FTIR Discussion for Ethanol Manufacturers

California Analytical Instruments
www.gasanalyzers.com

CAI Overview

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Company Information

BUILDING 1

BUILDING 2

Experience:
- Over 30 years in Business
- Over 20,000 Analyzers

Markets:
- Industry and Automotive

Personnel:
- ~50 employees

Headquarters:
- 2 Adjacent Buildings
- (Approx. 27,000 square feet)

CAI Products

600 Series

- NDIR – CO, CO_2, CH_4, SO_2
- FID/HFID – Total Hydrocarbons
- CLD/HCLD – NO, NO_2, NO_x
- Oxygen Analyzers

Other

- FTIR
- Photo acoustic Multi-gas Analyzers
- Zero Air Generators – ZAG
- Multipoint Samplers
- Custom Sample Conditioning
- Land Fill Gas Systems
- Automotive Test Systems
- Boiler Monitoring Systems
- Other Custom Systems

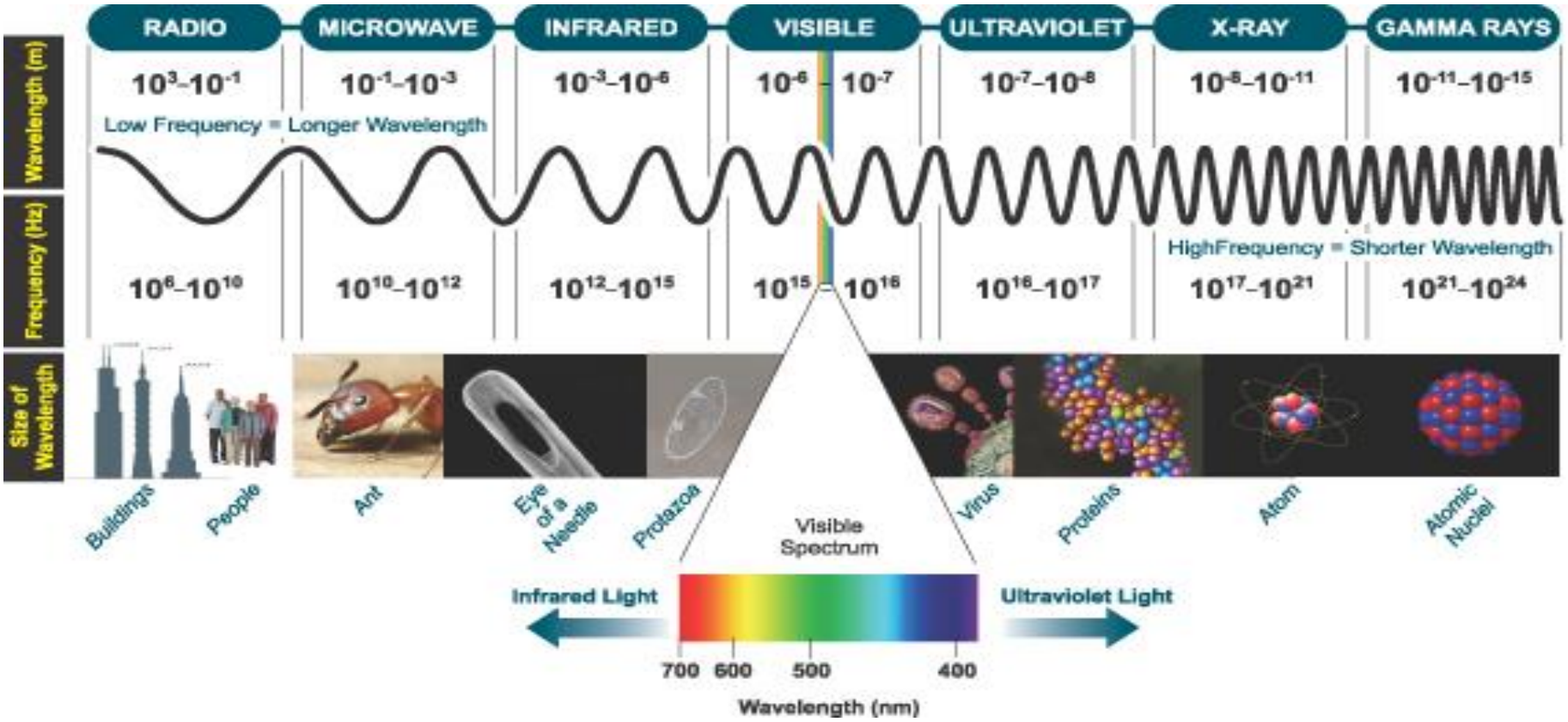
FTIR Basics

- FTIR – Stands for Fourier Transform Infrared Radiation Spectroscopy
- The Fourier transform is a mathematical function that converts from the time domain to the frequency domain:

$$\hat{f}(\xi) = \int_{-\infty}^{\infty} f(x)\, e^{-2\pi i x \xi}\, dx$$

- Infrared is radiation from a specific region of the light spectrum where most gas molecules absorb
- FTIR is a type of spectroscopy, which is the study of the interaction between matter (gases) and radiated energy (or light)
- CAI's FTIR gas analyzer is utilized to analyze hot/wet gas samples for many components.

Light Spectrum



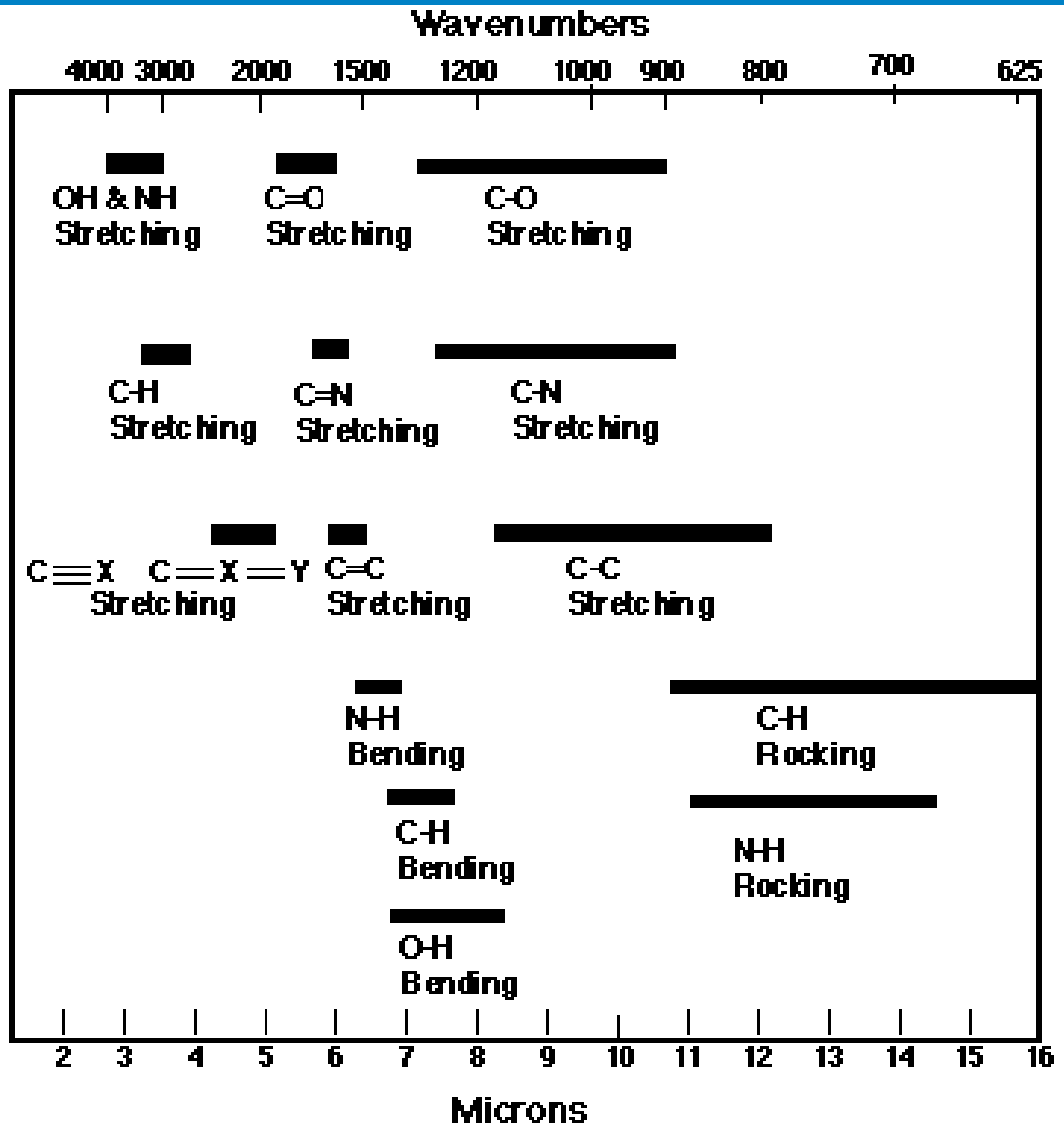
- Infrared is invisible light ranging from 1mm to 750nm in wavelength
- Infrared light can be divided into three parts:
  - Far infrared -1mm to 10µm
  - Mid infrared - 10µm to 2.5µm ← most components have strongest absorption here
  - Near infrared - 2.5µm to 750 nm


FoxTrot
by Bill Amend
DO YOU SELL ULTRAVIOLET BULL?
EXCUSE ME?
WHAT ABOUT REGULAR VIOLET BULL?
NO.
BLUE BULL?
NO.
GREEN BULL?
YELLOW BULL?
ORANGE BULL?
NO.
NO.
NO.
RATS. OK, I'LL TAKE A RED BULL.
I WAS HOPING FOR SOMETHING A LITTLE HIGHER-ENERGY.
AT LEAST IT ISN'T INFRARED BULL.
www.foxtrot.com

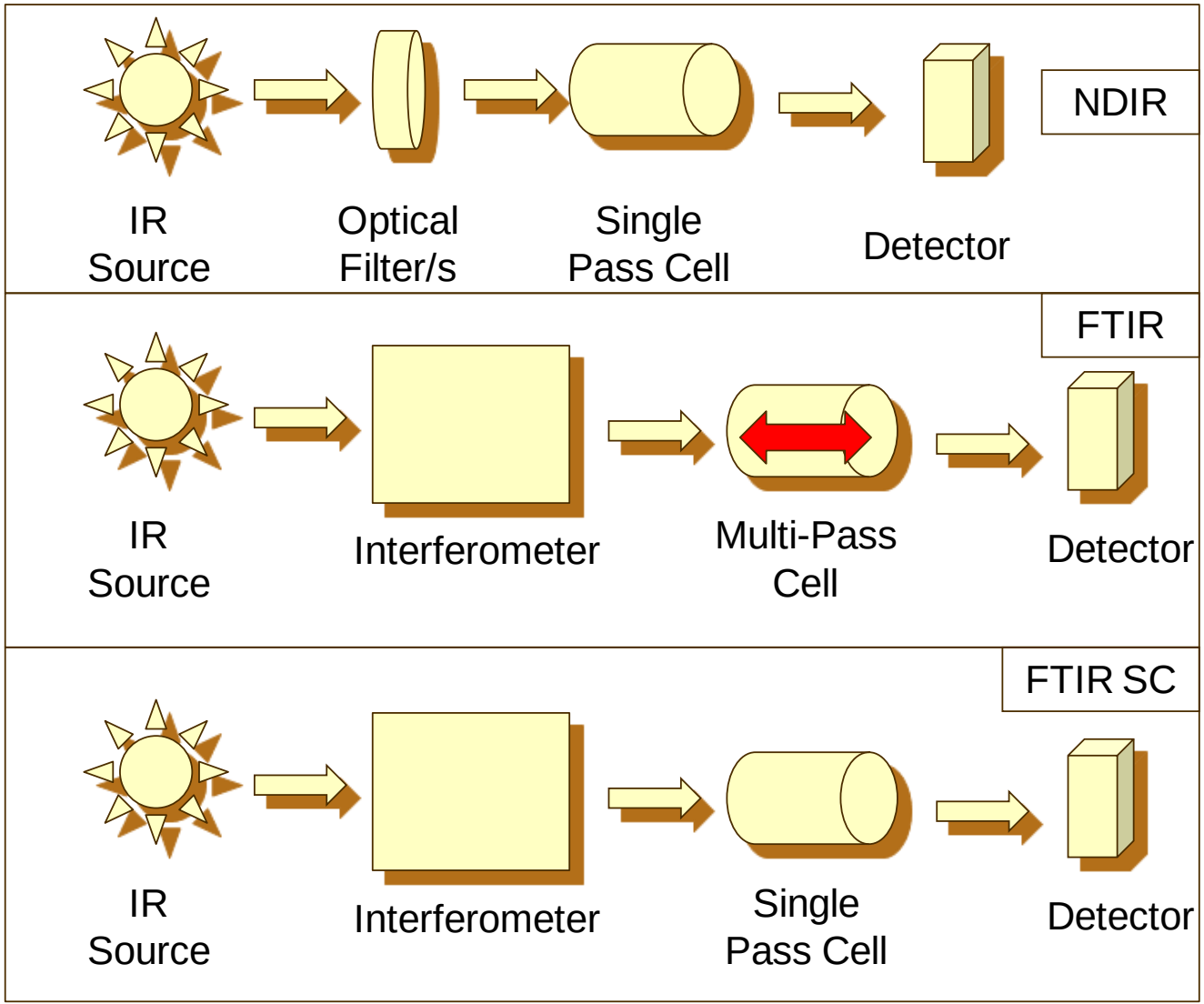
IR Absorbing Molecules

- Not every molecule absorbs infrared light
  - Monoatomic
    - He, Ar, Ne, etc…
  - Homoatomic diatomic
    - N_2, O_2, H_2, etc…
- Several molecules do absorb infrared light
  - The CH_2 bond in hydrocarbons are a good example:

Symmetrical stretching | Asymmetrical stretching | Scissoring or bending | Rocking | Wagging | Twisting

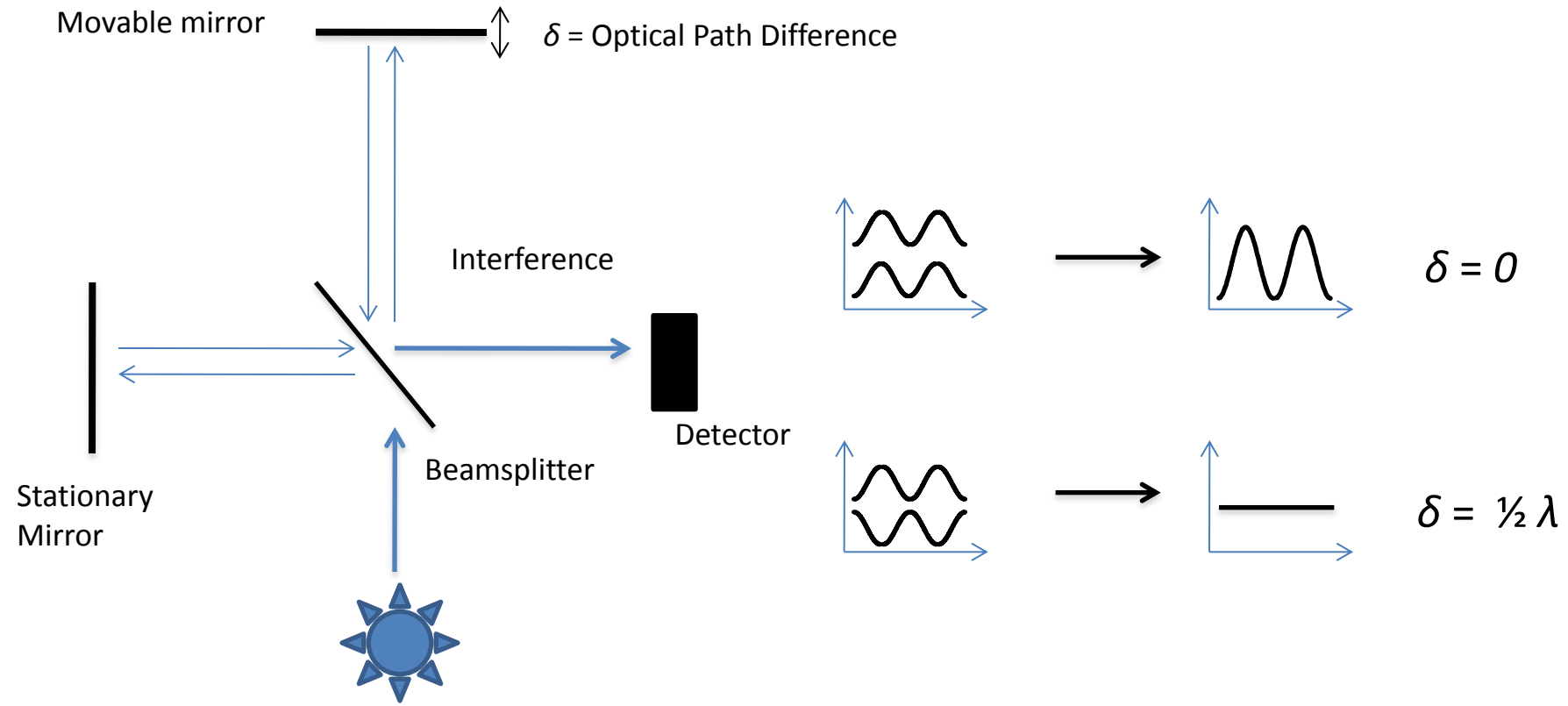

Wavenumbers
4000 3000 2000 1500 1200 1000 900 800 700 625
OH & NH Stretching
C=O Stretching
C-O Stretching
C-H Stretching
C=N Stretching
C-N Stretching
C≡X C=X=Y Stretching
C=C Stretching
C-C Stretching
N-H Bending
C-H Bending
O-H Bending
C-H Rocking
N-H Rocking
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Microns

NDIR Versus FTIR

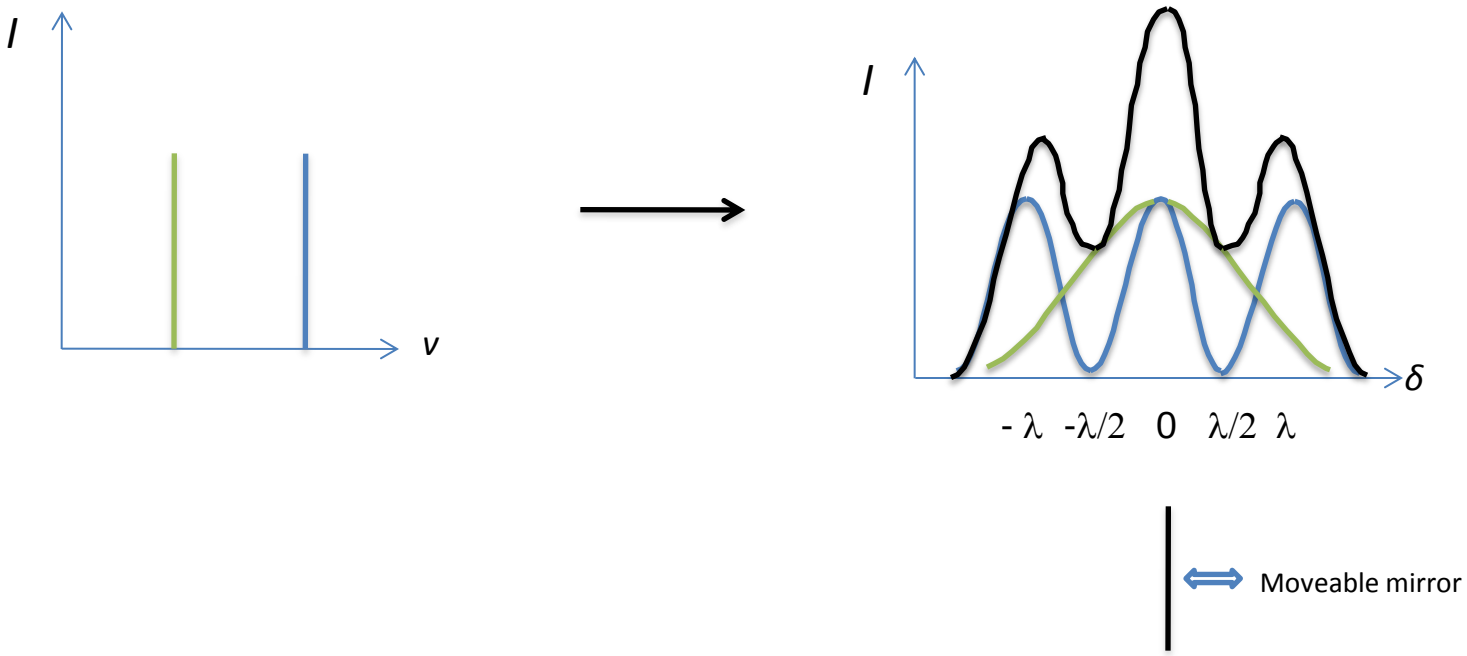


Michelson Interferometer

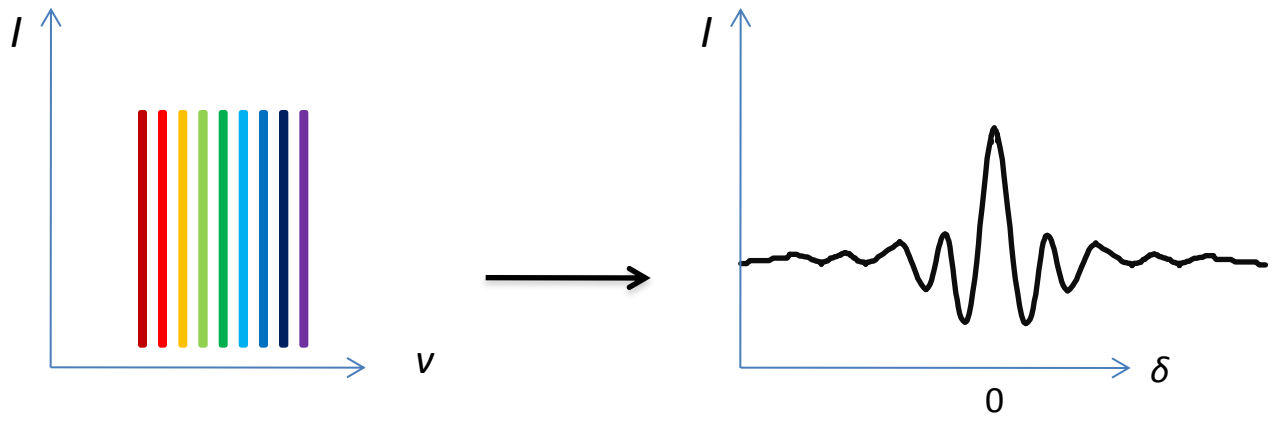
- The Michelson interferometer principle
- Monochromatic light



- Dichromatic source



- Broadband source



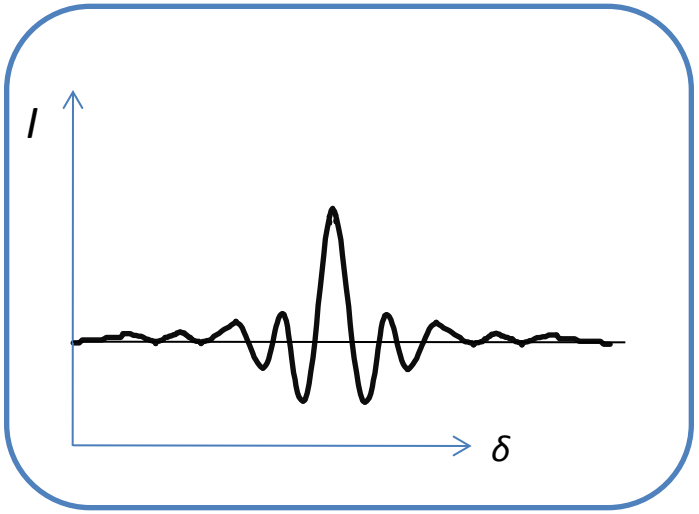
Continuous IR spectrum

Interferogram

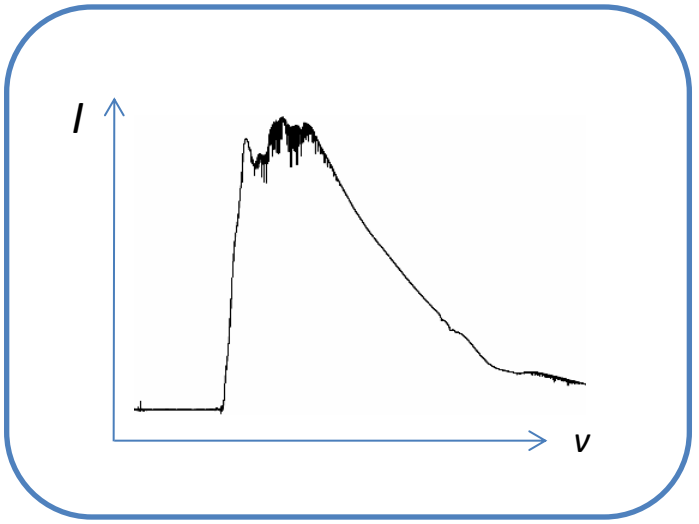
$$I(\delta) = \int_{-\infty}^{\infty} B(\nu)\cos(2\pi\nu\delta)d\nu$$

FT

$$B(\nu) = \int_{-\infty}^{\infty} I(\delta)\cos(2\pi\nu\delta)d\delta$$



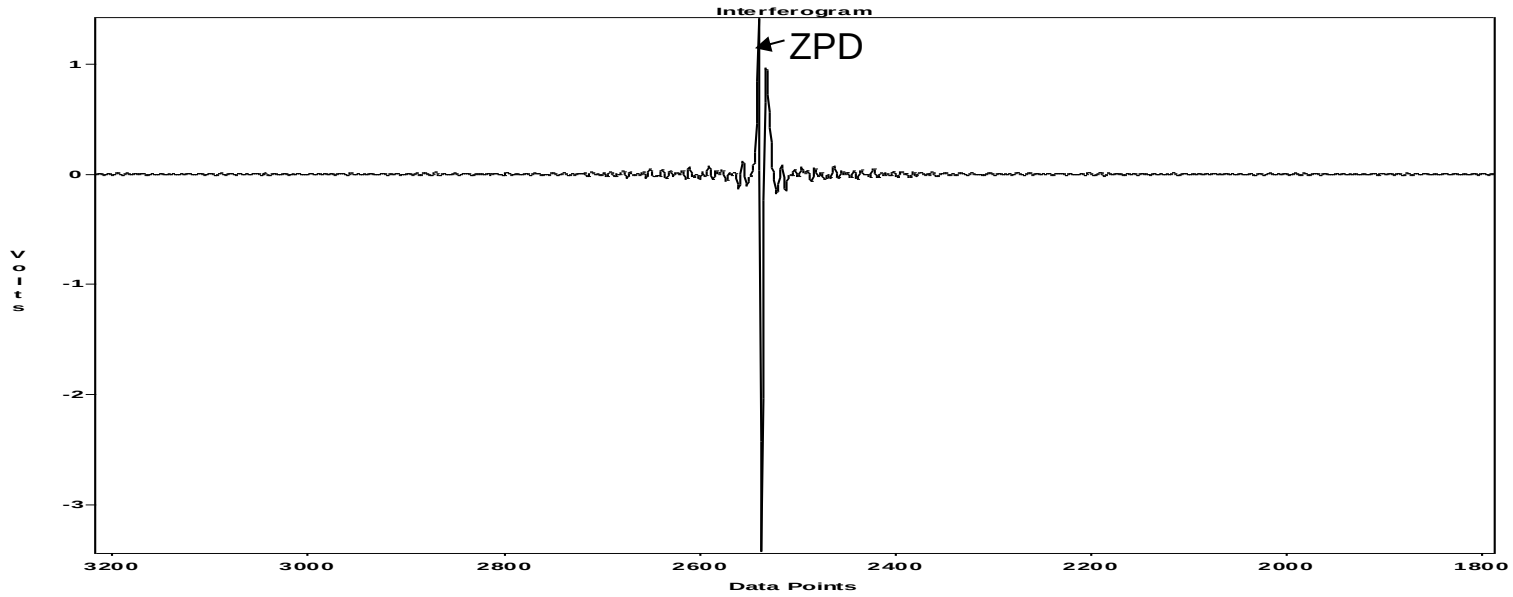
Time domain: *I* vs. *δ*



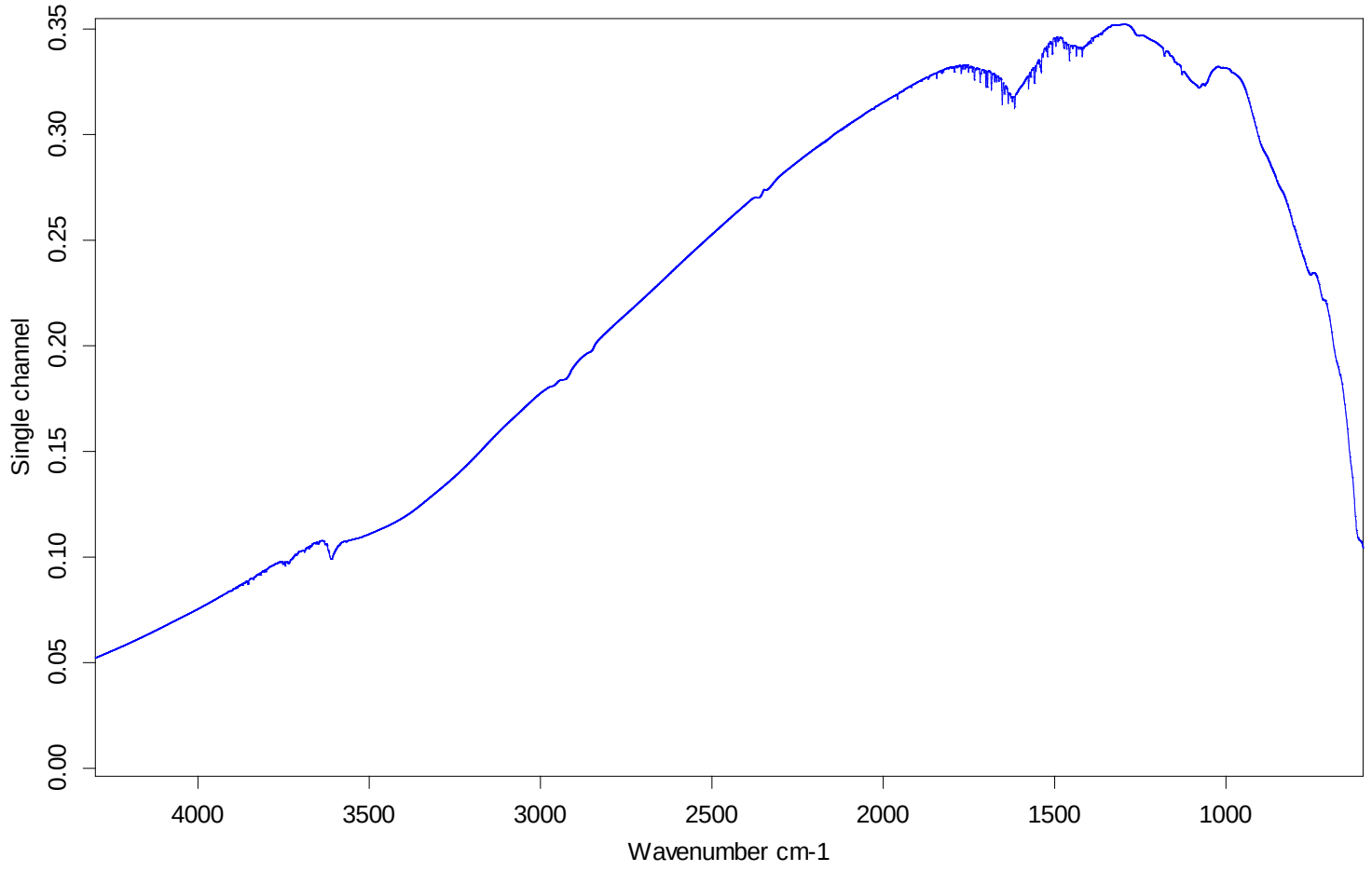
Frequency domain: *I* vs. *ν*

Fast Fourier Transform

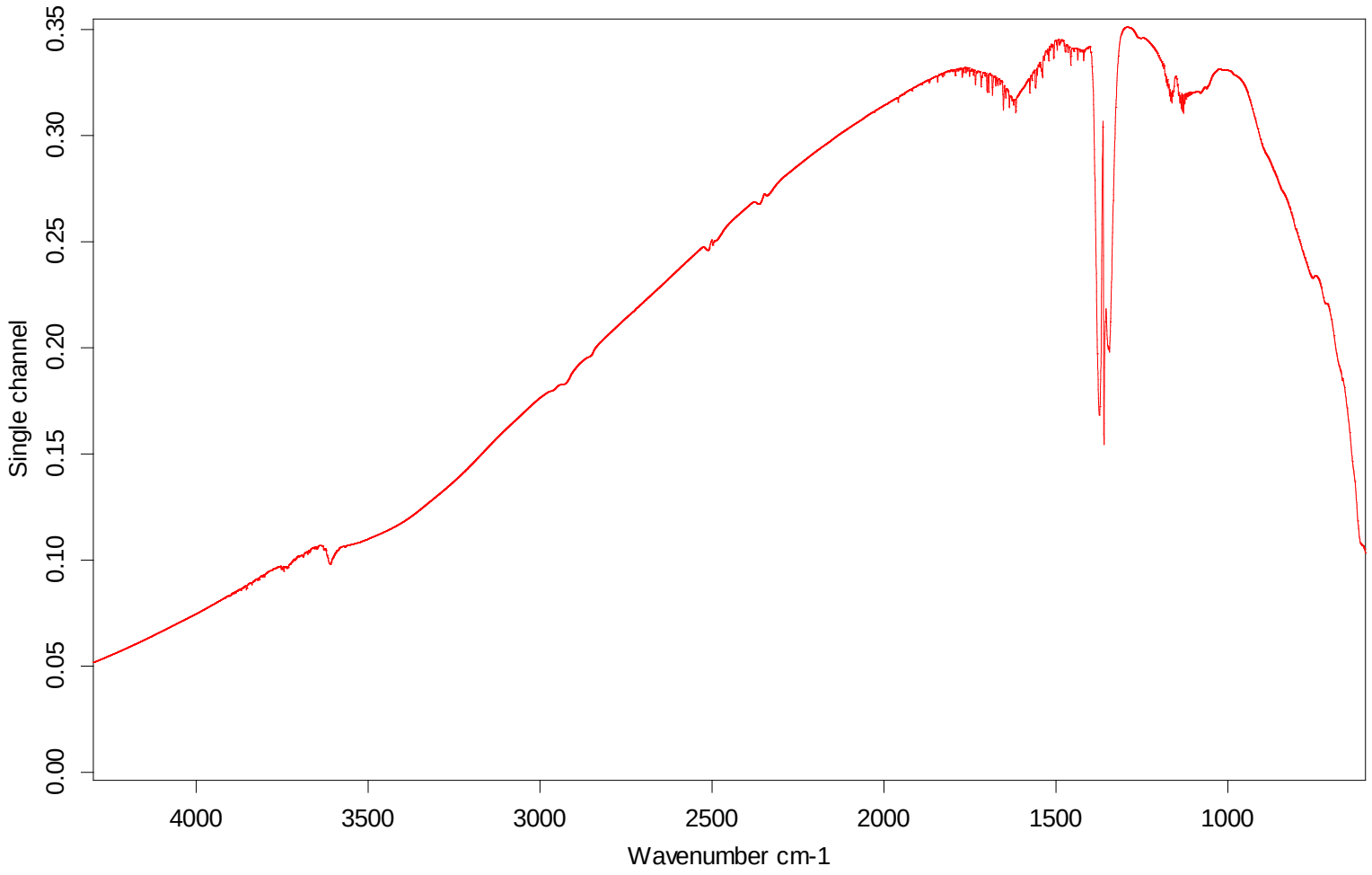
- The highest peak intensity is attained when AB=AC
- The maximum of the highest intensity peak is called the zero path difference (ZPD) point
- After the interferogram has been created by the instrument, the Fourier transform is applied to it, which then results in a single beam spectrum



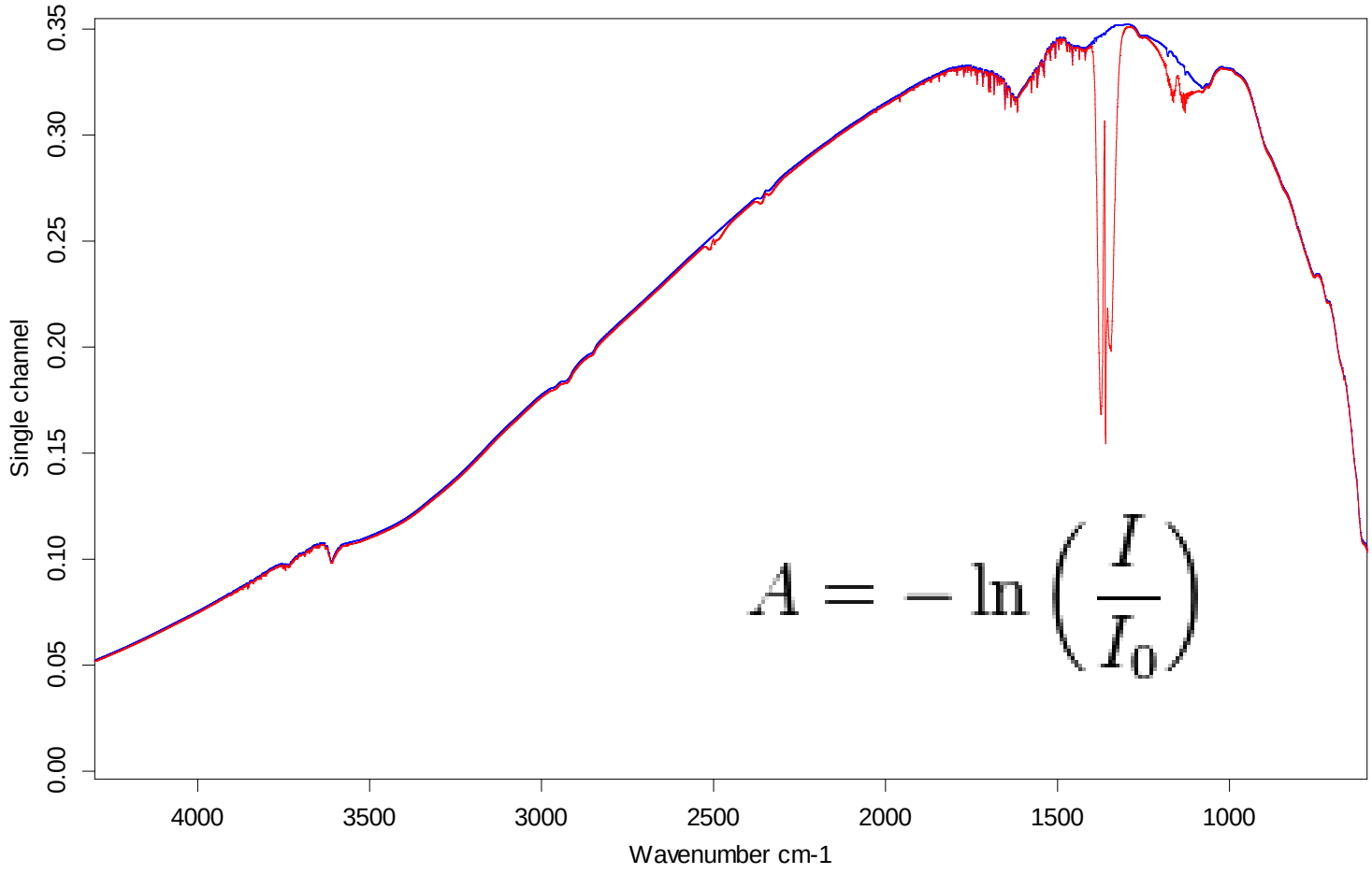
Single Beam Spectrum (Background)



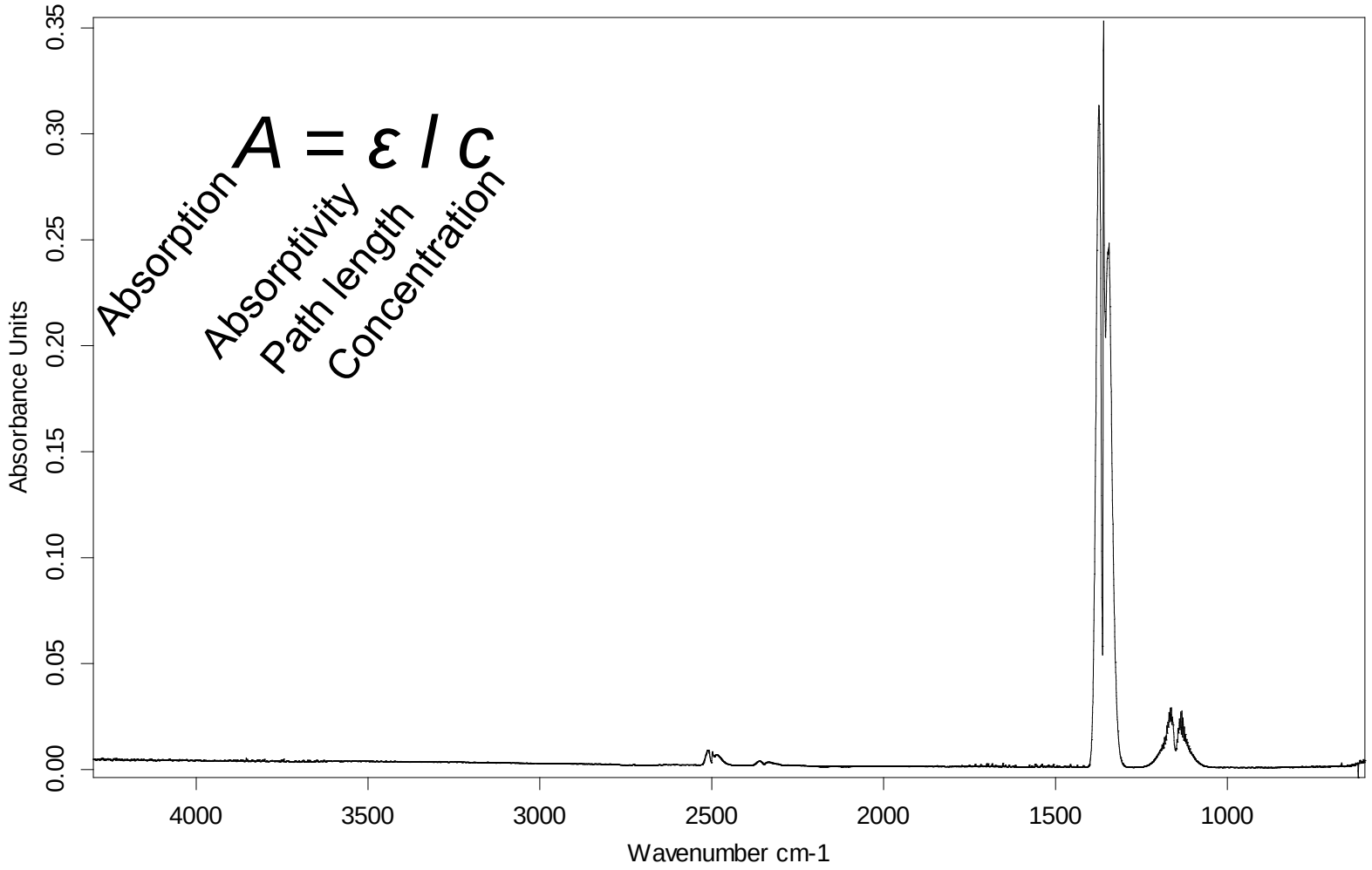
Single Beam Spectrum (Sample)



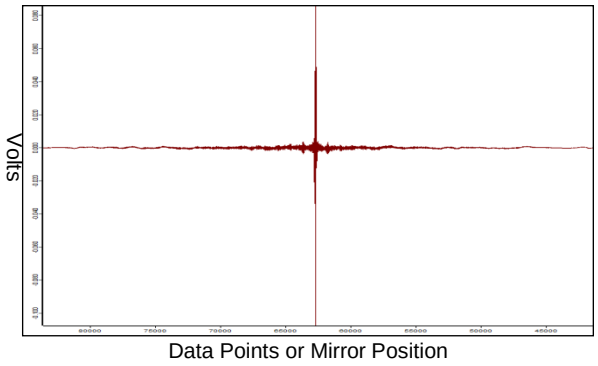
Single Beam Spectrum (Background + Sample)

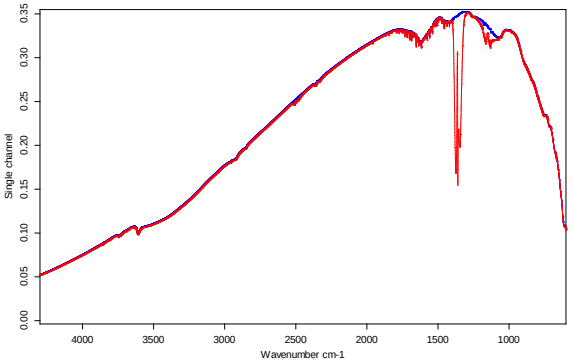


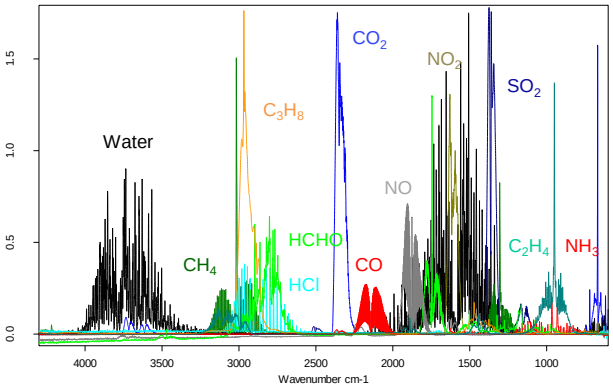
Absorbance


A = ε / c
Absorption
Absorptivity
Path length
Concentration
Absorbance Units
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
4000
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

Measurement Processing







Interferogram → *Signal Processing & Fourier Transform* → Single Beam → *Normalization ratio sample to reference* $A=Log_{10}(I_0/I)$ → Absorbance Spectrum ready for speciation / quantification

CAI FTIR

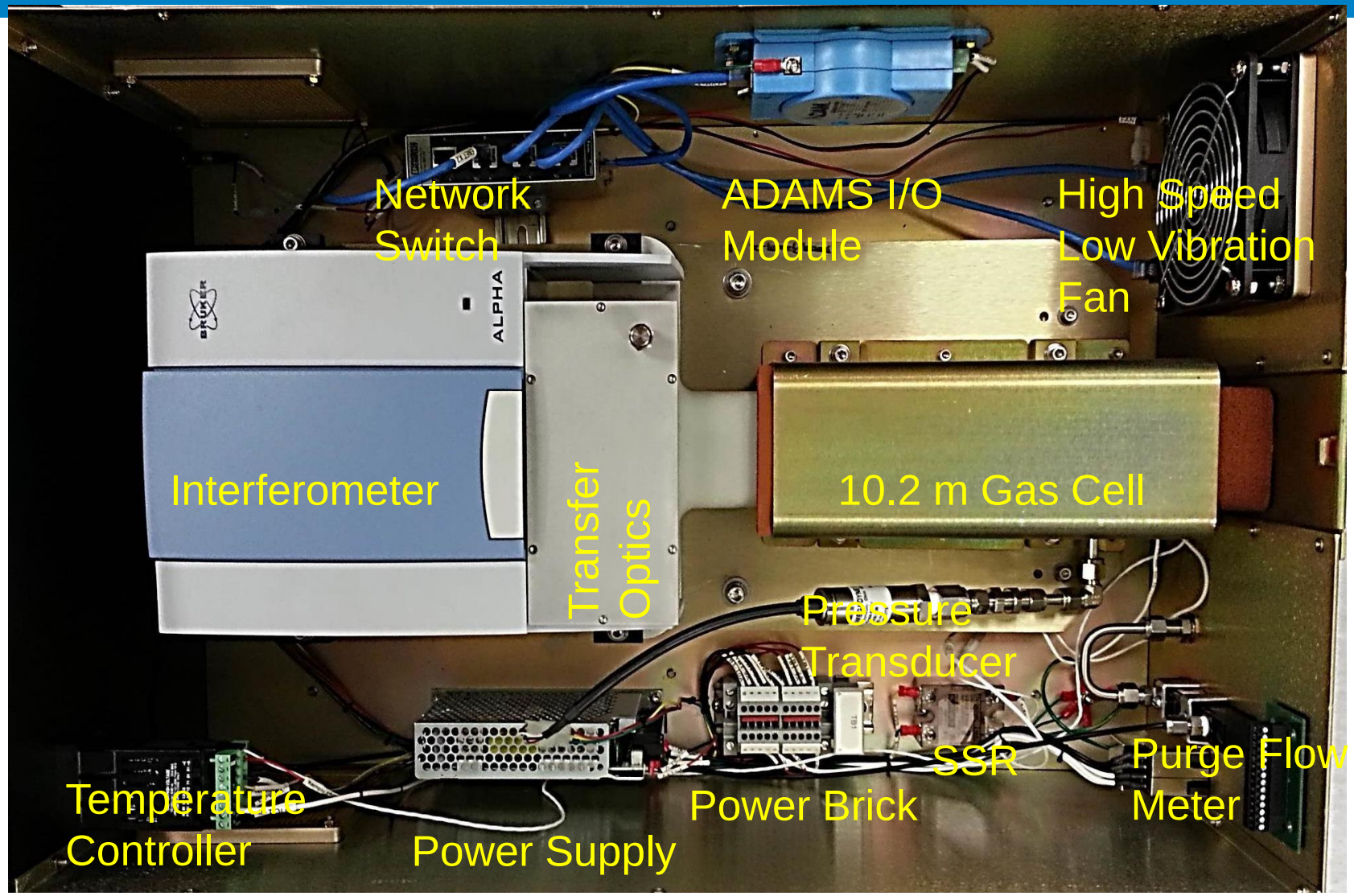
FEATURES

- Measures multiple components simultaneously
- Can measure most components from sub-ppm to percent levels
- Sample Cell is heated to 50°C or 191°C
- Fast Response
- Small Form Factor
- Ease to use software interface
- NO LIQUID NITROGEN REQUIRED

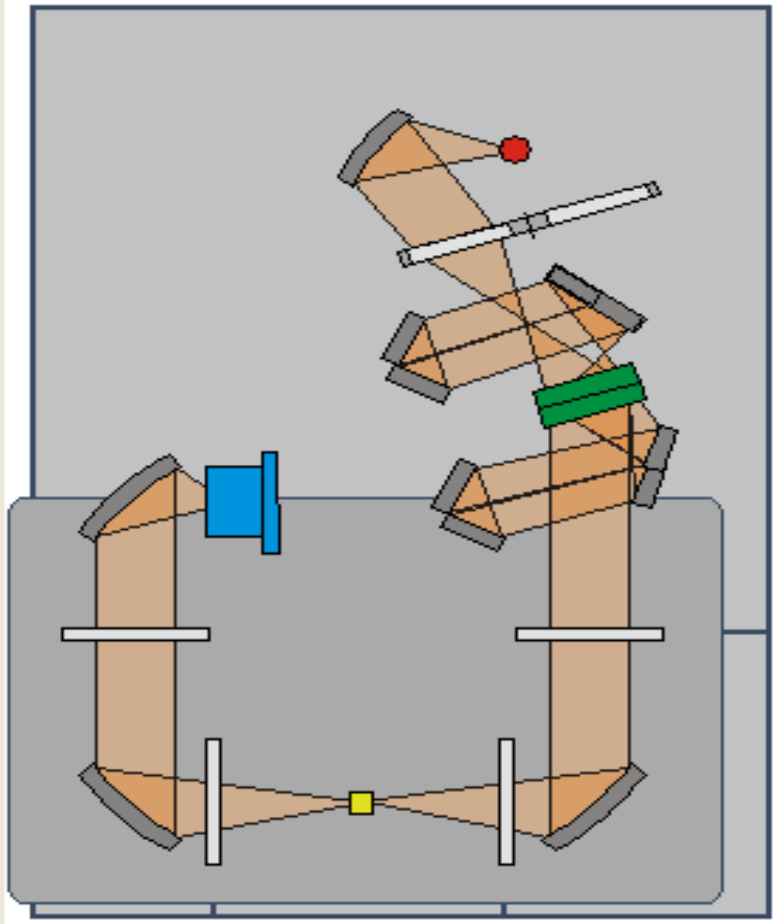
BENEFITS

- Only need one analyzer - saves money & space
- Flexibility for many applications
- Ambient or hot/wet applications – no need for sample conditioning
- Easily catches spikes in concentrations
- Transportable or rack mountable
- Anyone can operate and communicate
- Eliminates the hassle and cost of liquid N2

700 Series FTIR—Internal Components



600/700 Series FTIR—Interferometer Optical Path



FTIR—Requirements

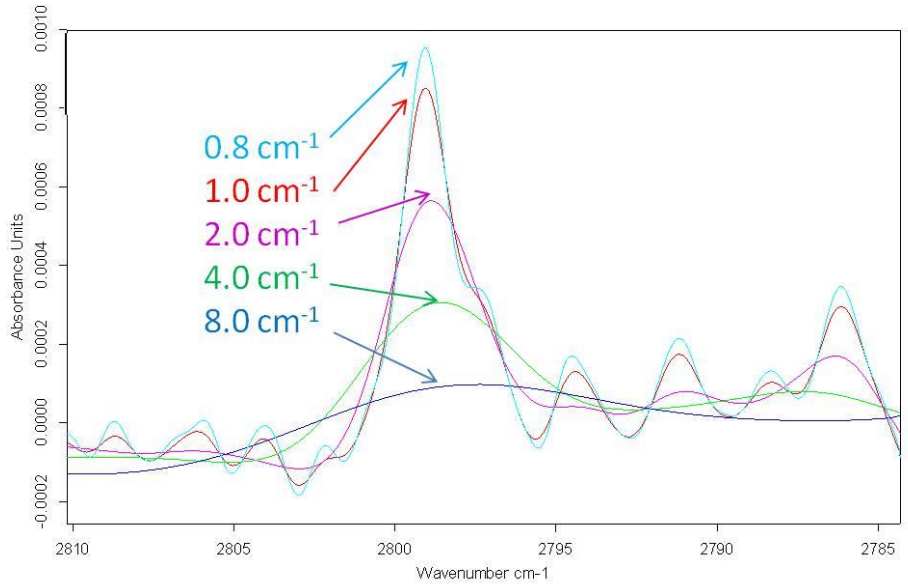
- 0.5 lpm N_2 or ZAG optics purge (maintaining rate).
- N_2 or ZAG for Baseline measurement
- Heated Sample Filter
- If 191˚ C is required:
  - Appropriate heated lines, heated pump, temp controllers
  - Sample probe (if needed)

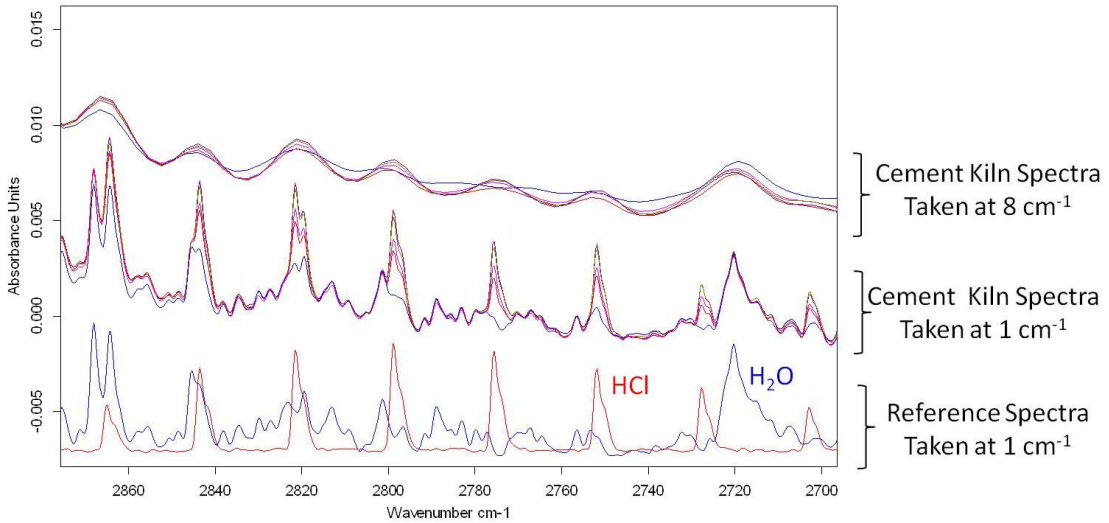
- Consumables
  - 5 year IR Source replacement
  - 19 year Laser replacement

- Cell life
  - Varies based on operating conditions.

Importance of High Resolution

Resolution (cm^{-1})	Noise	Signal	S/N
0.8	0.000528	0.001016	1.93
1	0.000441	0.000913	2.07
2	0.000230	0.000549	2.39
4	0.000131	0.000370	2.82
8	0.000051	0.000164	3.24





Low resolution has high signal to noise which is great for a single gas bottle.

However overlapping peaks are difficult to separate in real world examples

FTIR—Gas Spectra

Acetaldehyde:
CH3CHO 65.3 ppm

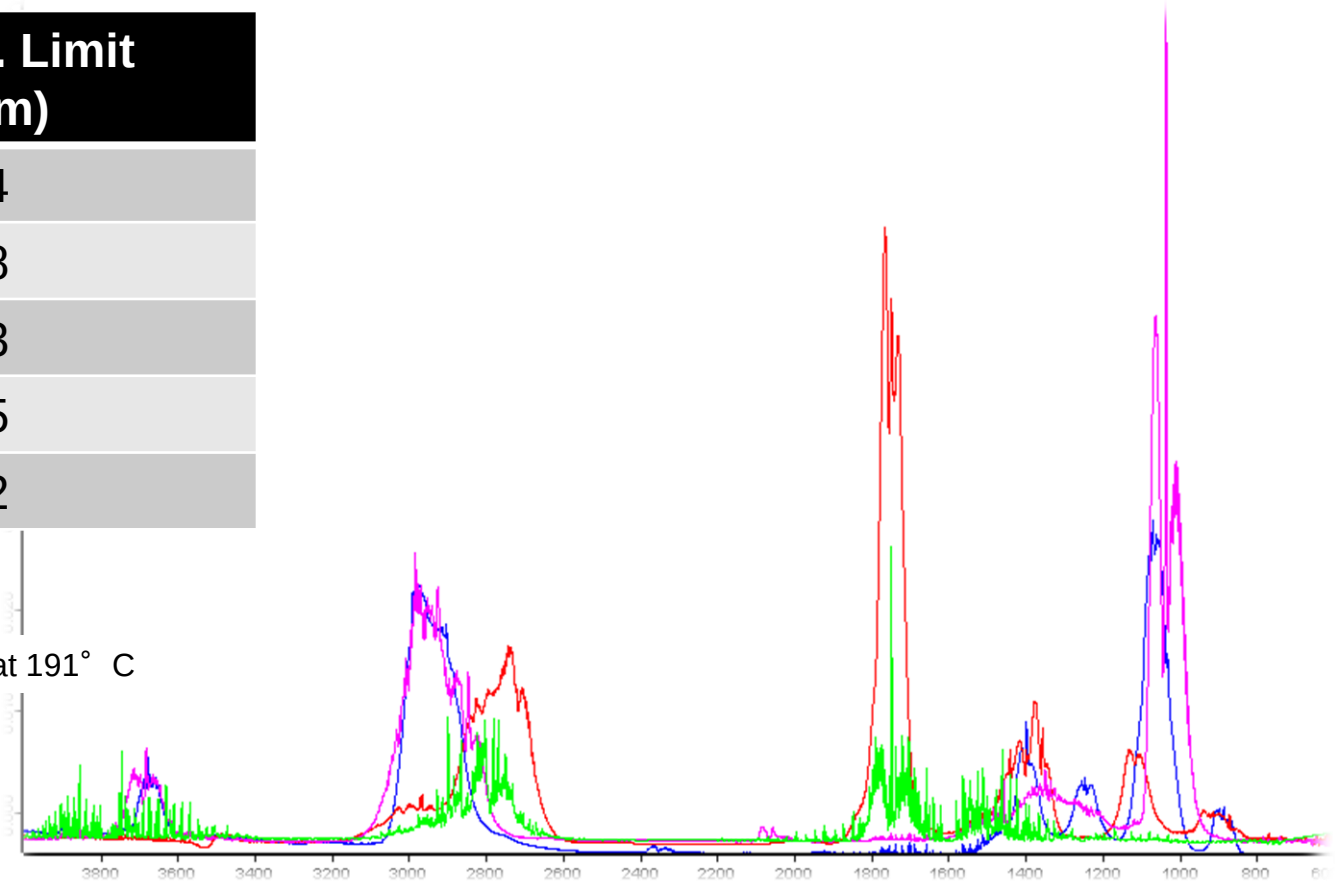
Methanol:
CH3OH 65.4 ppm

Ethanol:
C2H6O 51.7ppm

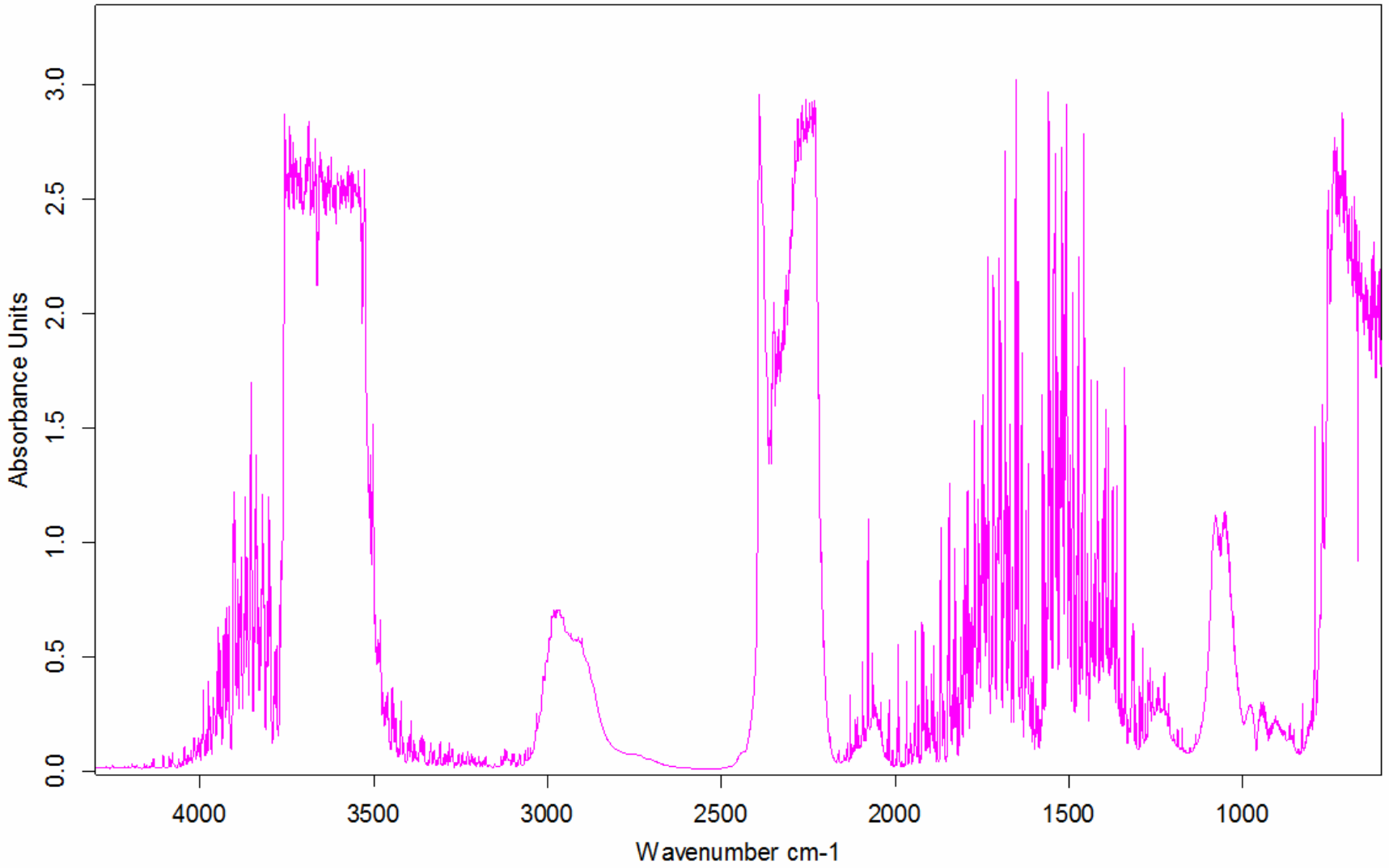
Formaldehyde:
HCHO 14.3ppm

Component	Det. Limit (ppm)
Acetaldehyde	0.14
Formaldehyde	0.08
Formic Acid	0.23
Methanol	0.05
Ethanol	0.42

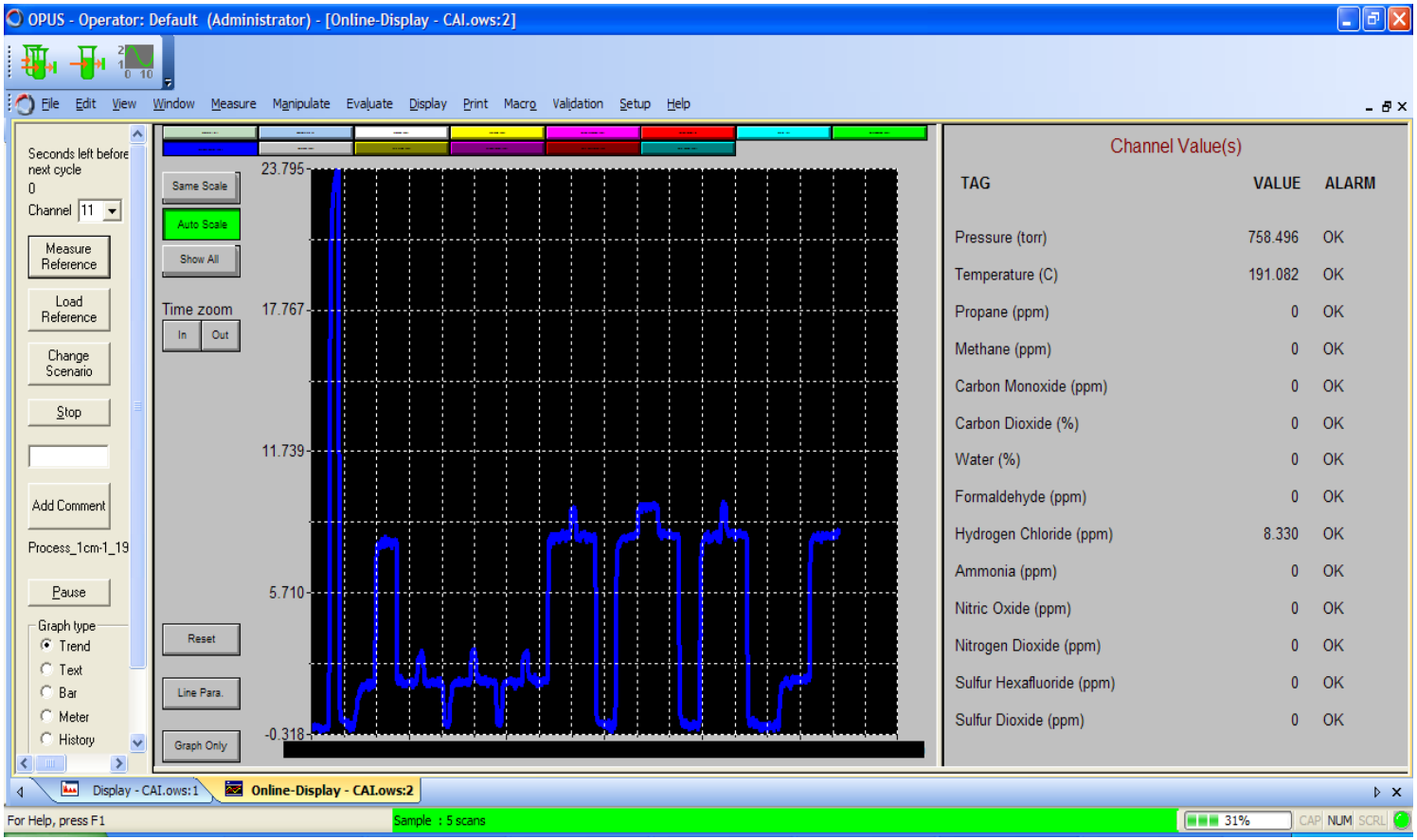
-Dry gas, single component values at 191˚ C



Ethanol Plant Spectrum



FTIR—Process



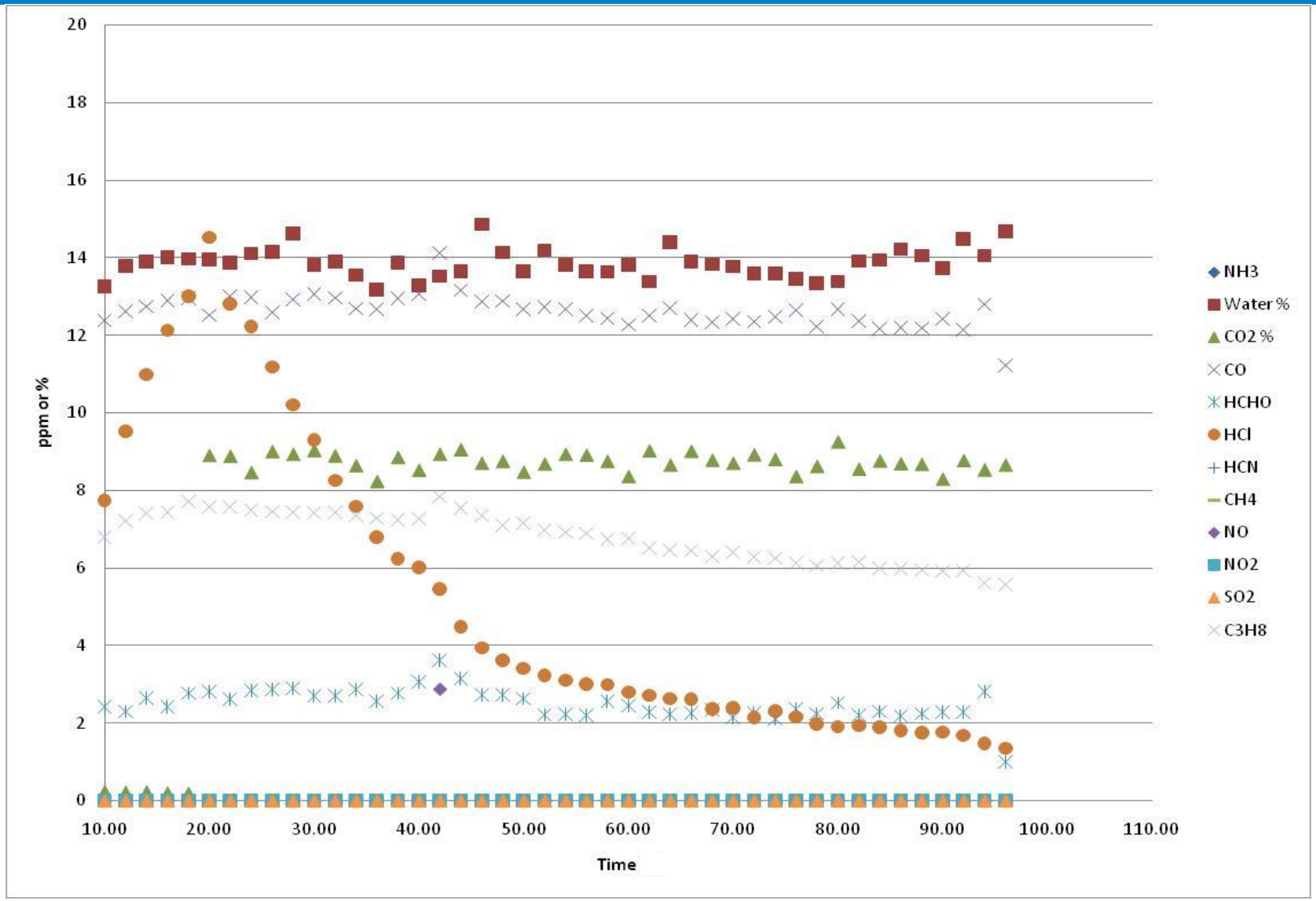
Includes auto ranging, pressure compensation, span correction, and LOD

FTIR - Installation at NE Ethanol Plant

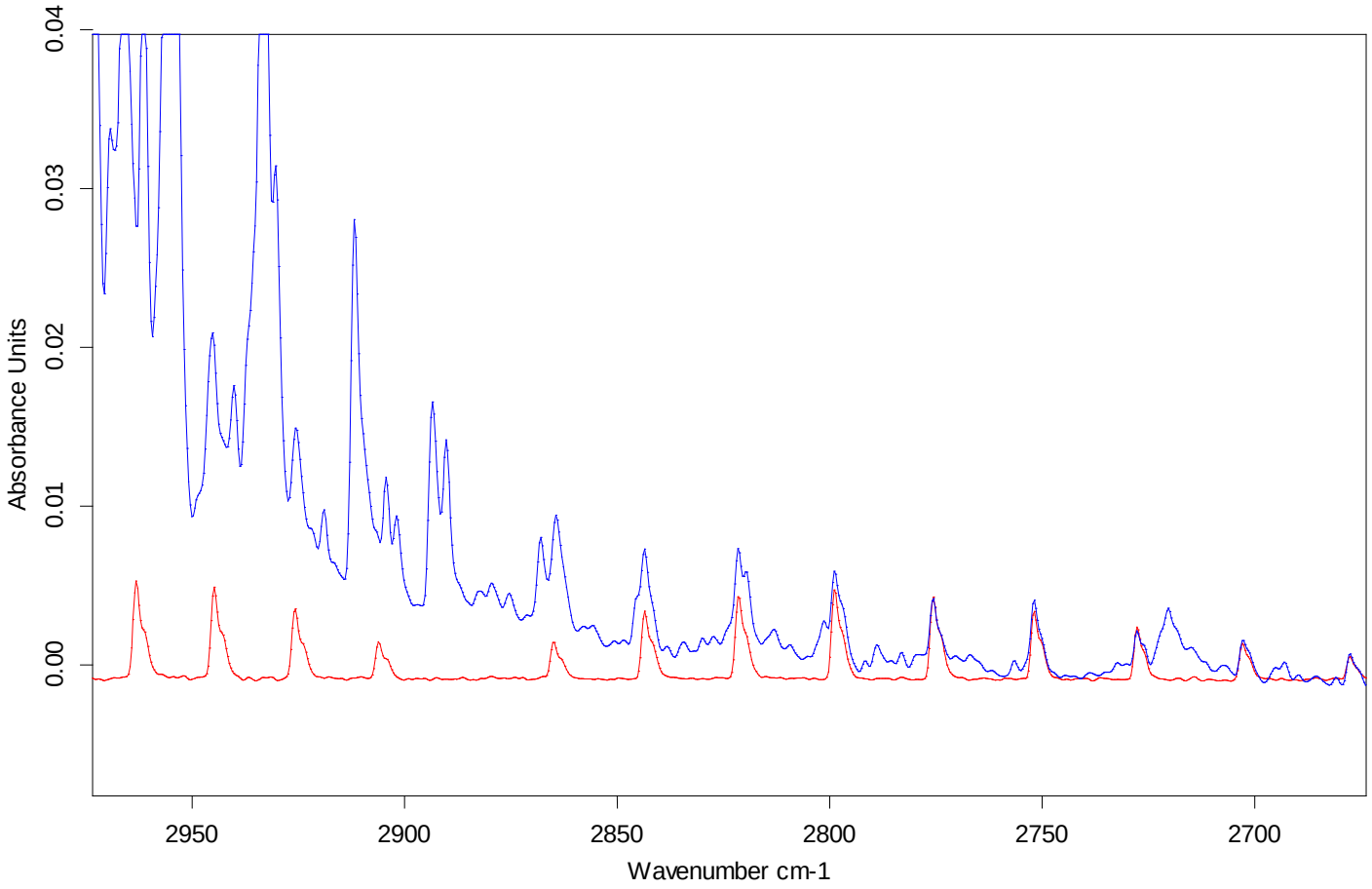
FTIR—Data Can Be Reworked

- Other instruments can only record numbers
- FTIR records spectra *and* displays numbers
- Spectra can be reviewed and reanalyzed in the case of any issue

FTIR—Example Data

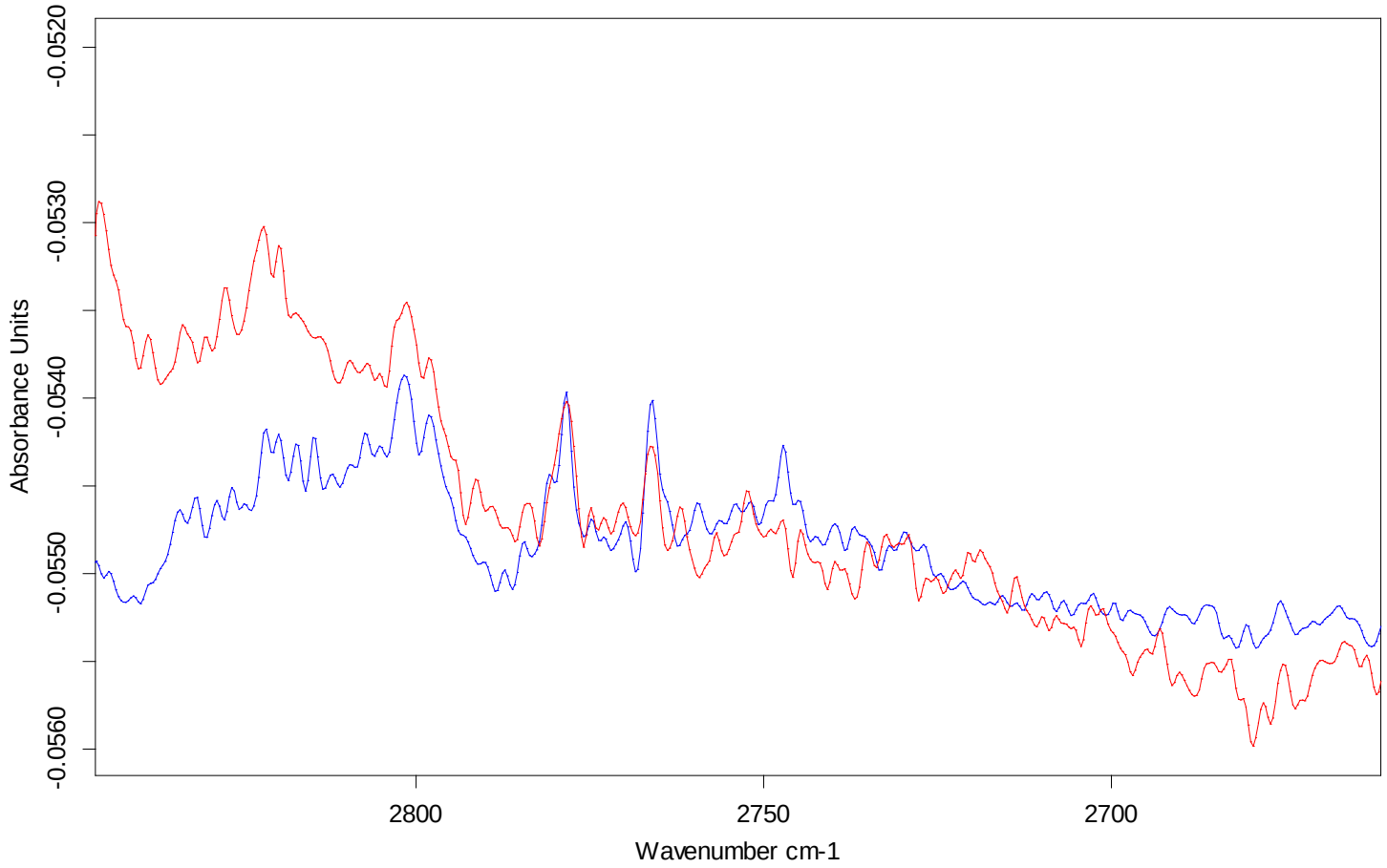


HCl in the Stack



- HCl spectra was reviewed to confirm measurement results

HCHO in the Stack



- HCHO spectra was reviewed to confirm measurement results

Current Application List

Cement
Stack Testing
Natural Gas Compressors
Diesel Engine
Catalysis
Pharmaceutical
Electric Utility Plant
Aerospace
Solid Fuel Burning
Municipal Waste Incineration
Process Control
Thermal Soil Remediation
Gas Purity
Jet Turbine
Ethanol Plant
Agriculture

FTIR—Low Cost of Ownership

- Laser – 19 year life
- IR Source - 5 year life, user replaceable
- Rocksolid™ Interferometer – Gold Mirrors, High throughput, Permanent alignment
- Process – Allows anyone to operate

CAI FTIR Advantages

- No liquid N2 Required
- Small Form Factor
- No Sample Pressure Restrictions
- ZnSe Beam-Splitter (for Humidity Protection)
- 19 year Laser Life
- 5 Year IR Source Life
- Partial Least Squares (PLS) Quantification
- 316SS Electro-Polished Cell Standard
- Digital & Analog Inputs/Outputs
- Minimal Service Required
- Library Search Capability
- Easy-to-Maintain
- Permanently Aligned – Dual Corner Cube Designed Interferometer (Pinned)
- Macros:
  - Makes Repetitive Tasks Easier
  - Allows User to Easily Customize each Application