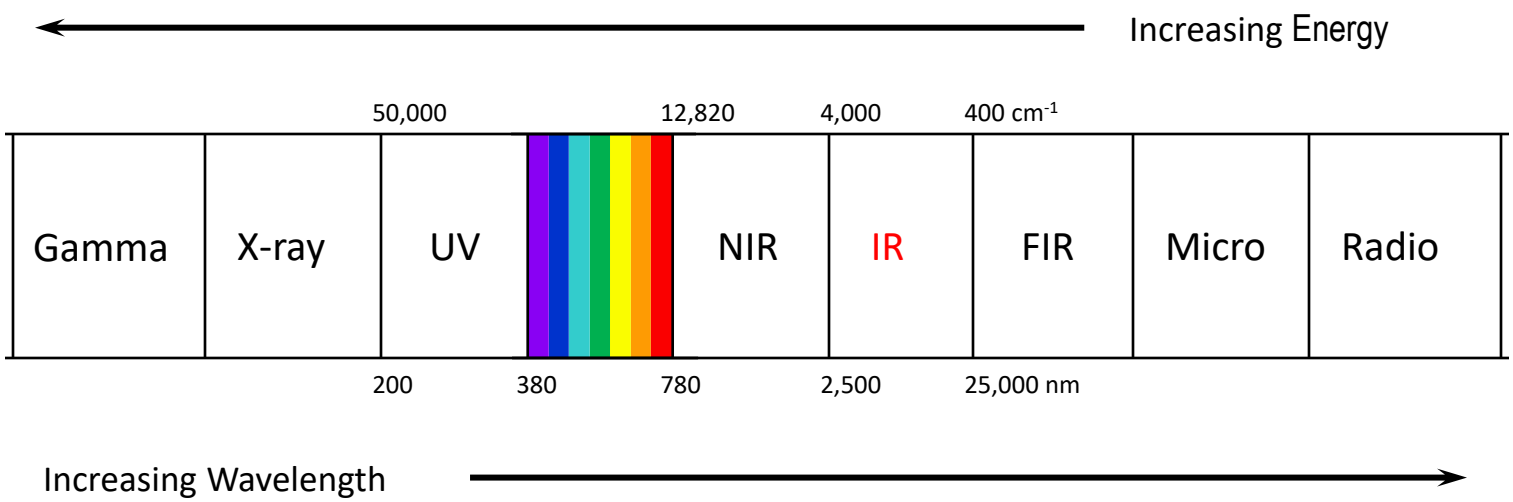
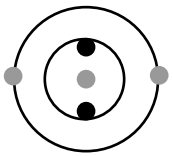
What is Infrared Spectroscopy?

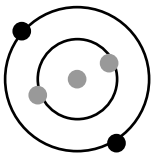
The electromagnetic spectrum





K- and L-shell electrons

X-ray diffr./fluor.

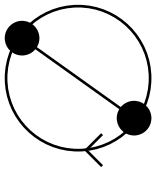


Valence electrons

UV-vis, fluor.

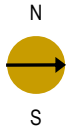
Molecular vibrations

FT-IR, Raman



Molecular rotations

FT-IR



Nuclear spin transitions

NMR

The infrared region of the electromagnetic spectrum…

The infrared region can be divided into **three** sub-regions:

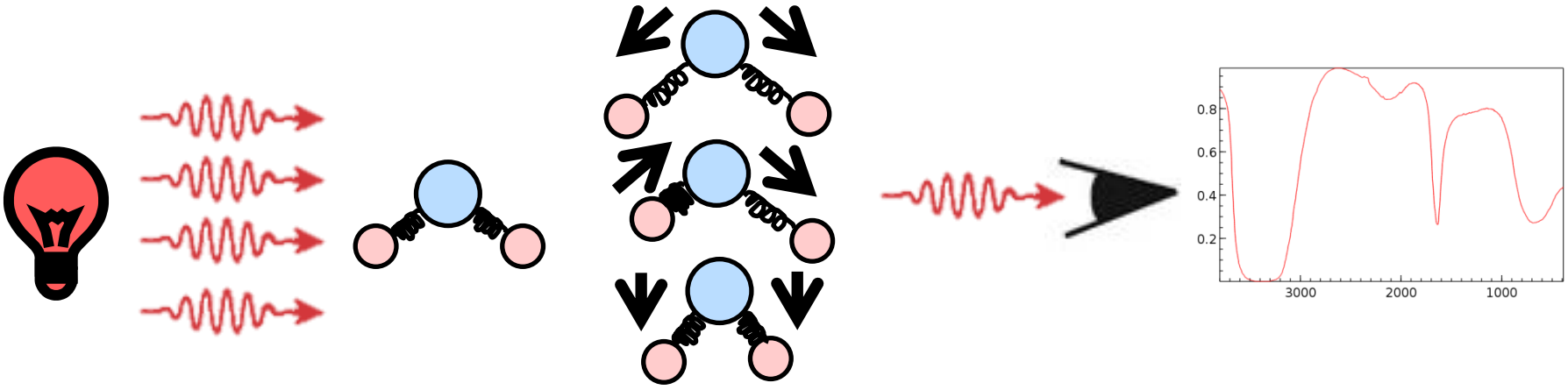
		Wavelength λ (μm)	Wavenumber $\bar{\upsilon}$ (cm^{-1})	Frequency v (Hz)
	Near IR	0.78 – 2.5	12800 – 4000	$3.8 \times 10^{14} – 1.2 \times 10^{14}$
	Mid IR	2.5 – 50	4000 – 200	$1.2 \times 10^{14} – 6.0 \times 10^{12}$
	Far IR	50 – 100	200 – 10	$6.0 \times 10^{12} – 3.0 \times 10^{11}$

- IR spectroscopists speak in ***wavenumbers***
- Number of waves per centimeter
- Inversely proportional to wavelength
- Directly proportional to energy

$$E = \frac{hc}{\lambda} = h\bar{\nu}$$

What happens when infrared radiation interacts with matter?

- When a molecule is radiated with IR light, some of the wavelengths will be ***absorbed***
- Promotes molecule into excited vibrational state
- Molecules absorb IR light at discrete frequencies depending on the types of ***chemical bonds*** present



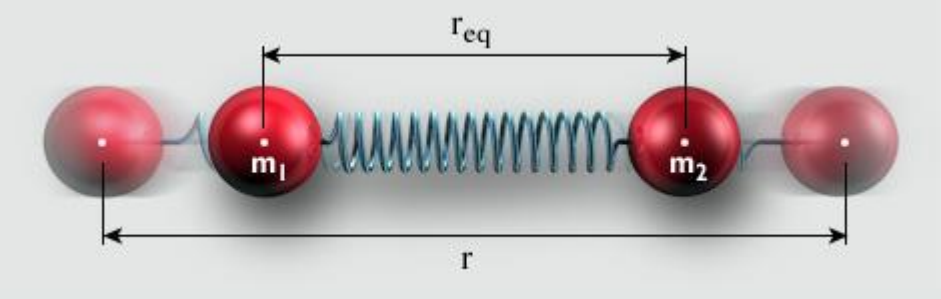
IR light Ground state Excited State Detector IR spectrum

(Absorption)

Molecular vibrations

- Atoms vibrate within molecules
  - stretching, bending
  - combinations
- Energy or frequency of vibration depends on:
  - mass of the atoms
  - strength of the bond
  - environment of the molecule
- Collective vibrations are unique to a given molecule
  - IR spectrum is considered a "molecular fingerprint"

"Ball and Spring" Model



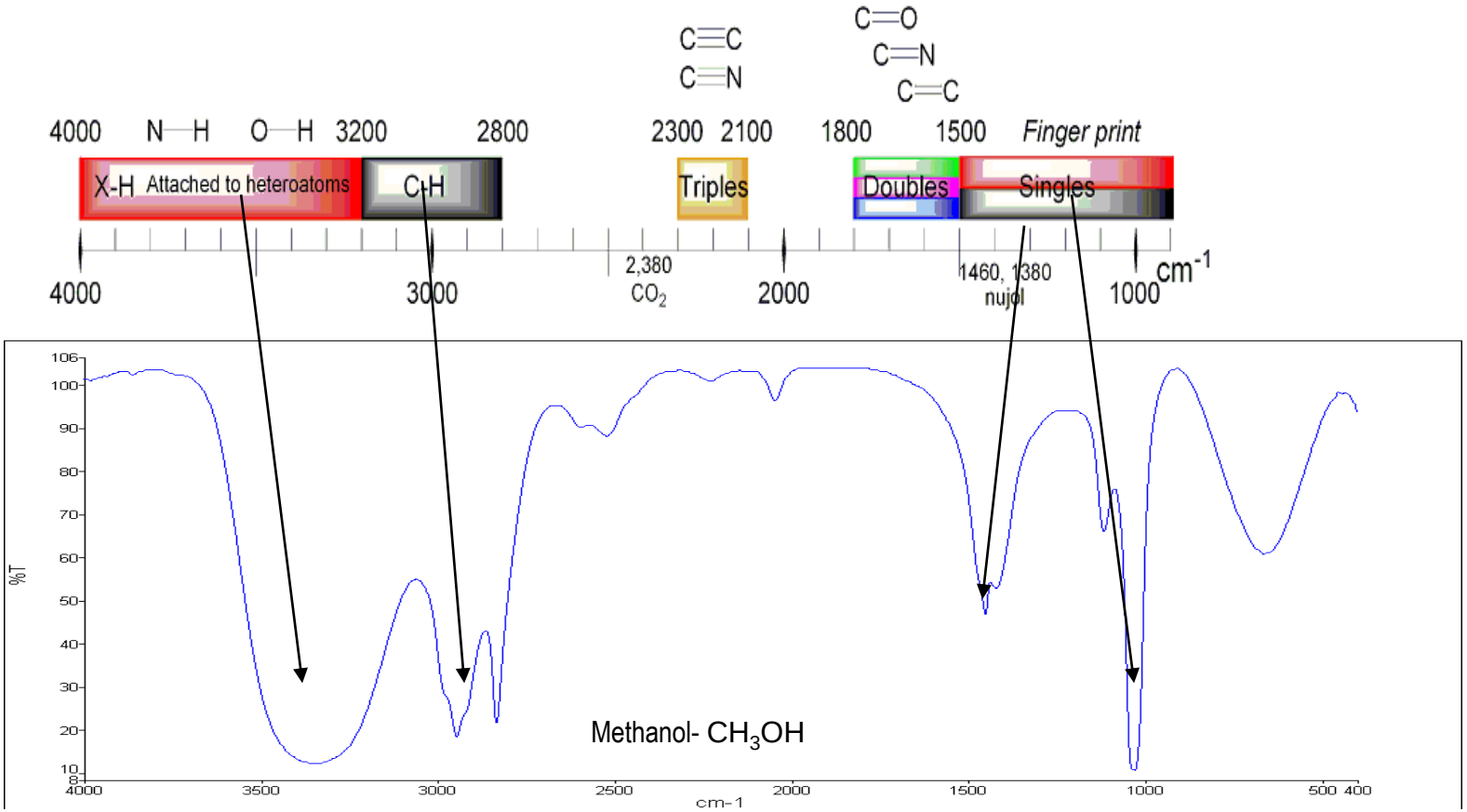
$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

k = force constant

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Typical mid-infrared spectrum

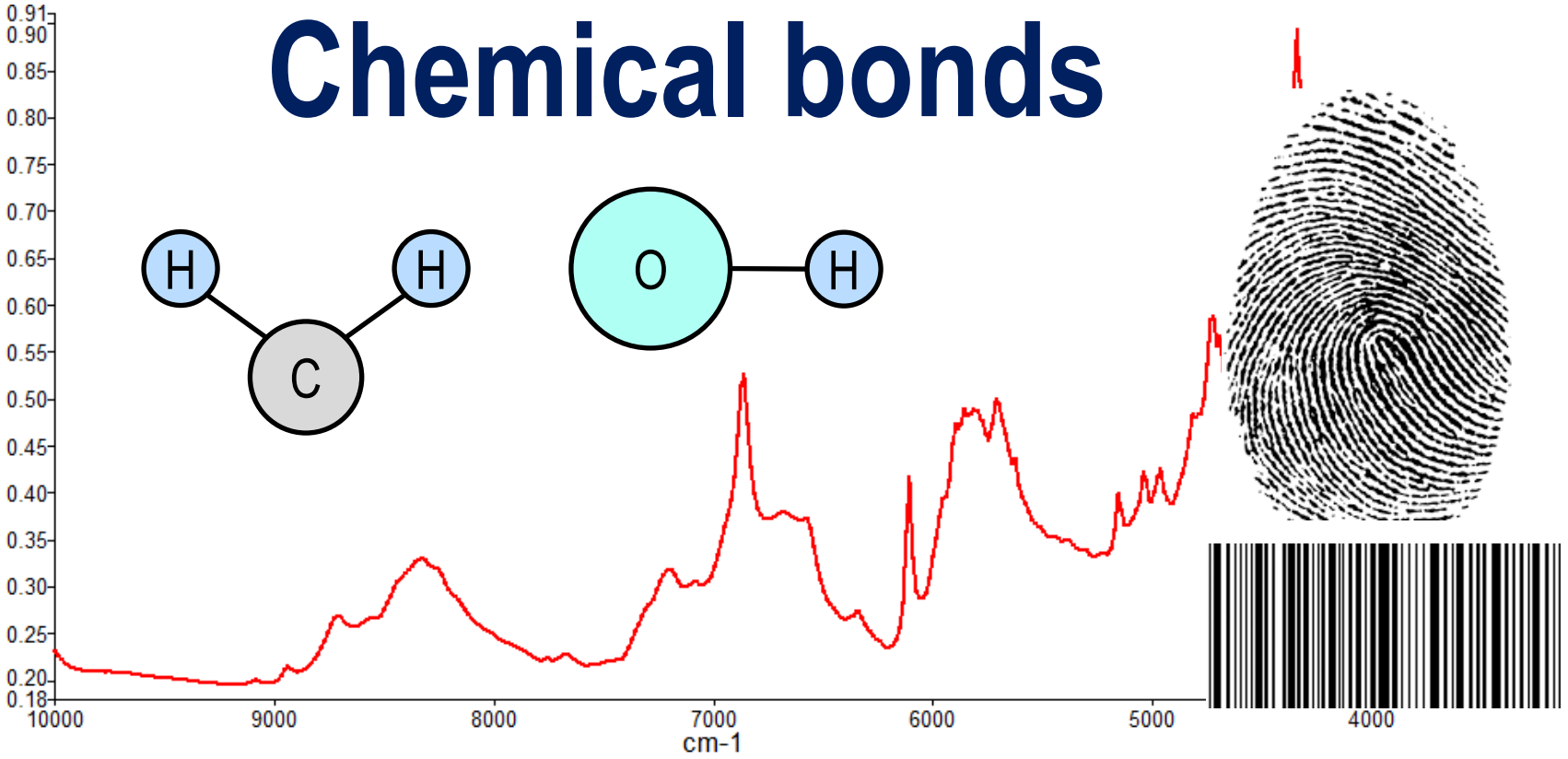
Functional groups within a molecule have characteristic peak positions



What happens as you add functional group?

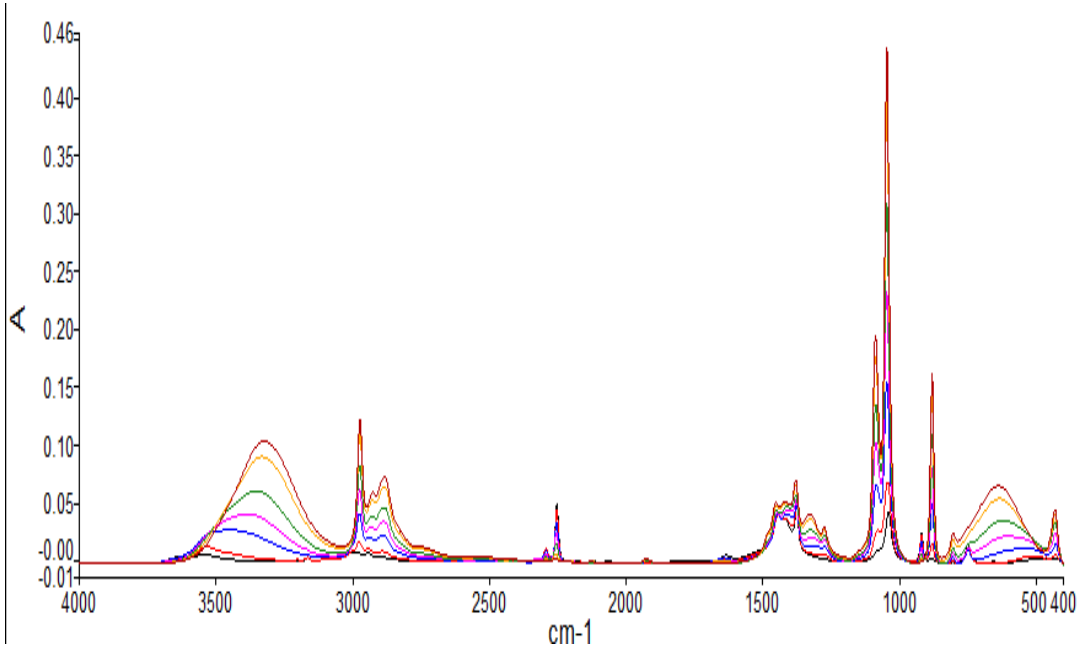
What does the infrared spectrum of a material tell us?

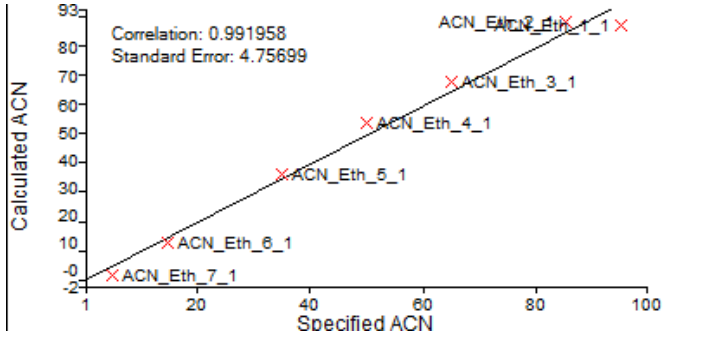
- FTIR measures the chemical structure of compounds
- Can be thought of as a '***fingerprint***' or '***barcode***' for a given compound

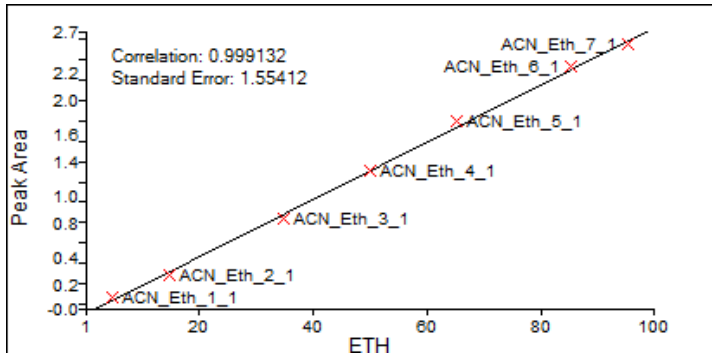


Quantitative analysis by IR

- Assign numerical value to constituent or property value based on spectroscopic data
- Requires correlation of spectral data with reference values determine by an independent technique
- Univariate or chemometrics (multivariate) analysis





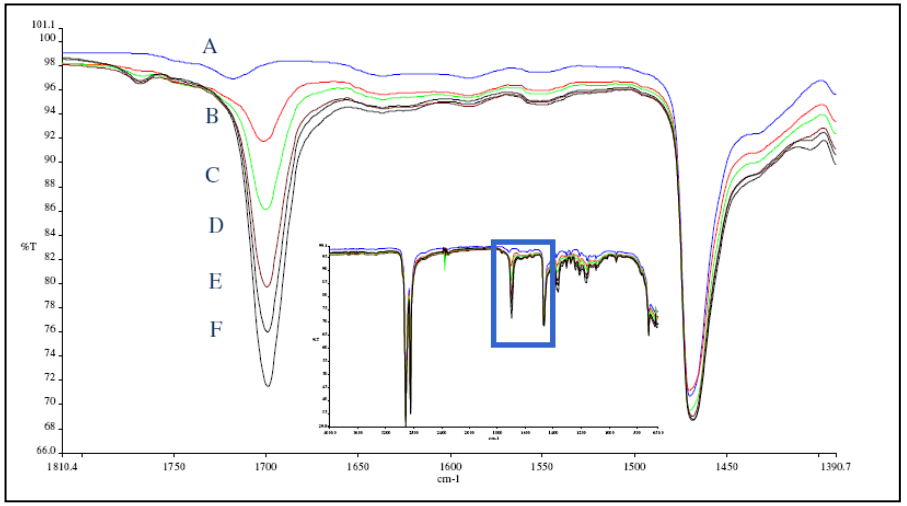


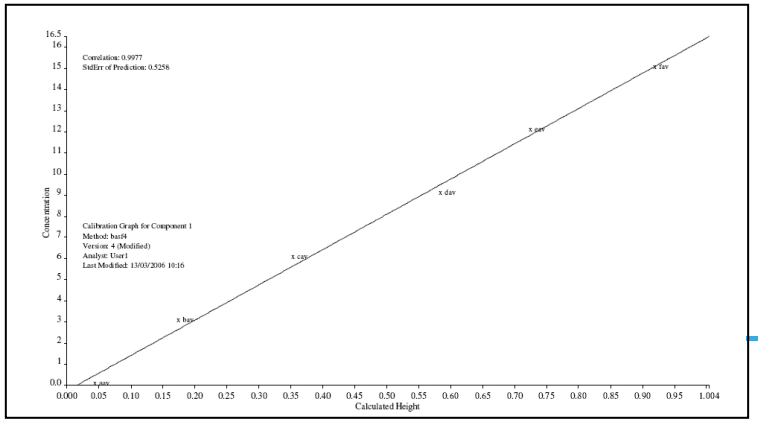
Beer's law calibration

- Univariate analysis
- Simple sample matrix
- Ability to assign concentration to a single peak or small region of spectrum
- Peak height/area, peak ratios
- Additive when multiple components are present
- Assumes linear relationship between measured absorbance and concentration

$$A = \varepsilon bc$$

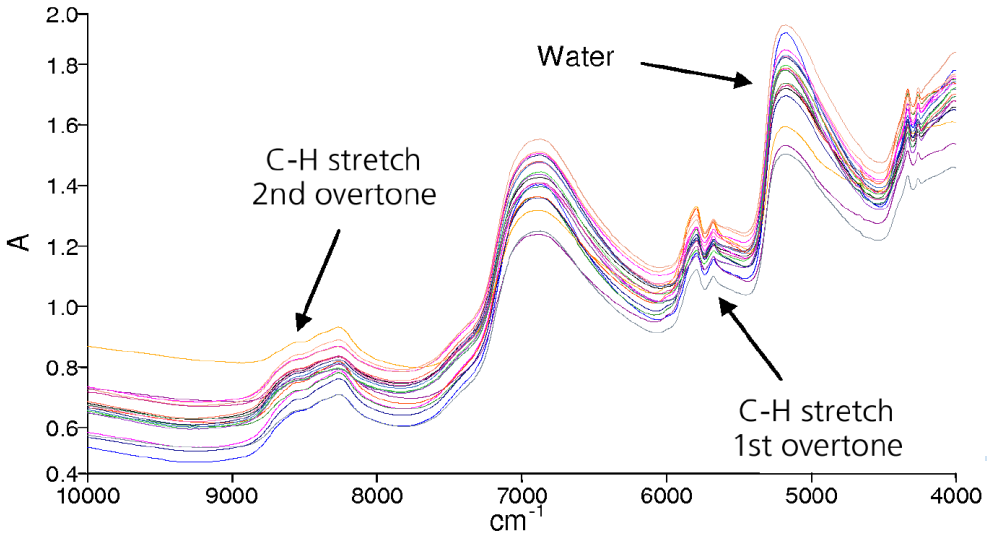
A = Absorbance
b = pathlength
ε = molar absorptivity
c = concentration





Introduction to chemometrics

- Application of *multivariate methods* for near-infrared data
- Utilizes entire spectrum
- Correlates spectral variance to property value
- Qualitative/classification
  - Principal component analysis (PCA)
  - Soft independent modeling of class analogy (SIMCA)
- Quantitative
  - Principal component regression (PCR)
  - Partial least square (PLS)



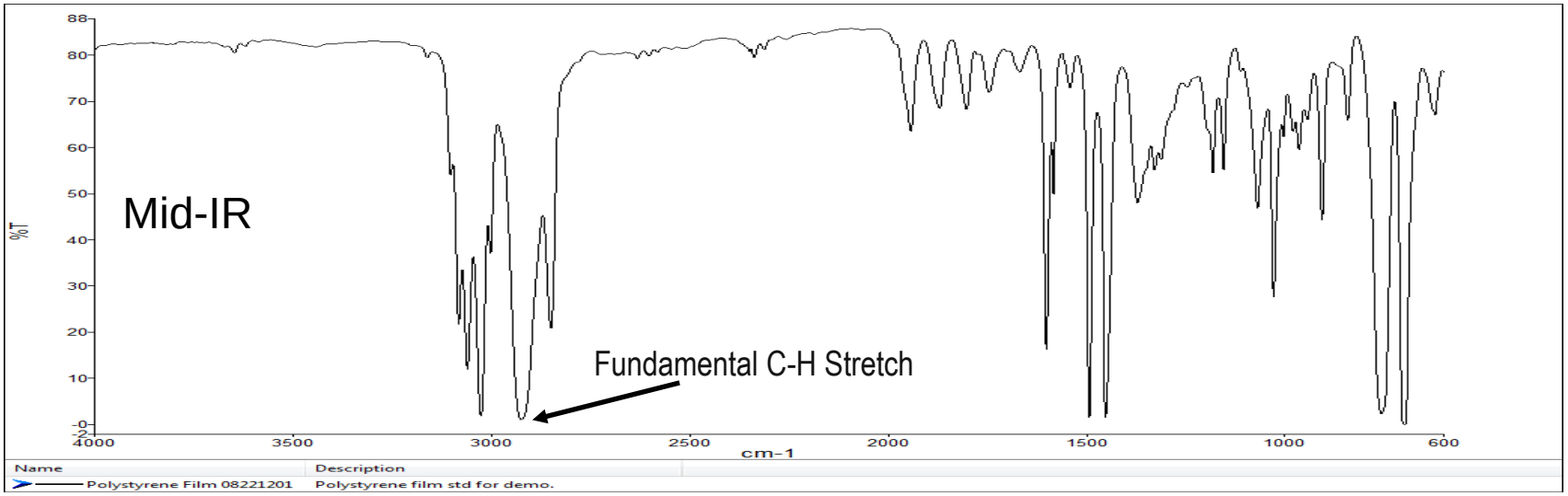
Comparison between mid-IR and Near-IR

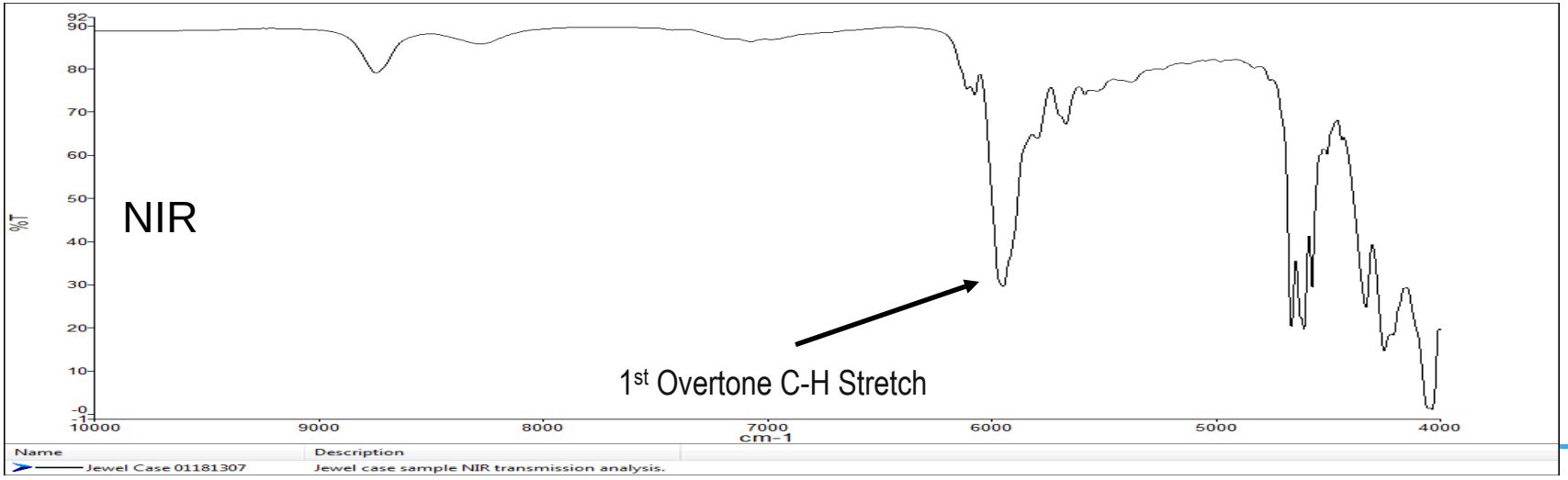
- Similarities
  - Measuring molecular absorptions
  - Molecule must have a dipole moment to be “IR active”
  - Fast data collection

- Differences

Mid-IR	*Near-IR*
4,000 – 400 cm^{-1}	12,000 – 4000 cm^{-1}
Primary vibrations	Overtone and combination vibrations
High structural selectivity	Low structural selectivity
Shorter pathlength	Longer pathlength
Smaller sample	Larger sample
more sample preparation	Less samples preparation
Beer’s Law calibration	Multivariate calibration
Good for homogenous materials	Good for heterogenous materials

Polystyrene thin film analysis





Mid-IR Applications for Fuels

FTIR methods for hydrocarbons

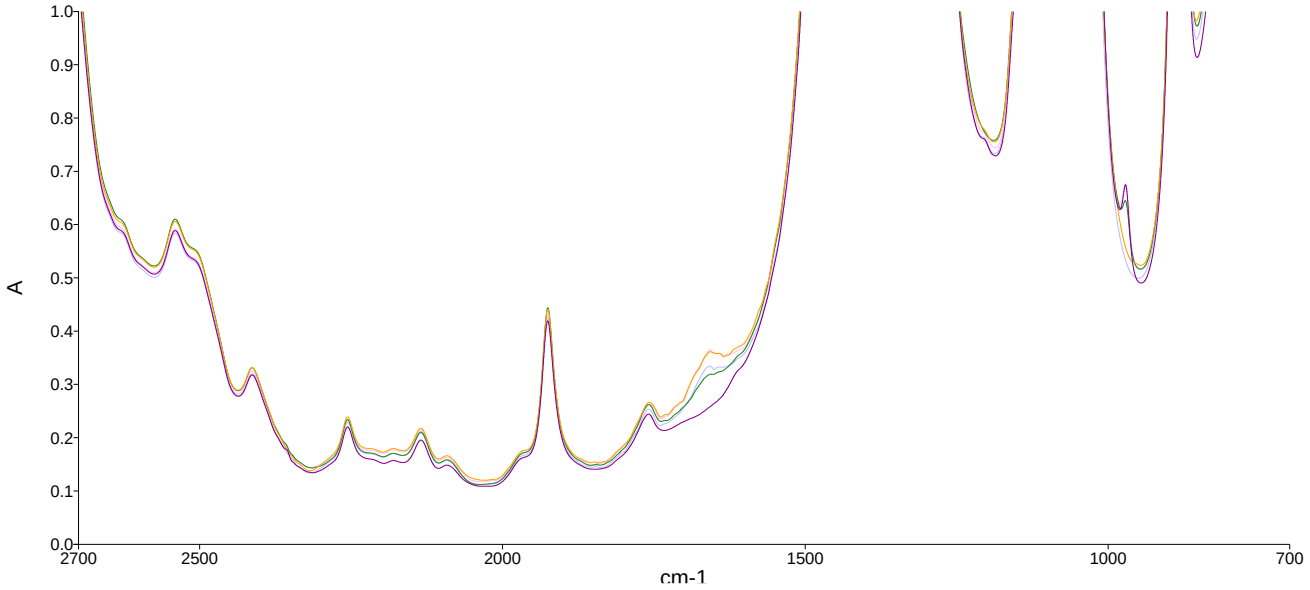
- Fuels Analysis
  - EN 14078 – Fatty Acid Methyl Esters (FAME) in middle distillates fuels
  - ASTM D7371 – FAME analysis in Biodiesel
  - ASTM D5845 – Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol, and tert-Butanol in Gasoline by Infrared Spectroscopy
  - ASTM D6277 – Determination of Benzene in spark-ignition fuels
- Lubricants (oil and grease) analysis
  - ASTM E1412 – petroleum and synthetic lubricants, and hydraulic fluids
  - JOAP – petroleum, synthetic lubricants, and hydraulic fluids
- Environmental Hydrocarbon analysis
  - ASTM D7066-04 – Extraction into hydrocarbon-free solvent then transmission FTIR

Application 1: measuring contaminates in bioethanol - background

- Bioethanol can be produced by fermentation of sugars
- Fermentation produces bioethanol and by-products
- Bioethanol purity is important for suitability and performance as a fuel
- Regulatory bodies limit the allowable concentration of impurities and specify test methods
  - ASTM D4806: Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel
  - EN 15376: Automotive fuels – Ethanol as a blending component for petrol – Requirements and test methods
- Test methods can be time-consuming, use chemicals, and expensive
- FT-IR can be used as an alternative

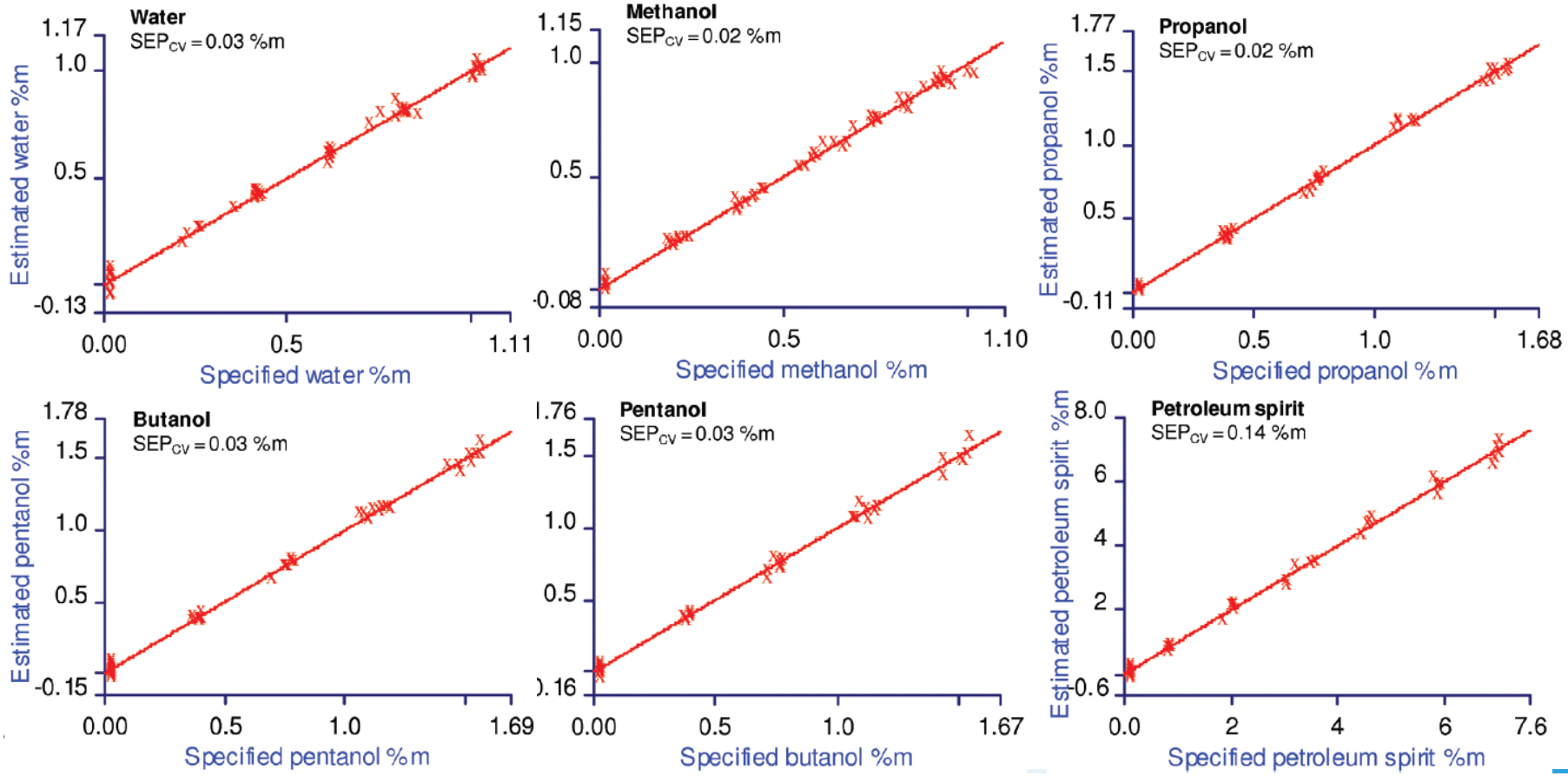
Measuring contaminates in bioethanol

- Contaminates measured
  - Methanol, water, C3-C5 alcohol, gasoline denaturant
- Method used
  - Mid-IR (FTIR) spectroscopy
  - Liquid flow cell with 0.1 mm pathlength
  - Less than 2 min analysis time per sample
- Samples
  - 60 ethanol samples spiked with contaminates in varying concentrations



Measuring contaminates in bioethanol

- Principal component regression (PCR) models were created
- Cross-validation results show good performance of models



Measuring contaminates in bioethanol

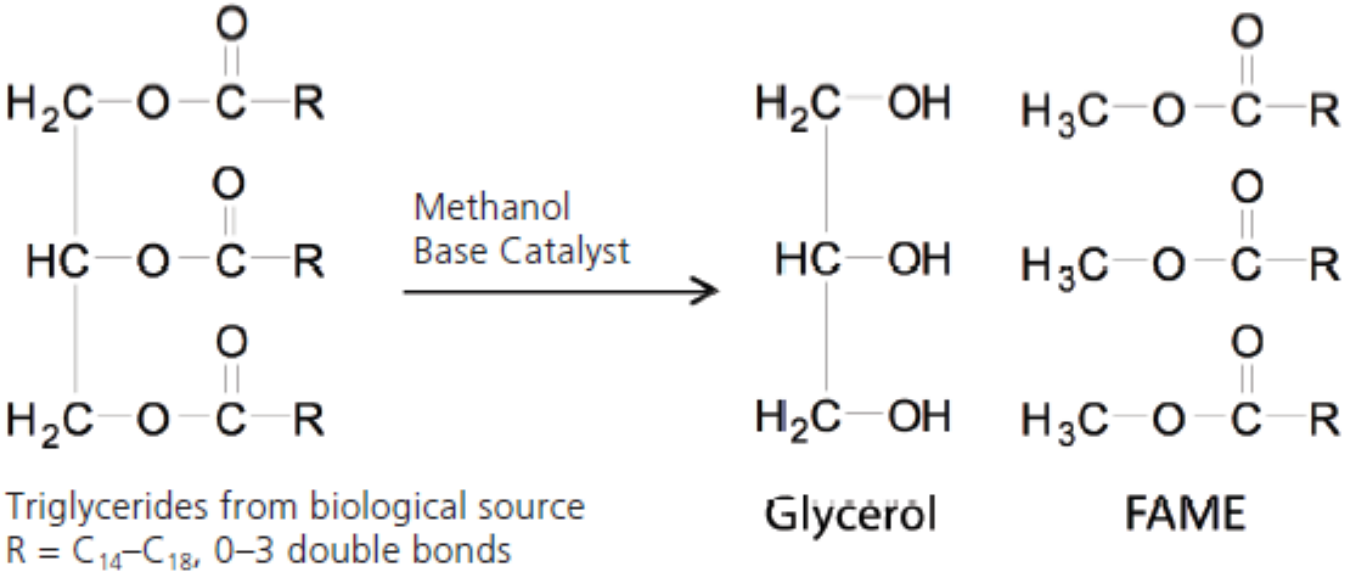
Maximum levels of impurities compared with detection limit of FTIR method

Parameter	ASTM D4806	EN 15376	FTIR LOD (5xSEP)
Water	1.0% v (1.3%m)	0.3%m	0.15%m
Methanol	0.5%v (0.5%m)	1.0%m	0.12%m
C3-C5 alcohols	N/A	2.0%m	0.48%m
Gasoline (denaturant)	1.96-5.0%v (~2-5%m)	N/A	0.7%m

- Results
  - Feasibility study – implementation required model validation and maintenance
  - Detection limit of FTIR method is defined as 5 times the standard error of prediction (SEP)
  - All detection limits are well below required minimum concentrations
  - All impurities detected simultaneously
  - 2-minute or less data collection time

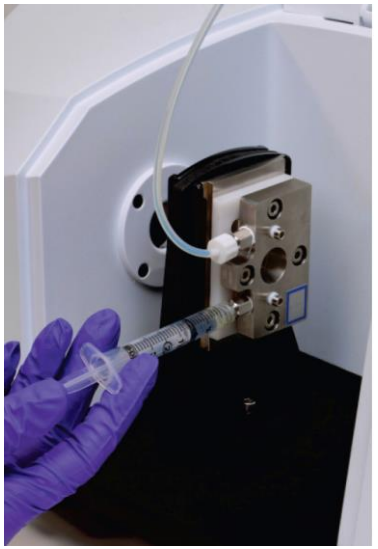
Application 2: FAME concentration in biodiesel

- Biodiesels can be produced from renewable biological sources and used oil waste streams
- The transesterification reaction converts triglycerides to glycerol and fatty acid methyl esters (FAME)
- ASTM D6277 and EN 14078 are two methods for measuring FAME (biodiesel) concentrations in petroleum diesel.

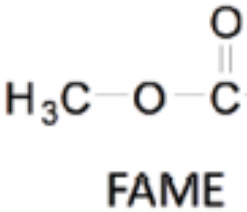


FAME in Biodiesel (EN 14078)

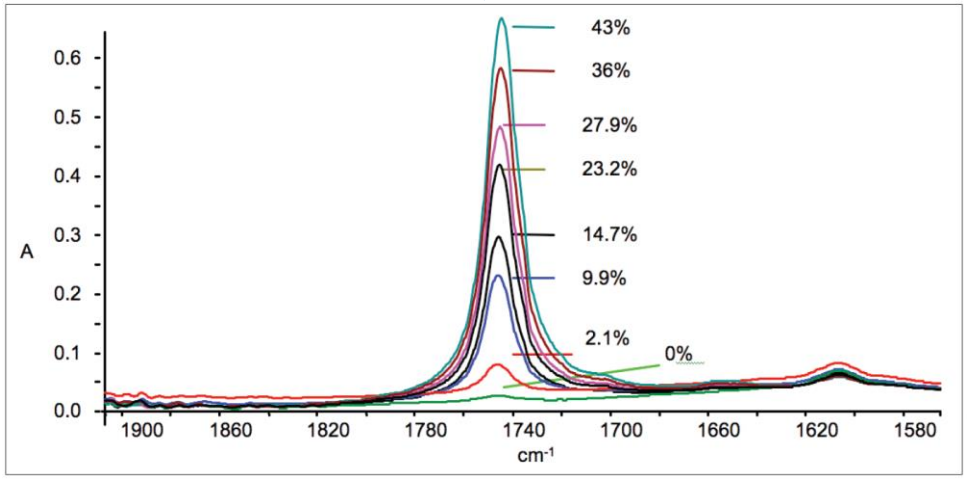
- EN 14078 – Liquid petroleum products – Determination of fatty acid methyl esters (FAME) in middle distillates infrared spectroscopy method
- Liquid Flow Cell – Beer's Law method based on the carbonyl (C=O) absorption band at 1745 cm-1

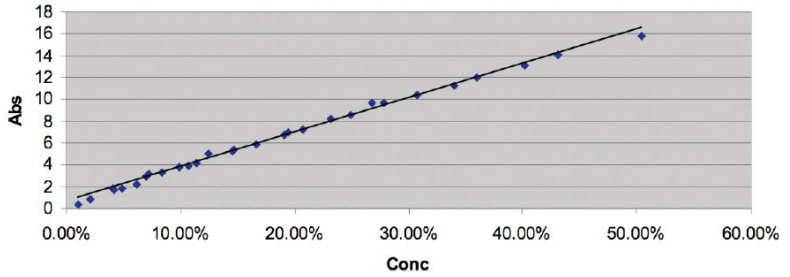


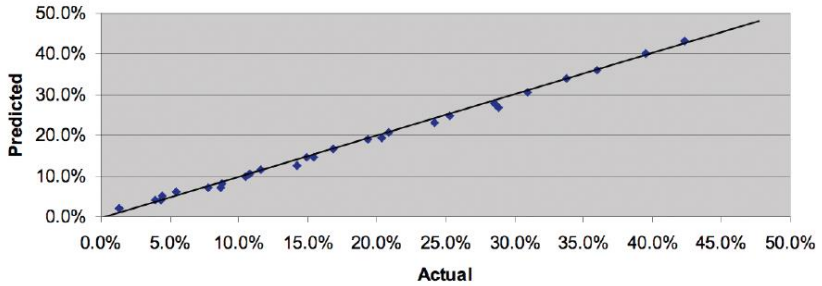
FTIR liquid flow cell



FAME



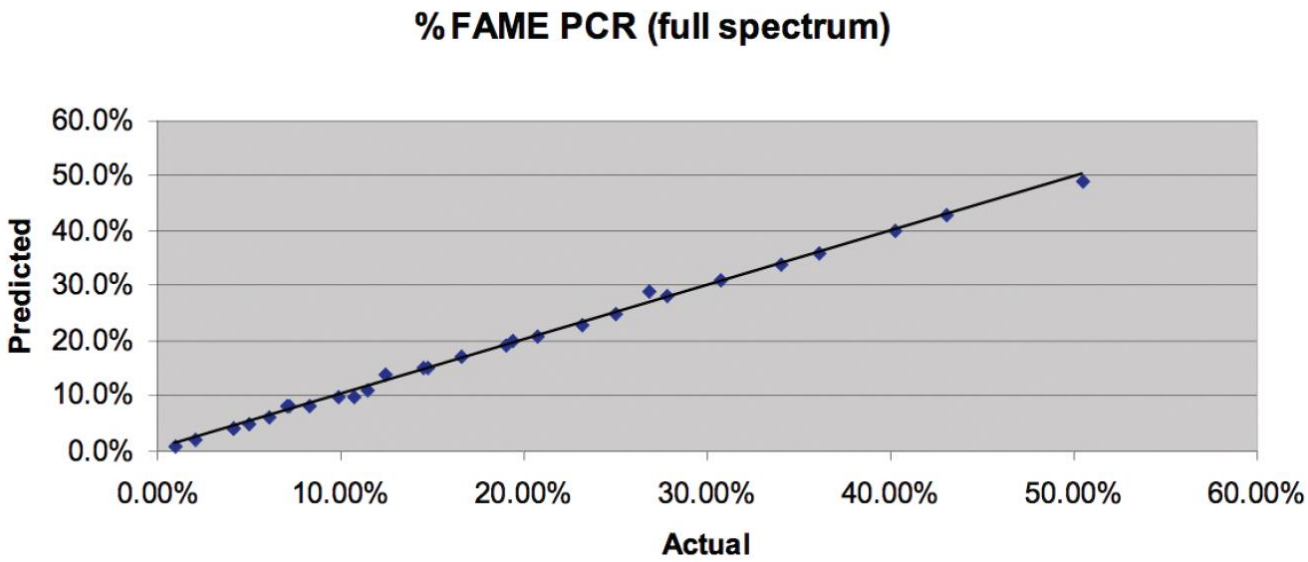




FAME in Biodiesel (ASTM D7371)

- ASTM D7371: Determination of biodiesel (fatty acid methyl ester) content in diesel fuel oil using mid infrared spectroscopy
- UATR Method – Multivariate partial least squares (PLS) method

Attenuated Total Reflectance (ATR)



Application 3: FTIR characterization of biodiesel blends

- Purpose: Characterization of thermal and chemical properties of pure petroleum diesel and biodiesel blends
- Analytical techniques:
  - FTIR with ATR
  - Evolved gas analysis using TGA-FTIR hyphenation

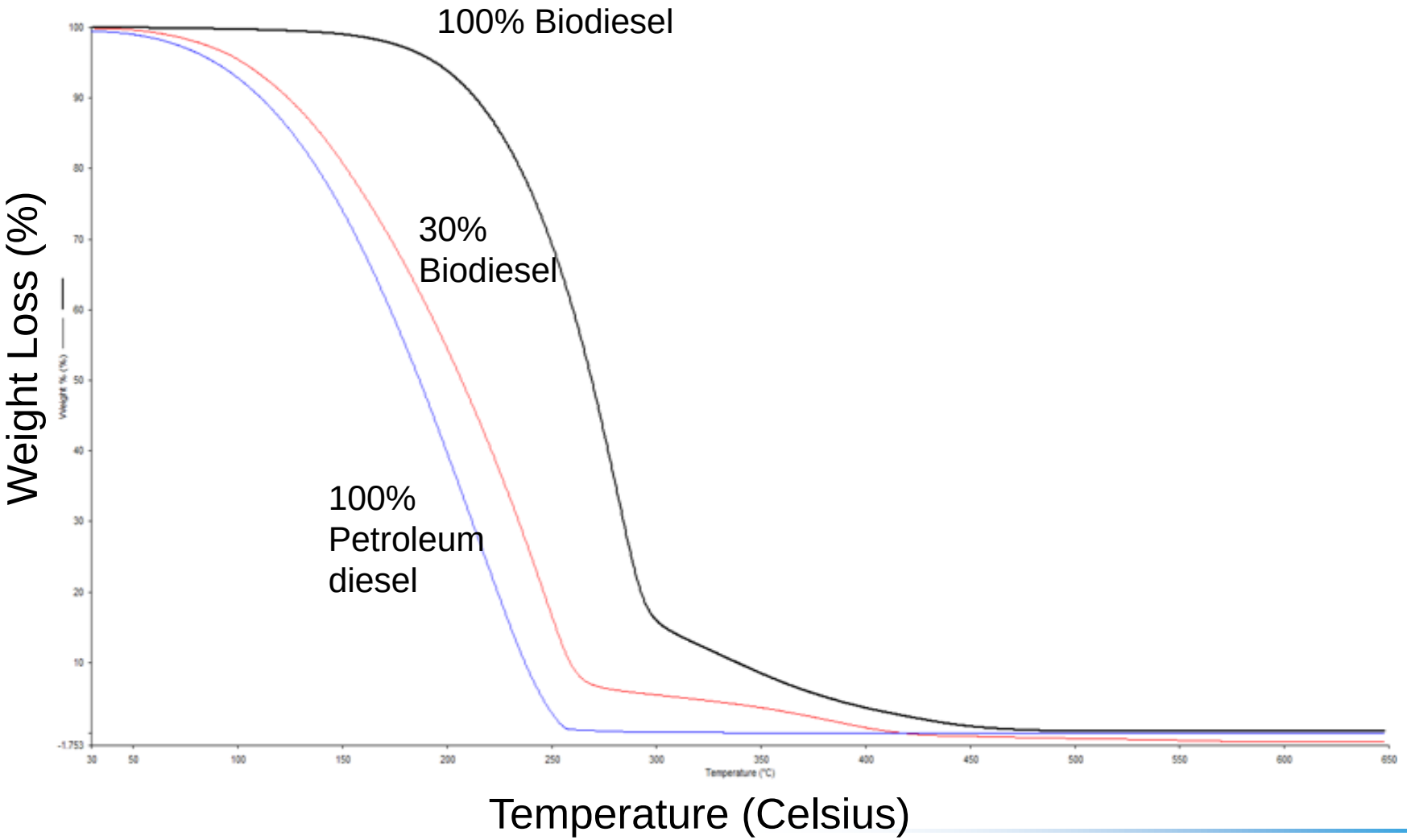
FTIR with ATR

TGA-FTIR for evolved gas analysis

Reference:
Locally Sustainable Biodiesel Production from Waste Cooking Oil and Grease Using a Deep Eutectic Solvent: Characterization, Thermal Properties, and Blend Performance. Neelam Khan, Sang H. Park, Lorraine Kadima, Carlove Bourdeau, Evelyn Calina, Charles Warren Edmunds, and David P. Pursell. ACS Omega 2021 6 (13), 9204-9212.DOI: 10.1021/acsomega.1c00556

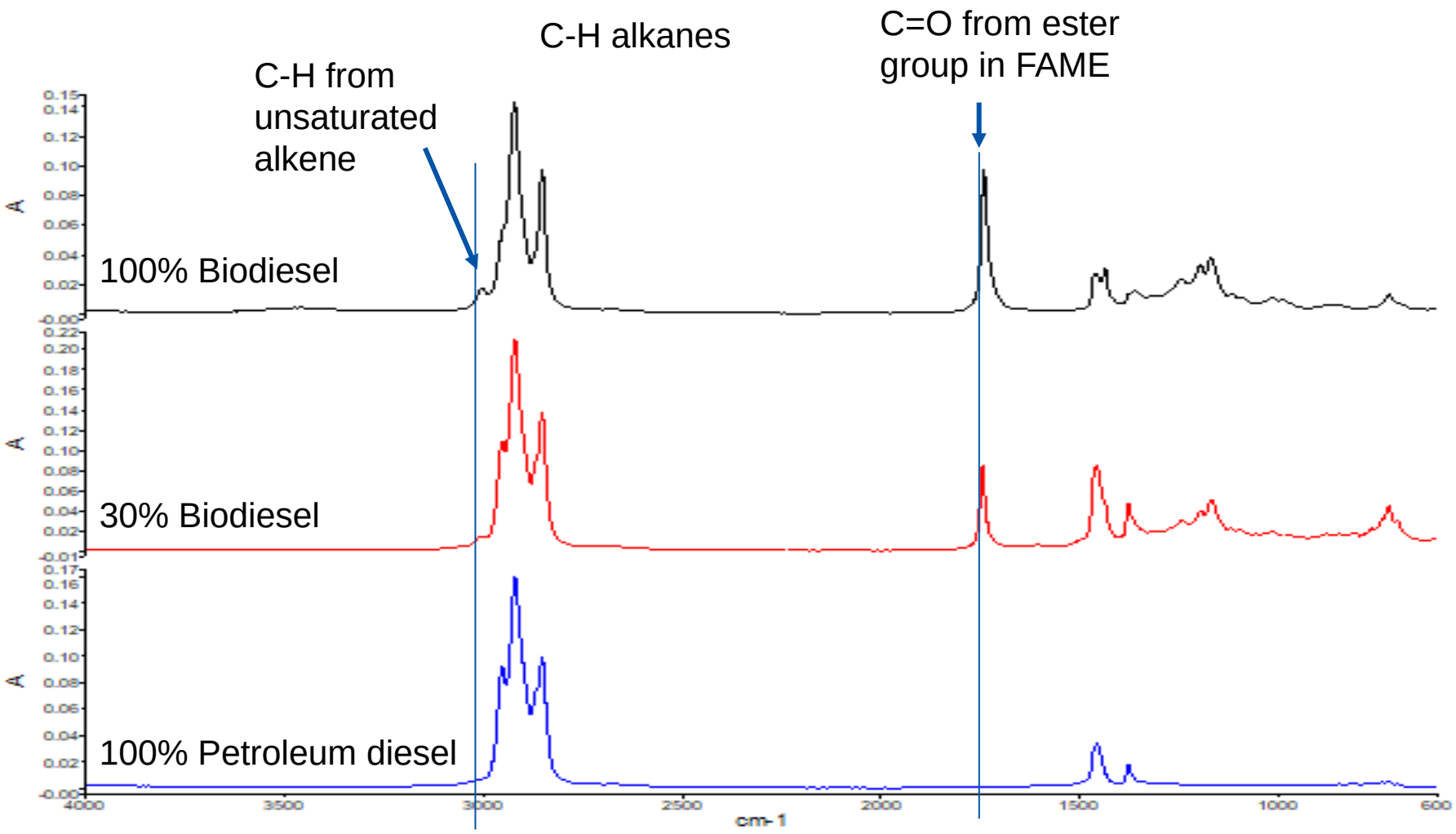
FTIR characterization of biodiesel blends

- Thermogravimetric analysis (TGA) – Weight loss data



FTIR characterization of biodiesel blends

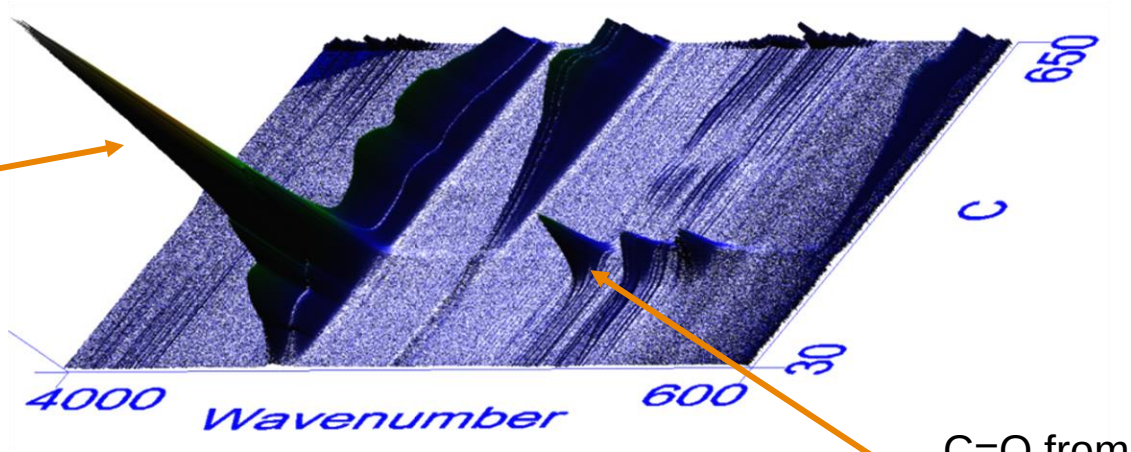
- FTIR spectra of liquid samples collected with ATR



FTIR characterization of biodiesel blends

- Evolved gas analysis TGA-FTIR data

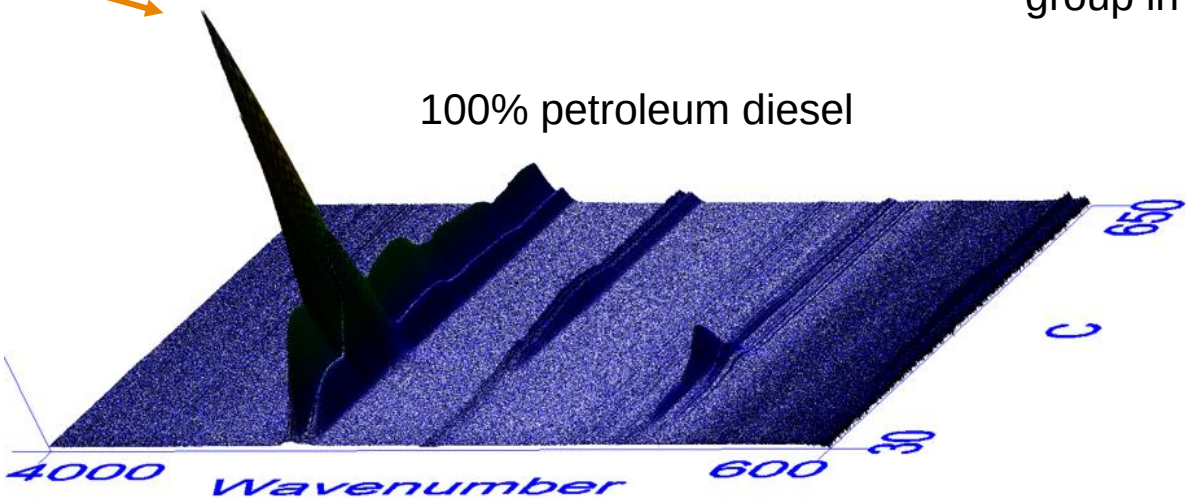
30% Biodiesel



C-H from diesel hydrocarbon

C=O from ester group in FAME

100% petroleum diesel



Conclusions

- FTIR Theory
  - Infrared spectroscopy probes the chemistry of the sample
  - The IR spectrum is a chemical finger-print
  - Data can be used for qualitative and quantitative analyses
  - Trade-offs between mid-IR and near-IR
  - Benefits of FTIR
- Applications
  - History of standard methods using IR spectroscopy for analyzing fuels
  - Routine measurements: Quality control and analysis of contaminates
  - R&D applications & Advanced applications

Thank You!

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