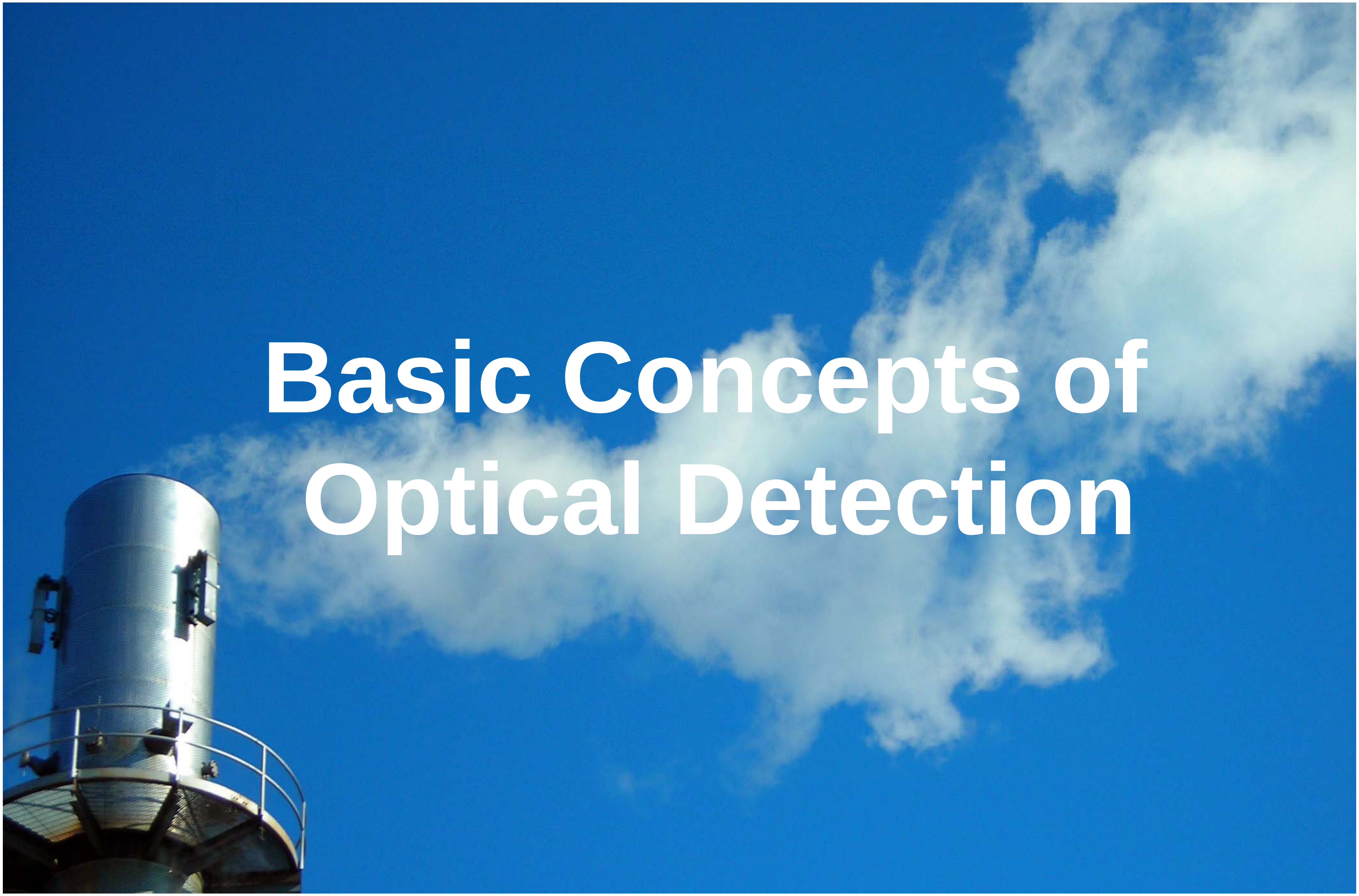
FTIR Systems & Operation

IMACC

INDUSTRIAL MONITOR AND CONTROL CORP.

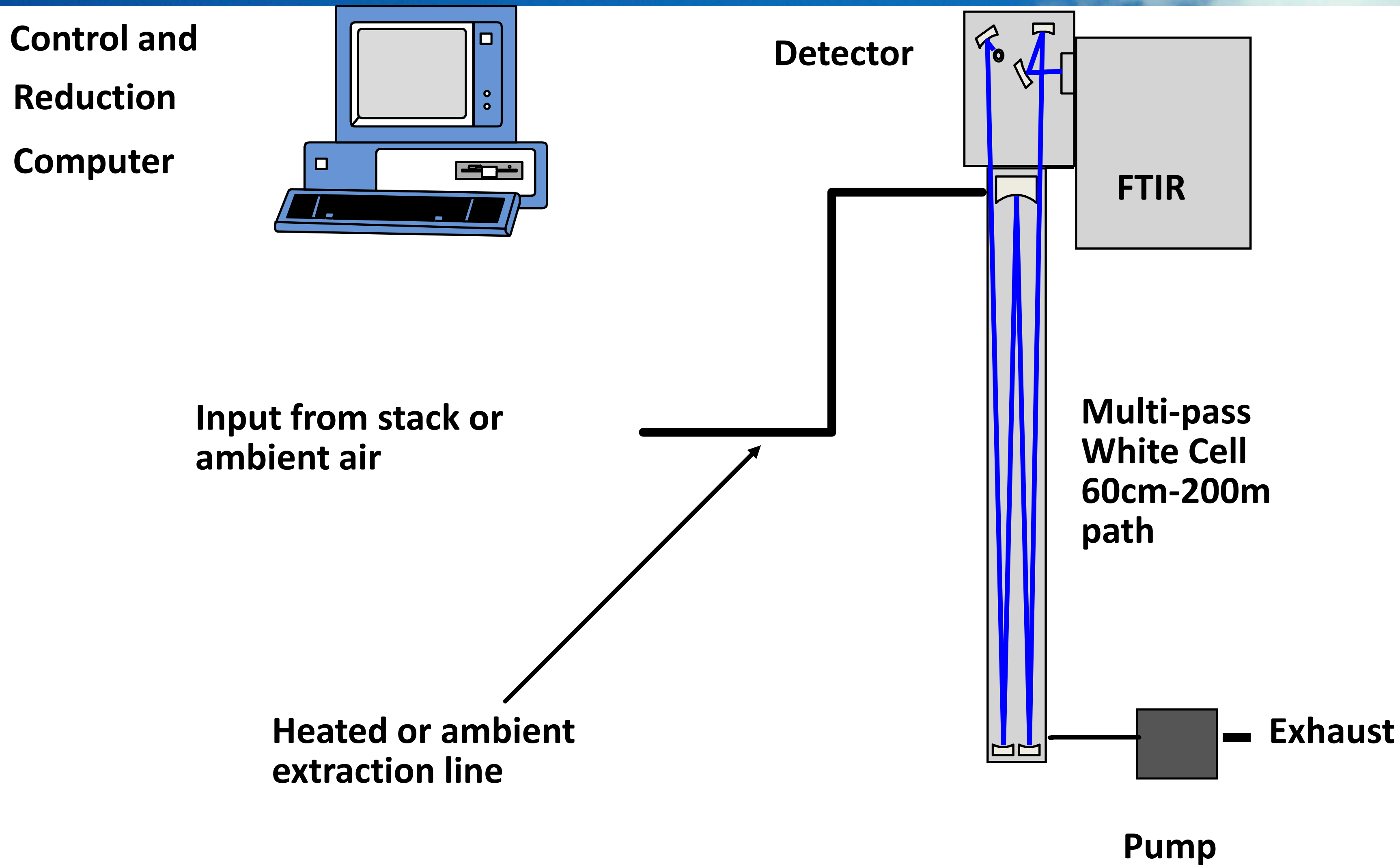


Basic Concepts of Optical Detection

Active & Passive Open Path FTIR

- Active transmission mode uses a light source in the FTIR which is modulated by the instrument and is then transmitted through the gas to be monitored.
- The transmitted beam is captured and analyzed to determine the compounds present and their concentrations.
- Analysis is done using reference standards for each compound collected under controlled conditions of: concentration, temperature, pressure, and path length

Typical Extractive FTIR System



Basic Concepts

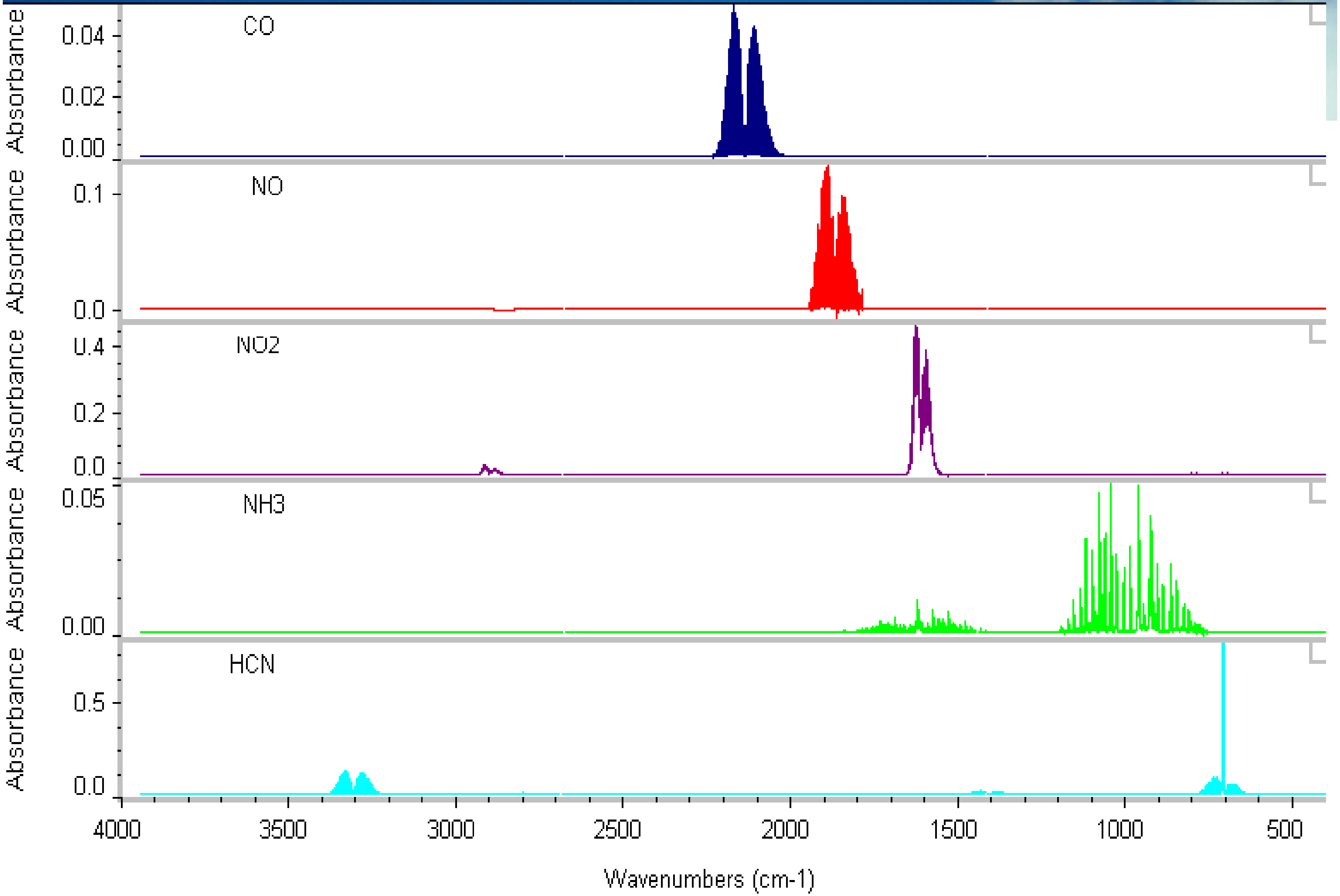
Most molecules absorb infrared (IR) light

- The patterns of IR wavelengths (colors) they absorb are unique to each molecule
- The amount of light they absorb is proportional to their concentration

As a Result:

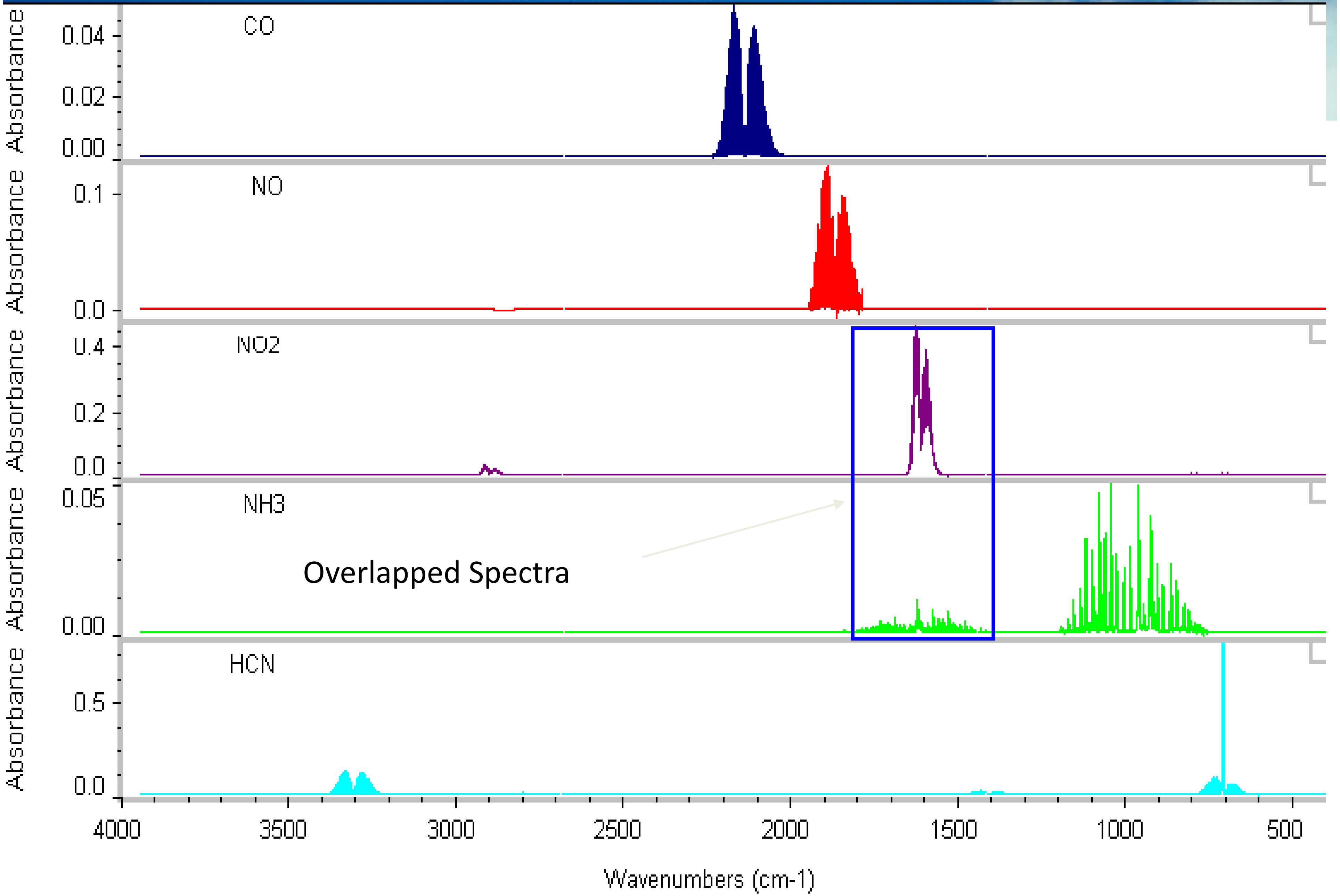
- The presence of specific compounds can be unequivocally determined by the absorption patterns
- The concentration of the compounds can be measured by the strength of the absorption patterns

Infrared Absorbance Spectra of Select Compounds

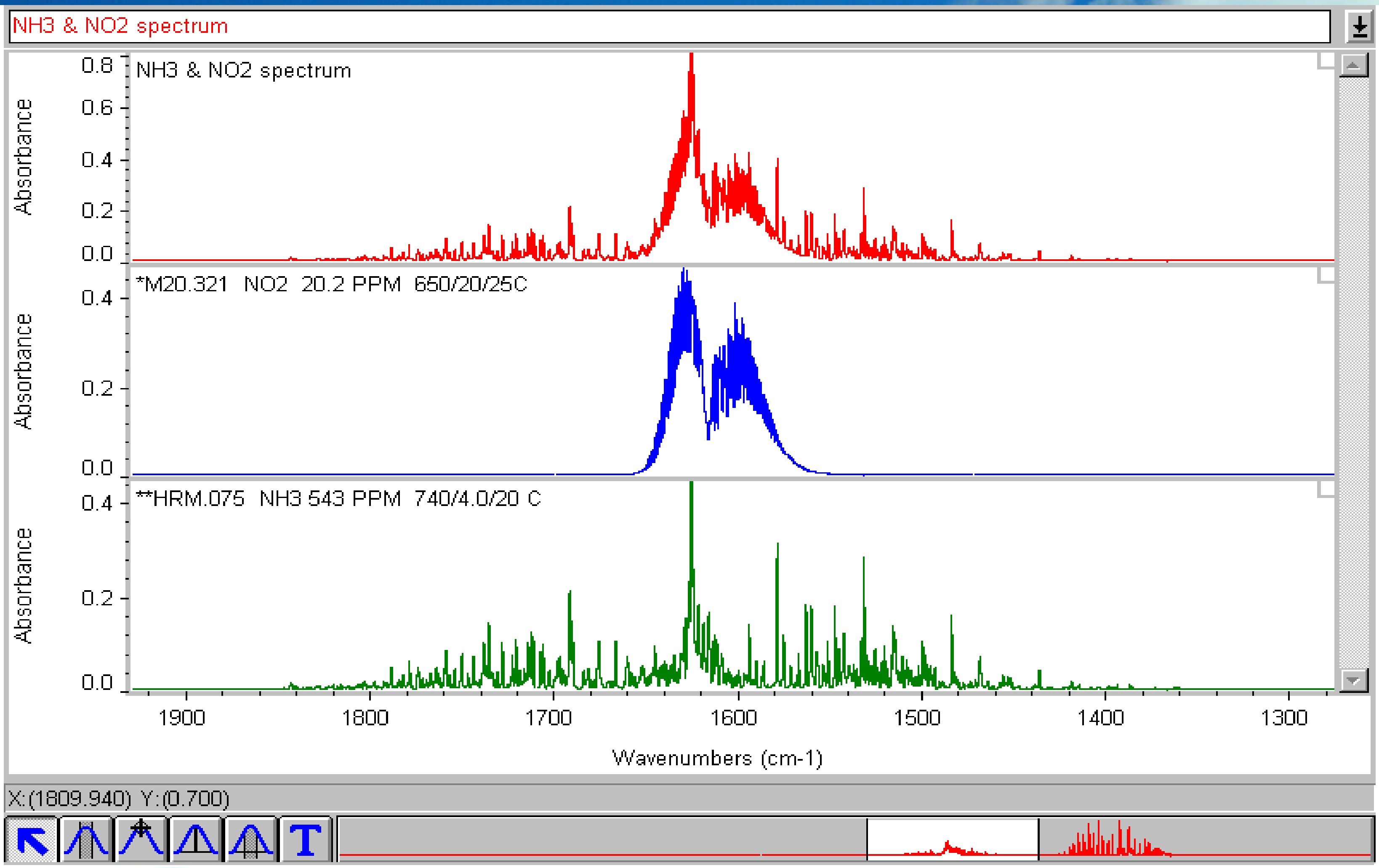


What About Overlapping Features?

Infrared Absorbance Spectra of Select Compounds



Overlapped Spectra of NO_2 and NH_3



What Can An FTIR Monitor Measure ?

Compounds Covered

- The FTIR can monitor most molecular species except for homonuclear diatomics (Cl_2, H_2, O_2, N_2, etc.)

- The detection limit varies by compound but all can be detected to sub ppm-levels with small systems and to the low ppb-level with larger systems

Detection Limits

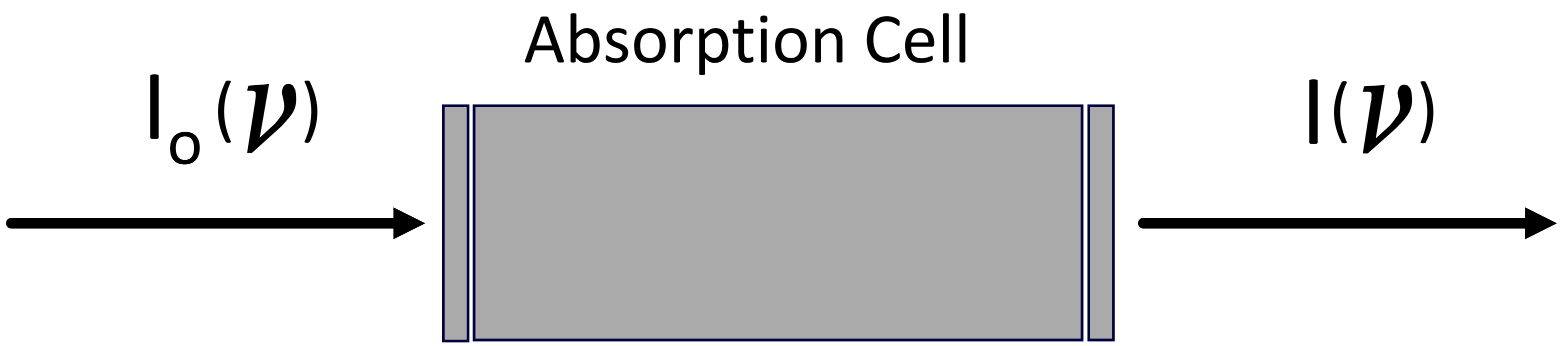
Species	300 Meter Open Path	100 Meter Cell*	Species	300 Meter Open Path	100 Meter Cell*
acetaldehyde	20	30	cyclohexane	3	5
acetic acid	5	7 SL	1,2-dibromoethane	5	7
acetone	30	10	m-dichlorobenzene	3	5
acetonitrile	50	70	o-dichlorobenzene	3	5
acetylene	2	2	p-dichlorobenzene	2	3
acrolein	5	7	1,1-dichloroethane	10	10
acrylic acid	10	5 SL	1,2-dichloroethane	30	40
acrylonitrile	6	10	1,1-dichloroehtylene	2	4
ammonia	2	3 SL	dimethylamine	20	30 SL
benzene	25	3**	dimethyl disulfide	10	15
1,3-butadiene	2	3	1,4 dimethyl piperazine	3	5
butane	HC		1,4 dioxane	2	3
butanol	15	20 SL	ethane	10	10
1-butene	10	15	etanol	10	10 SL
cis-2-butene	25	30	ethyl acetate	4	4
trans-2-butene	10	15	ethylamine	20	10 SL
butyl acetate	5	7	ethylbenzene	20	30**
carbon disulfide	dry only	50	ethylene	1	3
carbon monoxide	1	4	ethylene oxide	10	15
carbon tetrachloride	2	2	ethyl mercaptan	50	70
carbonyl sulfide	2	3	formaldehyde	5	8
chlorobenzene	10	10	formic acid	2	3 SL
chloroethane	10	15	furan	3	5
chloroform	2	2	halocarb-11 (CCl3F)	1	1
m-cresol	20	15	halocarb-12 (CCl2F2)	1	1
o-cresol	4	8	halocarb-22 (CHClF2)	1	1
p-cresol	10	15	halocarb-113 (CFCl2CF2Cl)	2	2

Detection Limits

Species	300 Meter Open Path	100 Meter Cell*	Species	300 Meter Open Path	100 Meter Cell*
hexafluoropropene	1	2	ozone	3	5
hydrocarbon continuum	10	15	pentane	HC	
hydrogen chloride	2	4	phosgene	1	2
hydrogen cyanide	5	4	phosphine	2	3
hydrogen sulfide	300	500	propane	10	10
isobutane	2	1	propanol	20	30 SL
isobutanol	4	6 SL	propionaldehyde	10	15
isobutyl acetate	5	7	propylene	4	10
isobutylene	4	4	propylene dichloride	10	15
isoprene	4	5	propylene oxide	10	15
isopropanol	10	10 SL	pyridine	20	20
isopropyl ether	10	5	silane	1	1
methanol	4	6 SL	styrene	1	2
methylamine	20	20 SL	sulfur dioxide	30	30
methyl benzoate	20	30	sulfur hexafluoride	<1	0.1
methyl chloride	60	80	1,1,1,2-tetrachloroethane	4	6
methylene chloride	5	8	1,1,2,2-tetrachloroethane	20	16
methyl ether	10	15	tetrachloroethylene	2	2
methyl ethyl ketone	40	60 SL	toluene	25	10**
methyl isobutyl ketone	15	25 SL	1,1,1-trichloroethane	4	10
methyl mercaptan	40	60	1,1,2-trichloroethane	10	15
methyl methacrylate	5	5	trichloroethylene	2	3
2-methyl propene	2	4	trimethylamine	10	15 SL
morphaline	2	3	1,2,4-trimethylbenzene	5	7
nitric acid	1	2	vinyl chloride	4	5
nitric oxide	25	20	m-xylene	10	10**
nitrogen dioxide	50	50	o-xylene	20	5**
nitrous acid	5	7	p-xylene	20	10**

Basic Equations
Transmission Mode

Transmittance of an Absorption Cell



$$\tau(\nu) = \frac{I(\nu)}{I_o(\nu)} = \begin{cases} 0\% \\ 100\% \end{cases}$$

Transmittance for Molecules

$$\tau(\nu) = I(\nu)/I_o(\nu)$$

$$= e^{-\kappa(\nu)\,C\,L}$$

Where:

k(n) = the gas absorption coefficient

C = the gas concentration

L = The optical path length

Transmittance for Molecules (cont.)

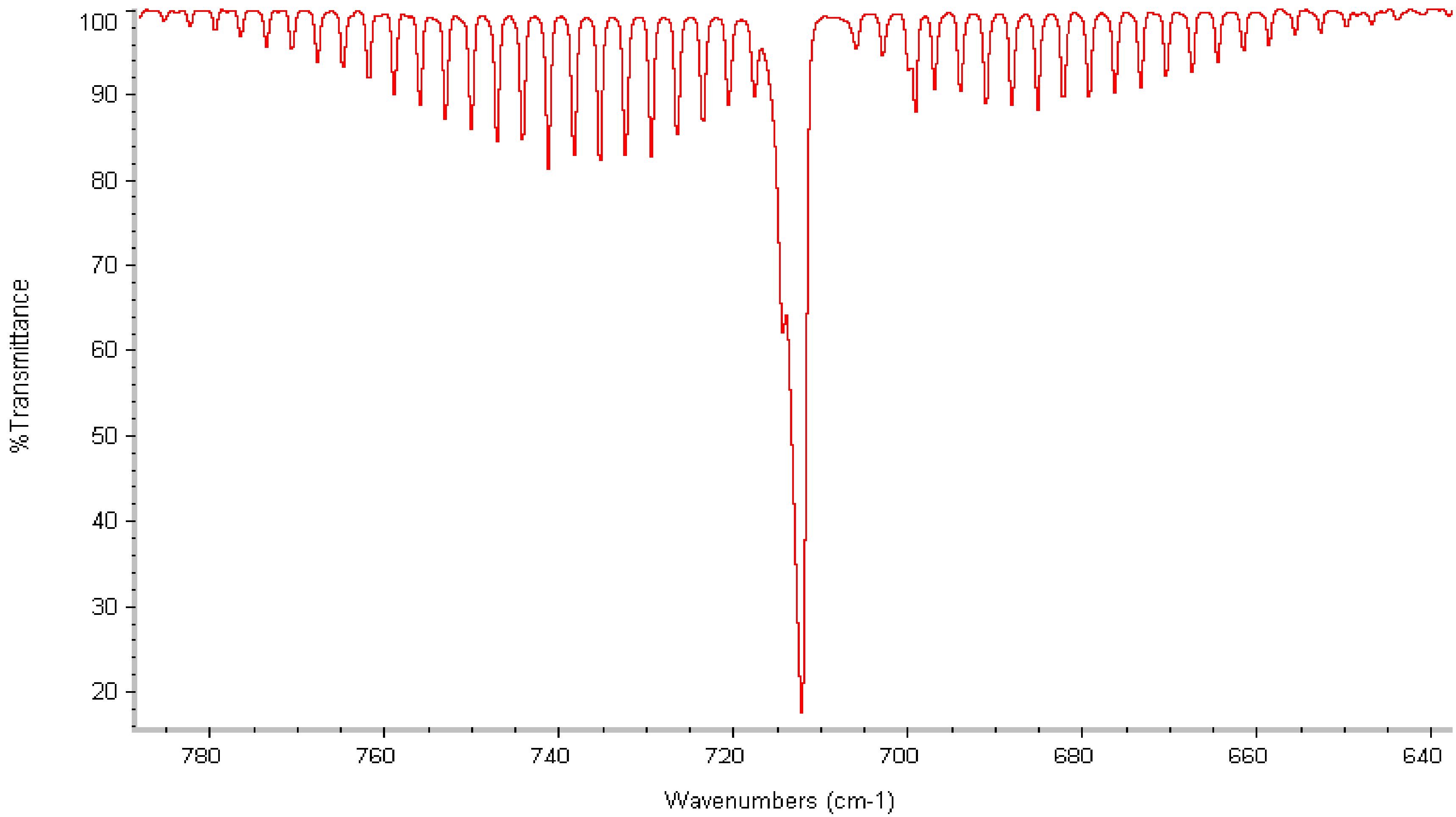
$$\text{Absorbance} = -\log_{10}\{t(n)\}$$

$$= -\log_{10}\{e^{-\kappa(\nu)\,C\,L}\}$$

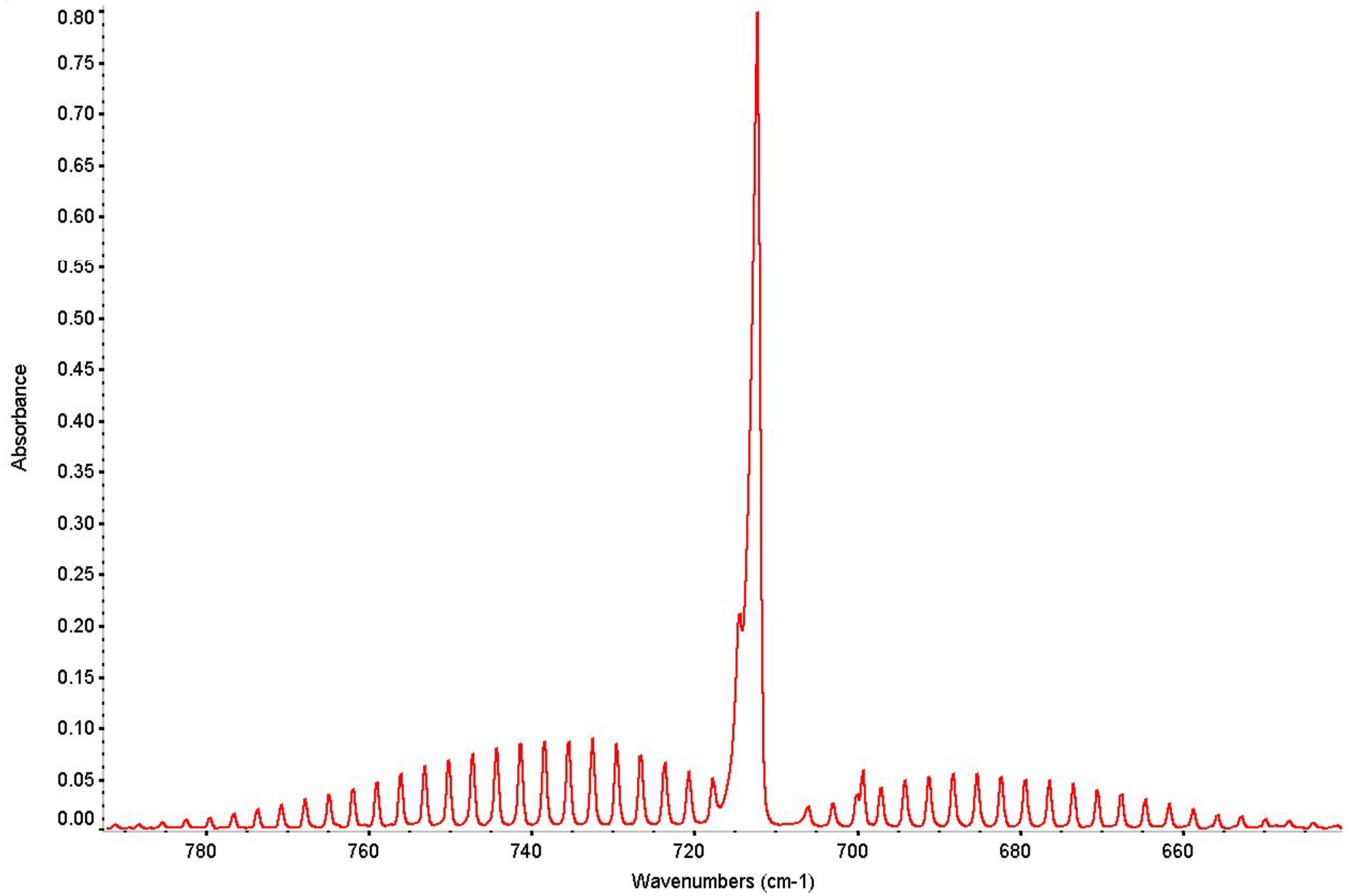
$$= (0.434)\,\kappa(\nu)\,C\,L$$

Scales as concentration times path length

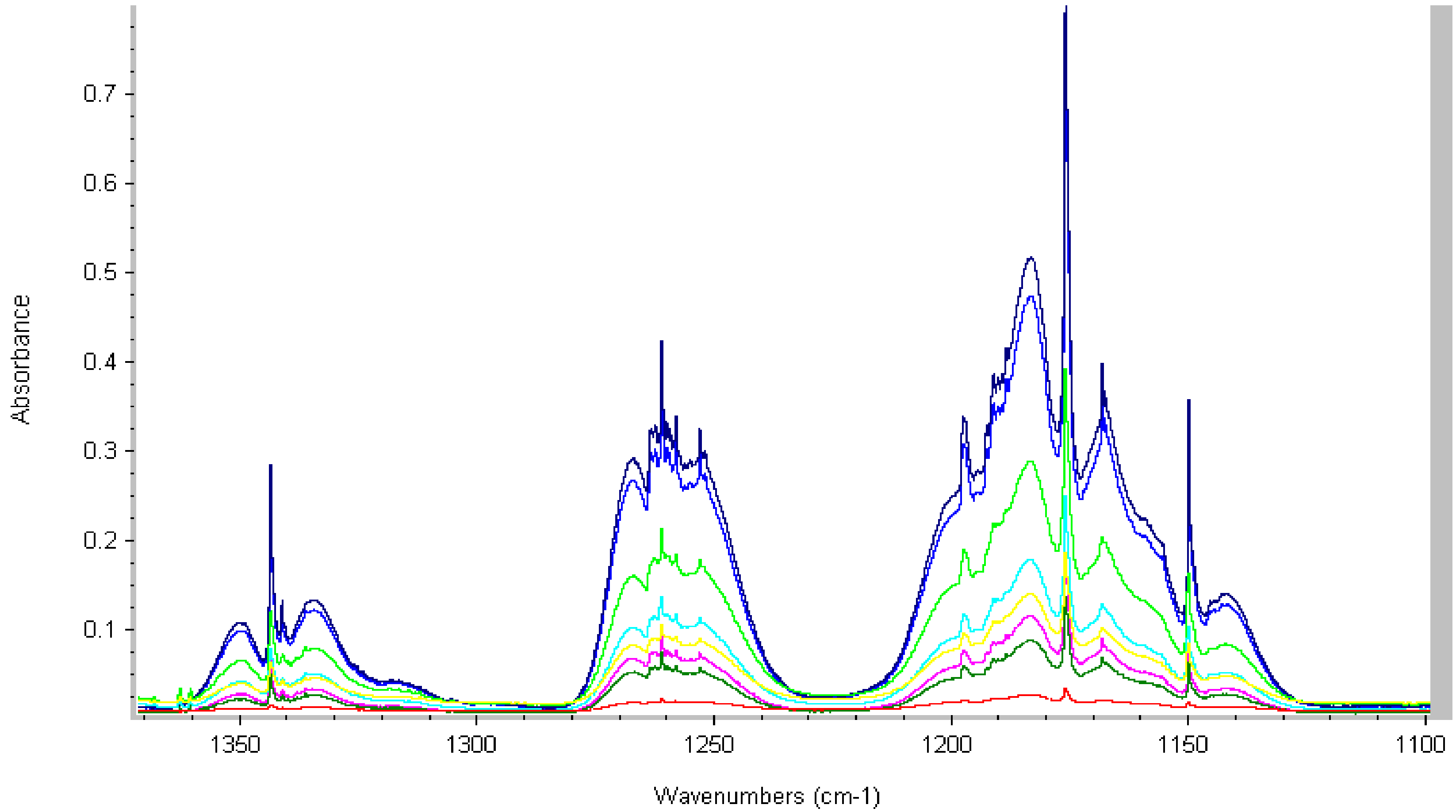
Transmittance Spectrum of HCN



Absorbance Spectrum of HCN

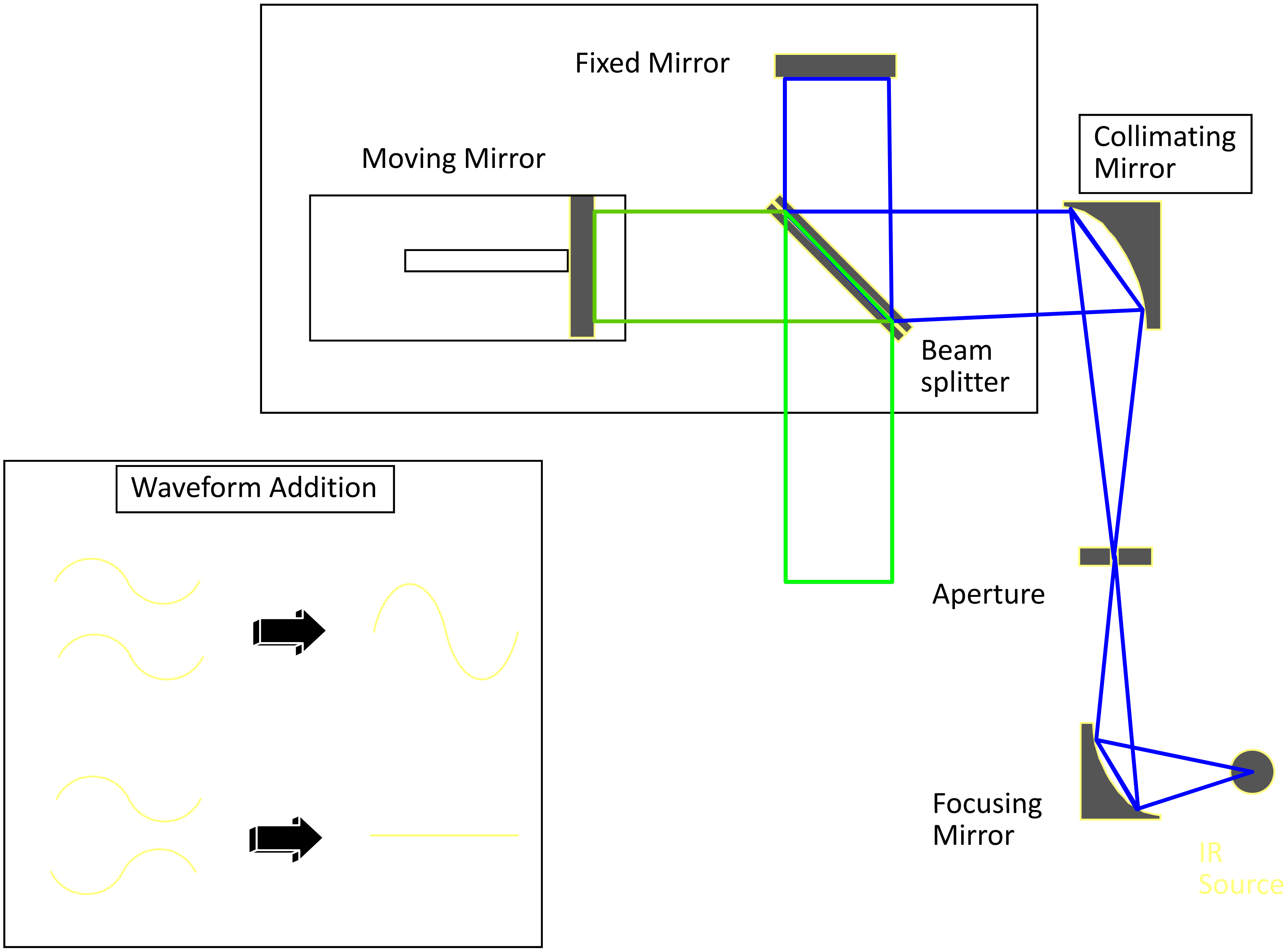


Measured Spectra of Phenol at Various Concentrations

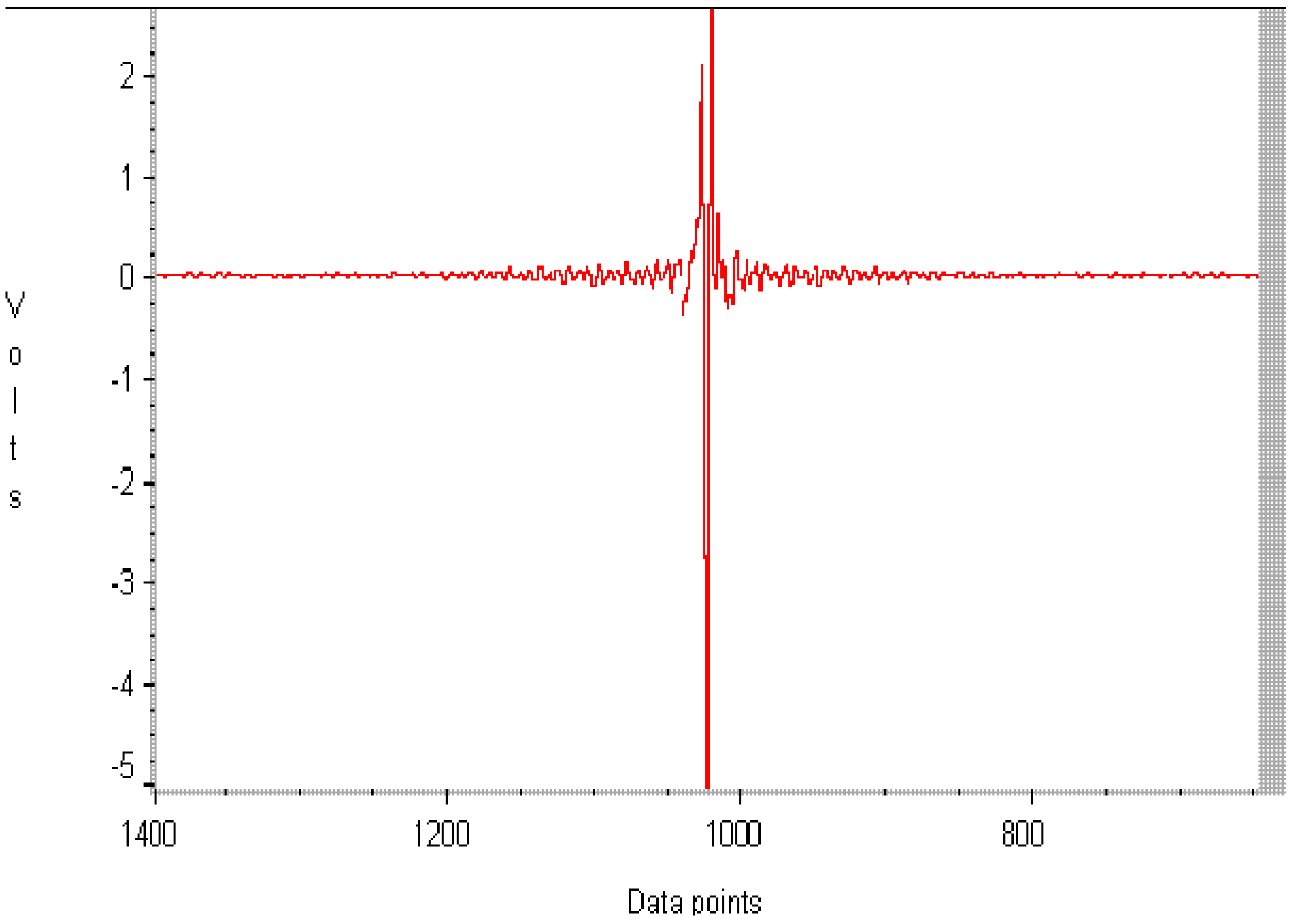


The Fourier Transform Infrared System (FTIR)

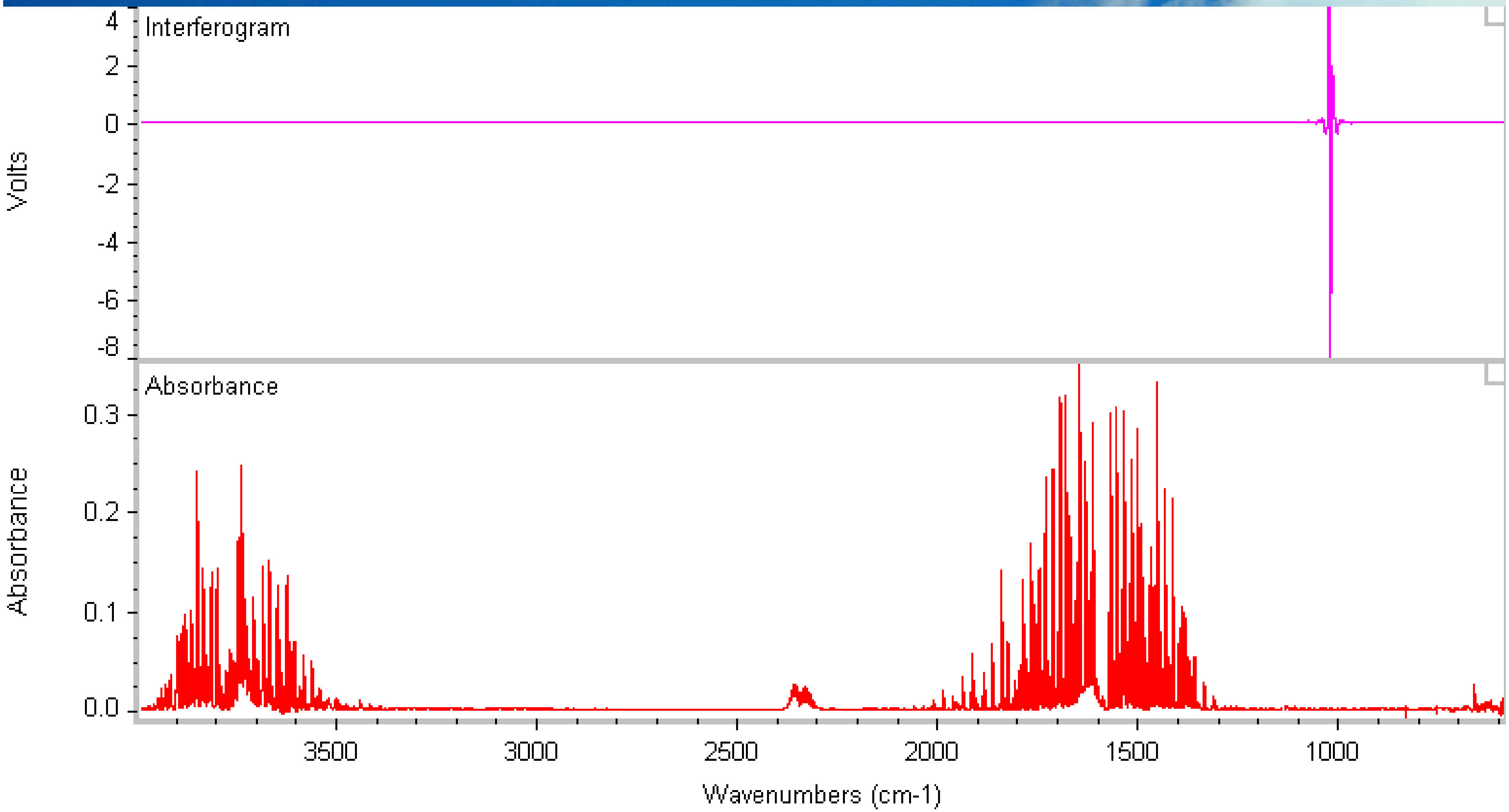
Schematic of FTIR Modulator



Typical FTIR Interferogram Near Center Burst

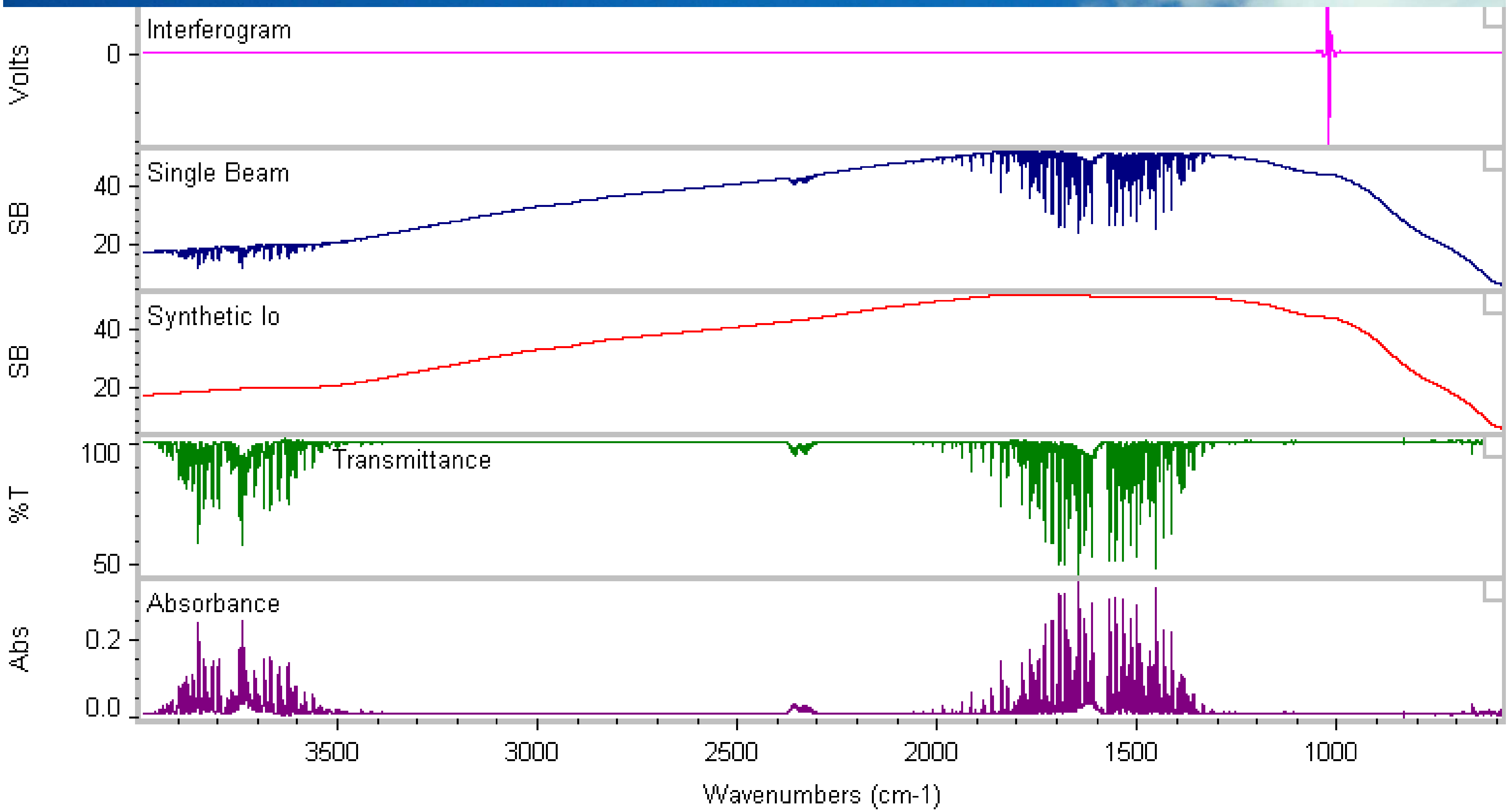


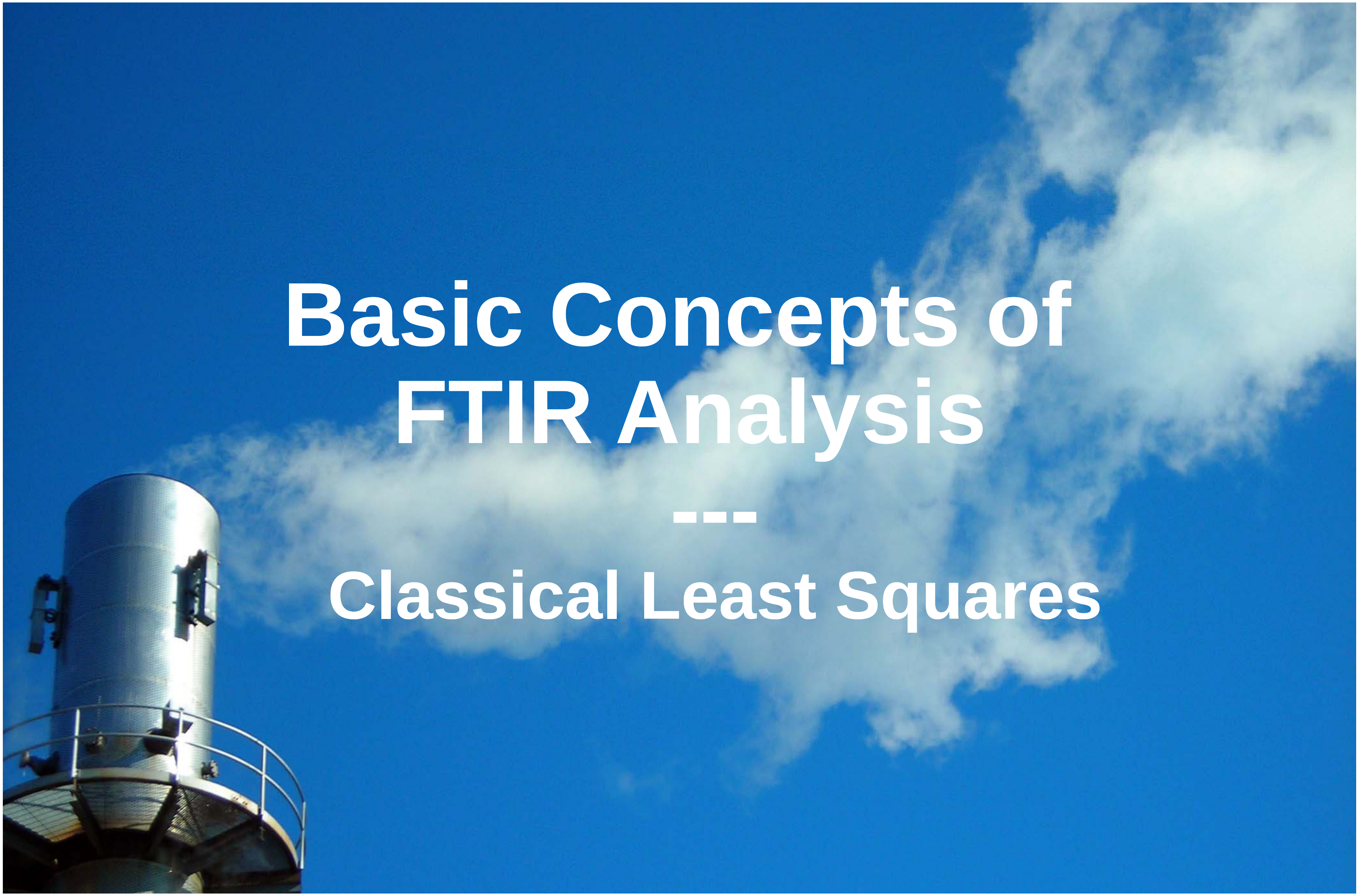
Interferogram & Absorbance Spectrum From FTIR



The FTIR Processing Sequence

FTIR Processing Sequence





Basic Concepts of FTIR Analysis

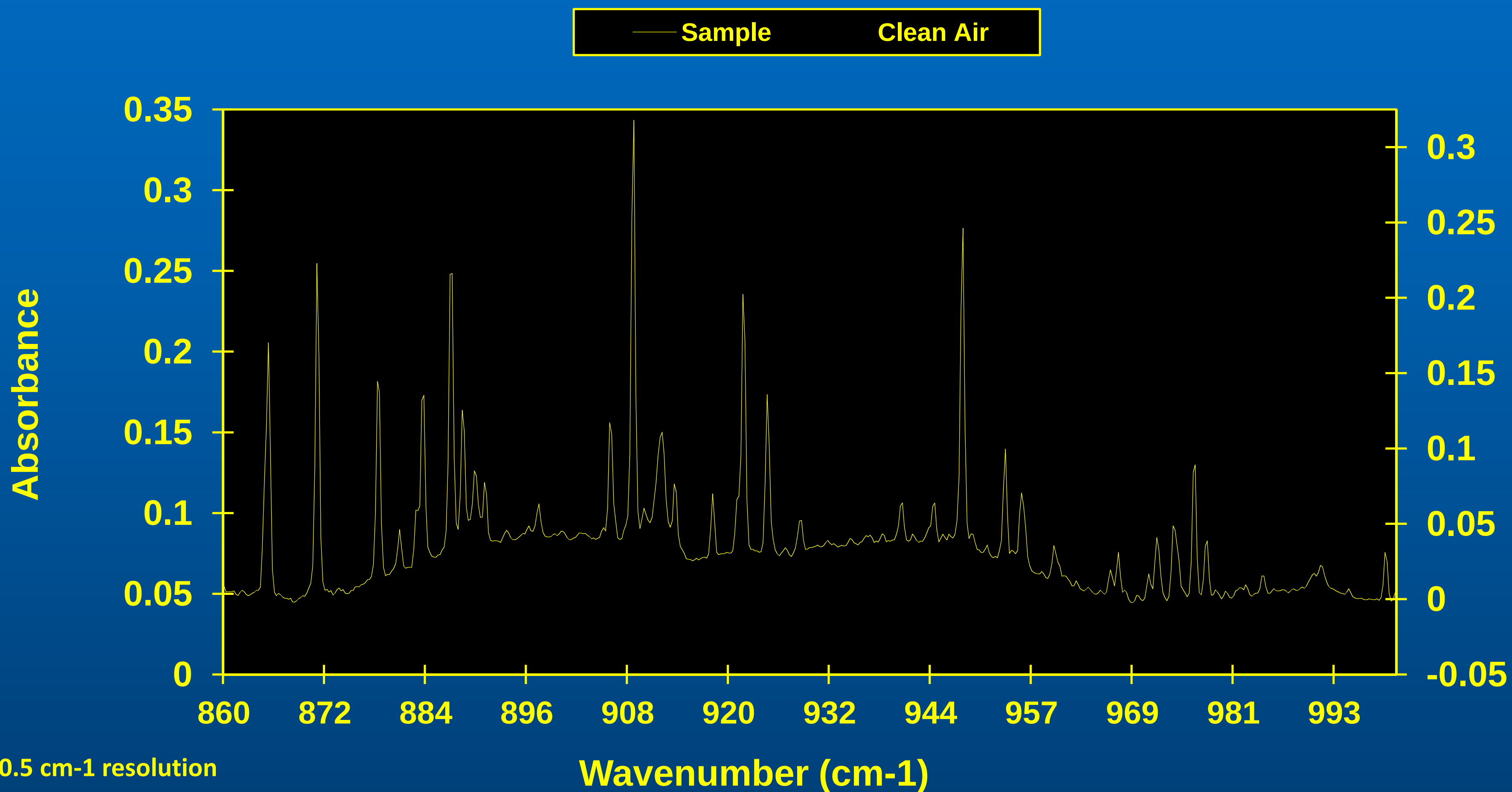
Classical Least Squares

Linear Least Squares Regions and Components

Region	H2O	CO	CO2	NH3	CH4	C2H4	C3H6	H2CO	CH3OH	C6H6	C7H8	ISBUT	13BUT	MXYL	MTBE	HCL	CH3CL	N2O	NO	SO2
743.50	I	-	S	-	-	-	-	-	-	-	-	-	-	-	-	-	I	-	-	-
766.25	I	-	I	-	-	-	-	-	-	-	-	-	-	S	-	-	-	-	-	-
889.50	I	-	-	I	-	-	-	-	-	-	-	-	S	-	-	-	-	-	-	-
937.50	S	-	I	S	-	S	S	-	-	-	-	S	-	-	-	-	-	-	-	-
1009.00	I	-	-	I	-	-	-	-	-	-	-	-	-	-	-	-	S	-	-	-
1035.50	I	-	I	I	-	-	-	-	S	S	S	-	-	-	-	-	I	-	-	-
1095.00	I	-	-	I	-	-	-	-	-	-	-	-	-	-	S	-	-	-	-	-
1148.00	I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	S
1900.00	I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	S	-
2138.50	I	S	I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2207.50	I	I	I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	S	-	-
2787.00	I	-	-	-	I	-	-	S	I	-	-	-	-	-	-	S	-	-	-	-
2932.50	I	-	-	-	S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Observed Spectrum

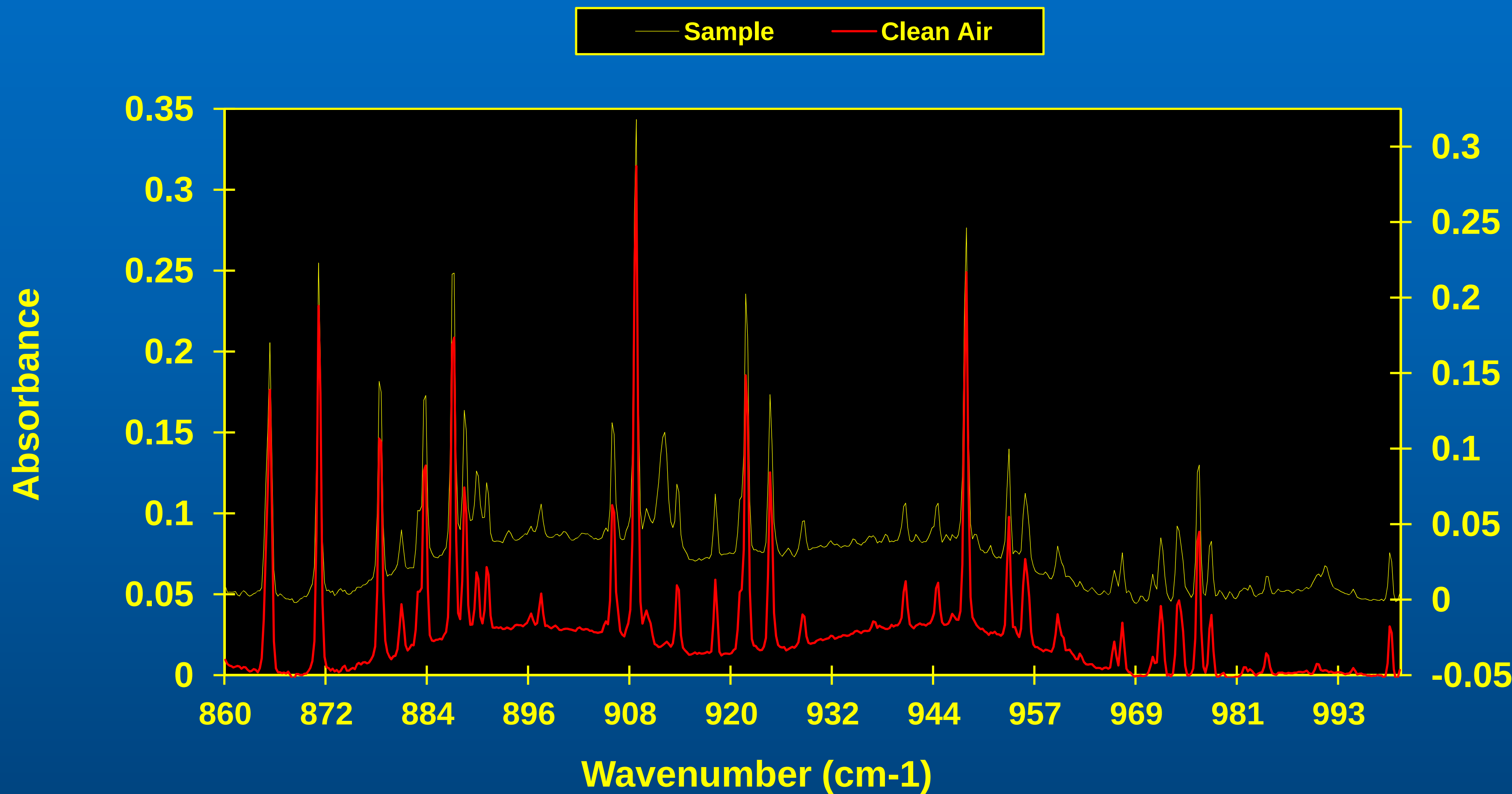
Houston, Texas 15 April 1991



0.5 cm-1 resolution

Observed Spectrum

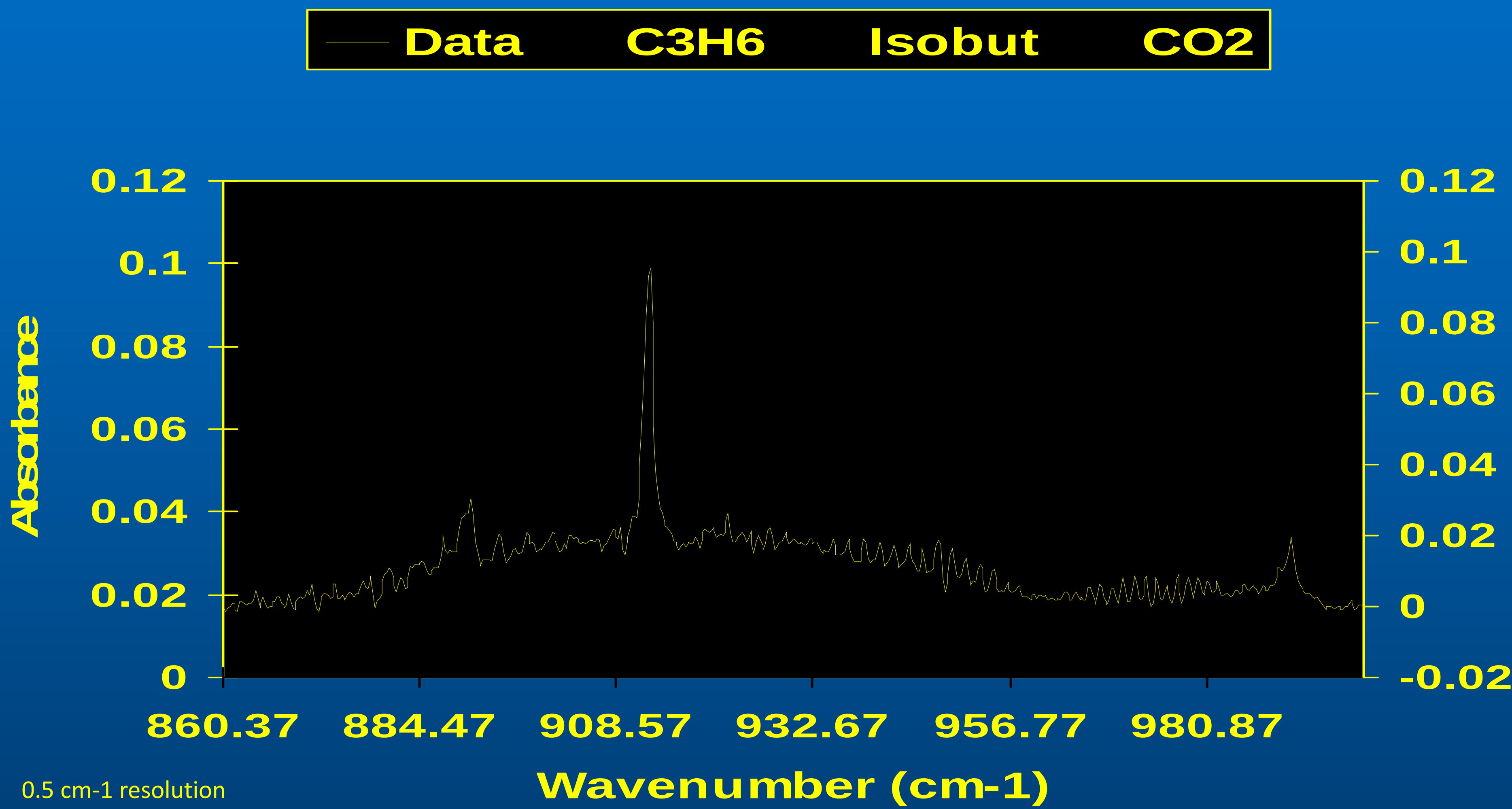
Houston, Texas 15 April 1991



0.5 cm-1 resolution

Difference Spectrum

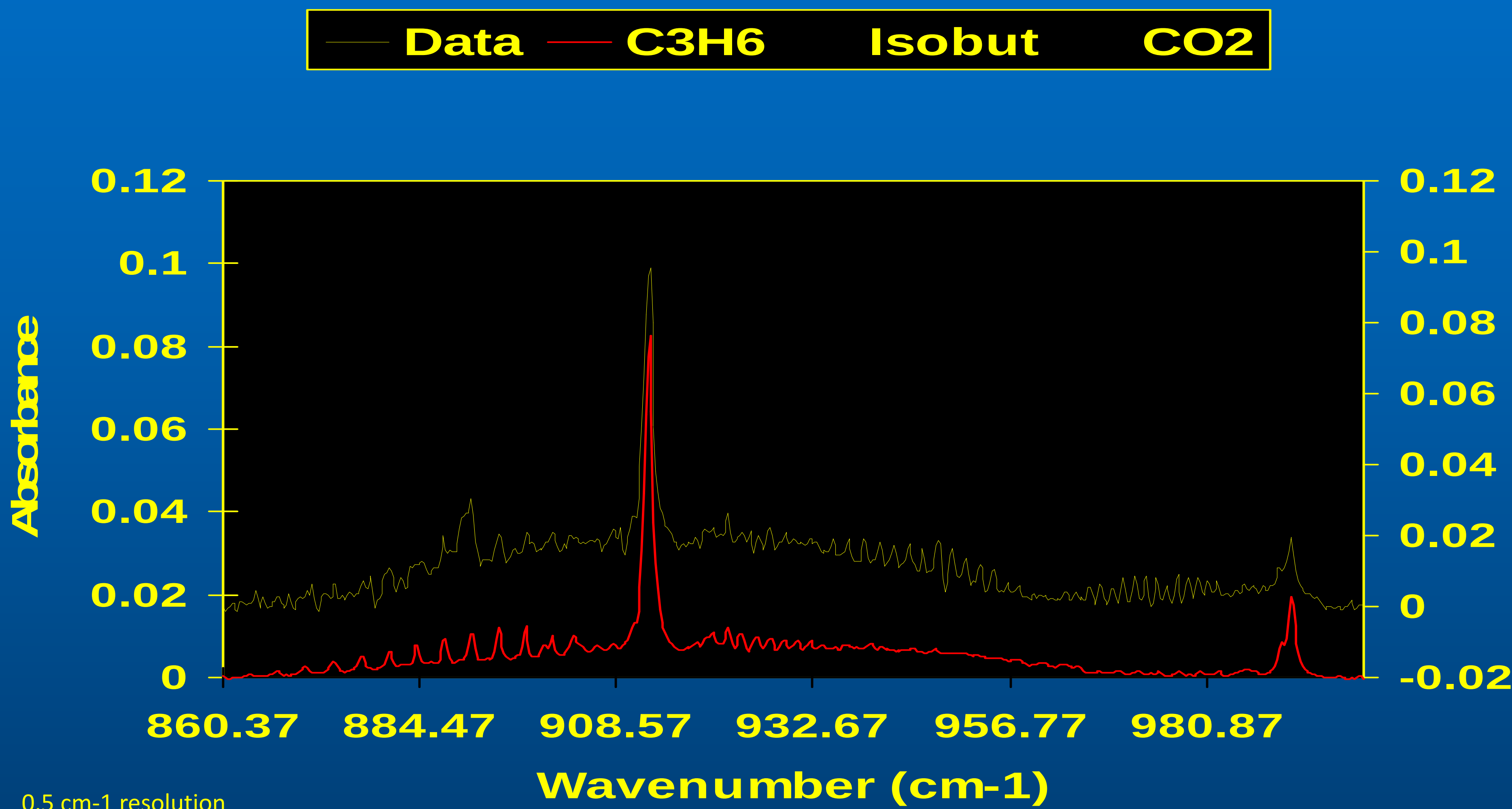
Reference File Overlays



0.5 cm-1 resolution

Difference Spectrum

Reference File Overlays



0.5 cm-1 resolution

Difference Spectrum

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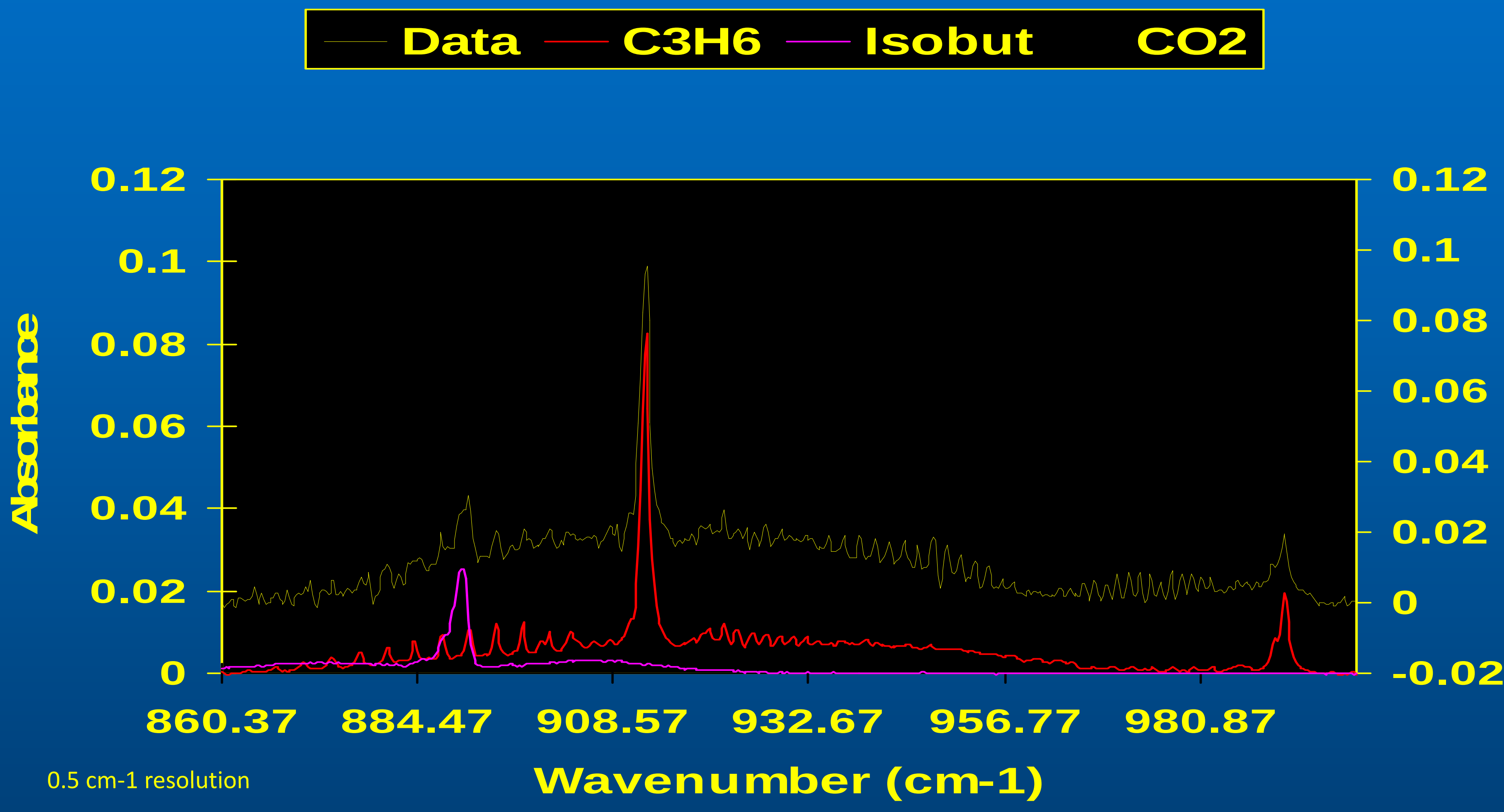
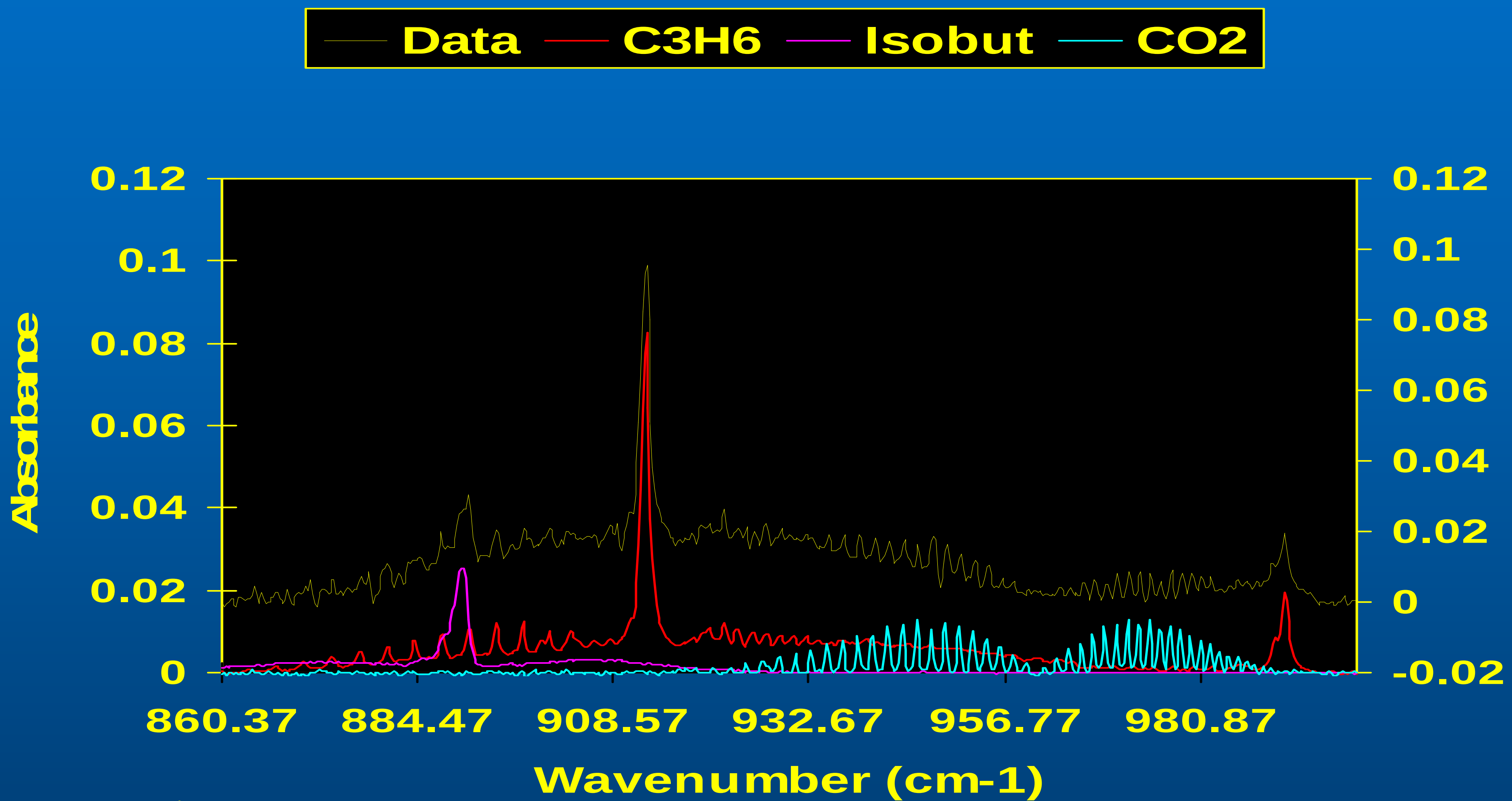


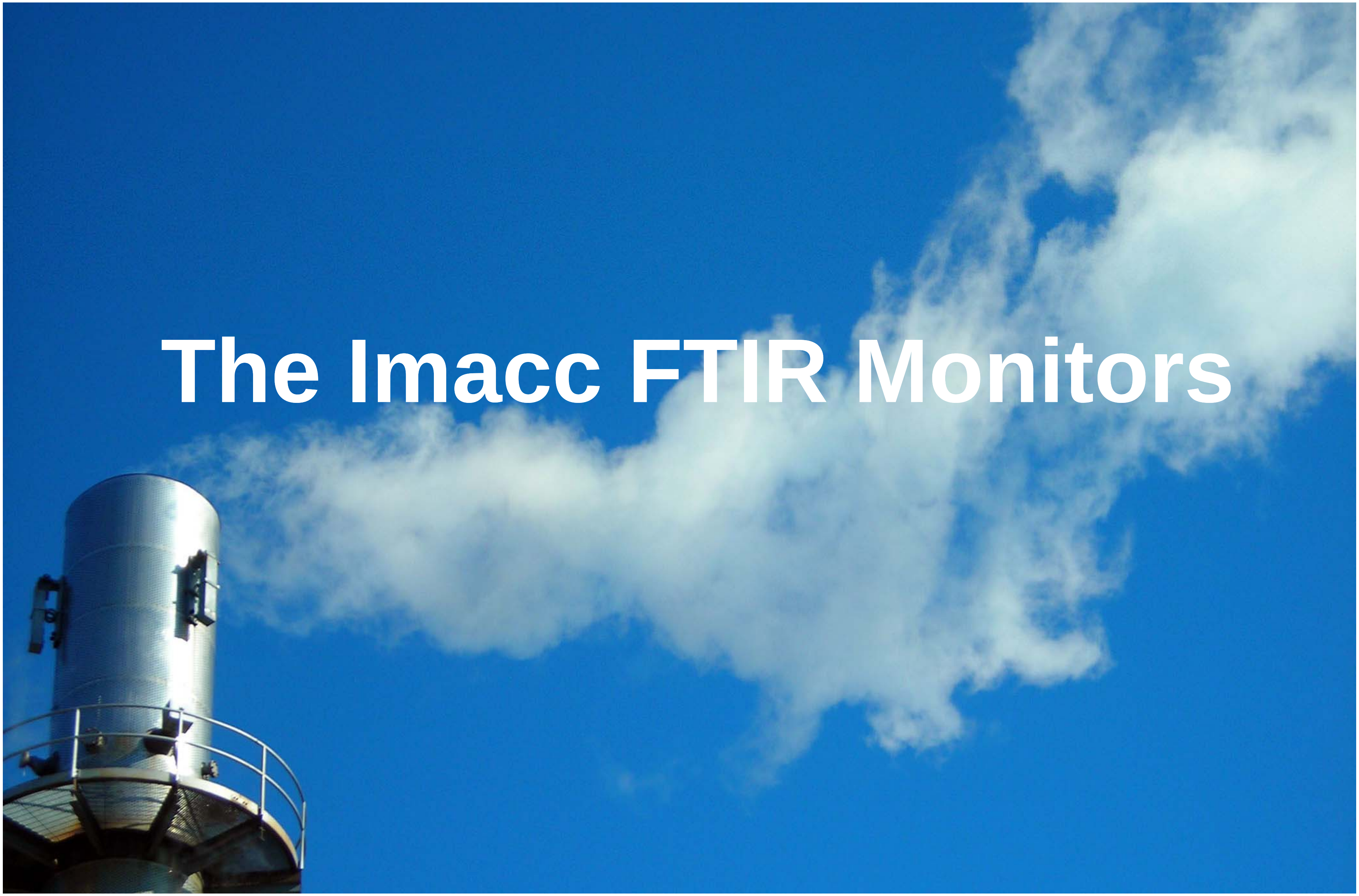
0.5 cm-1 resolution

Difference Spectrum
Reference File Overlays



0.5 cm-1 resolution

The Imacc FTIR Monitors



The Base Unit

- The unit utilizes a 0.125 cm^{-1} “dash-pot” interferometer with “dynamic alignment” both of which provide stability critical for field work
  - The “dash pot” consists of a graphite piston running in a precision glass tube, it has only one degree of freedom and as a result is very stable and immune to vibration
  - The “dynamic alignment” is laser controlled and actively aligns the FTIR thousands of times per second providing additional immunity to vibration and temperature variations

Base Unit Accessories

- The modular arrangement allows use of both cell-based and open-path accessories with one base unit
- The cell-based accessories are used for extractive monitoring in: ambient air, industrial process streams, stacks, or abatement systems
- The telescope-based accessories are used for open-path monitoring in: the ambient air, at the fence-line, or around process areas

Cell Based Accessories

- The cell-based accessories use heated cells and extraction lines at temperatures up to 200°C, allowing for monitoring of saturated process streams (hot/wet).
- Typical cell accessories include:
  - Fixed path cells: 5 cm and 10 cm (% concentrations)
  - Variable path cells

    1 m to 10 m cell (0.1 ppm)

    4 m to 32 m cell (20 to 50 ppb)

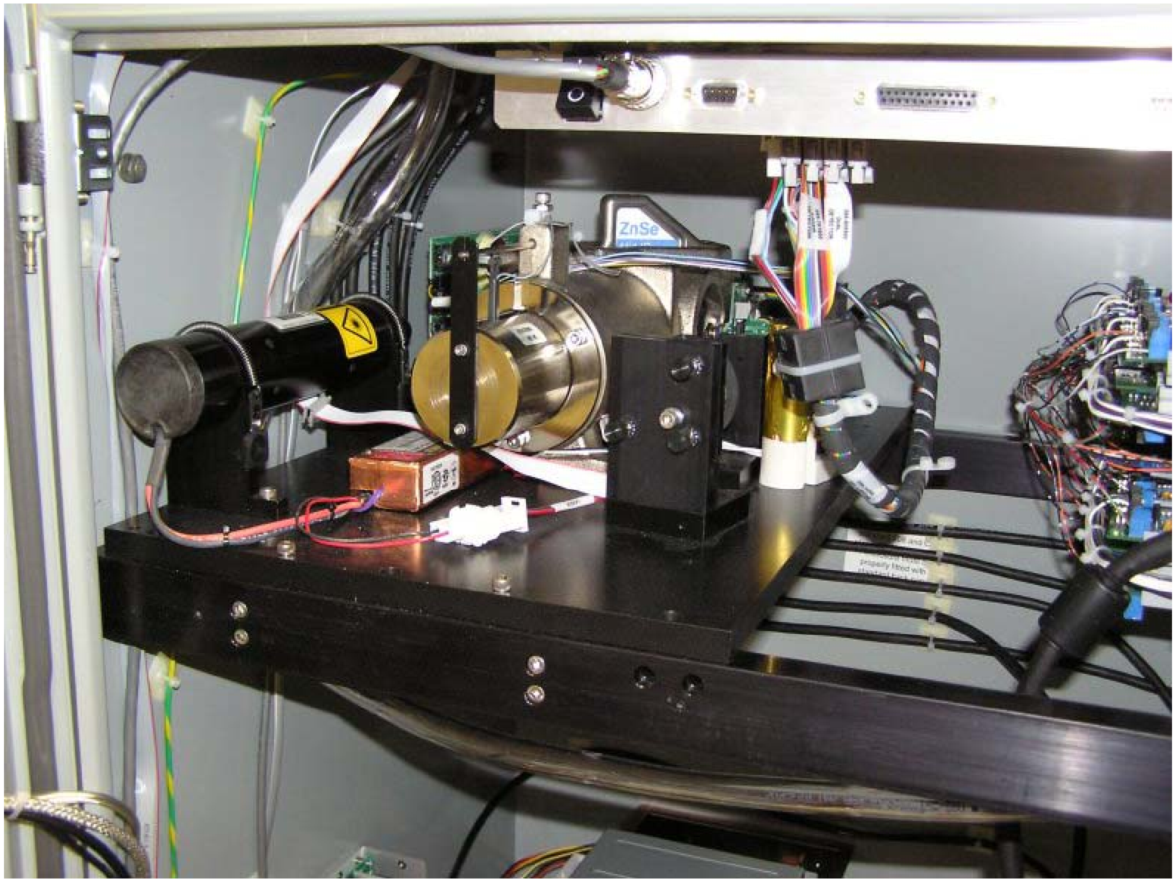
    12 m to 80 m cell (3 to 10 ppb)

    24 m to 150 m cell (1-5 ppb)

Shell Cell-Based Monitor

Interior of Shell System

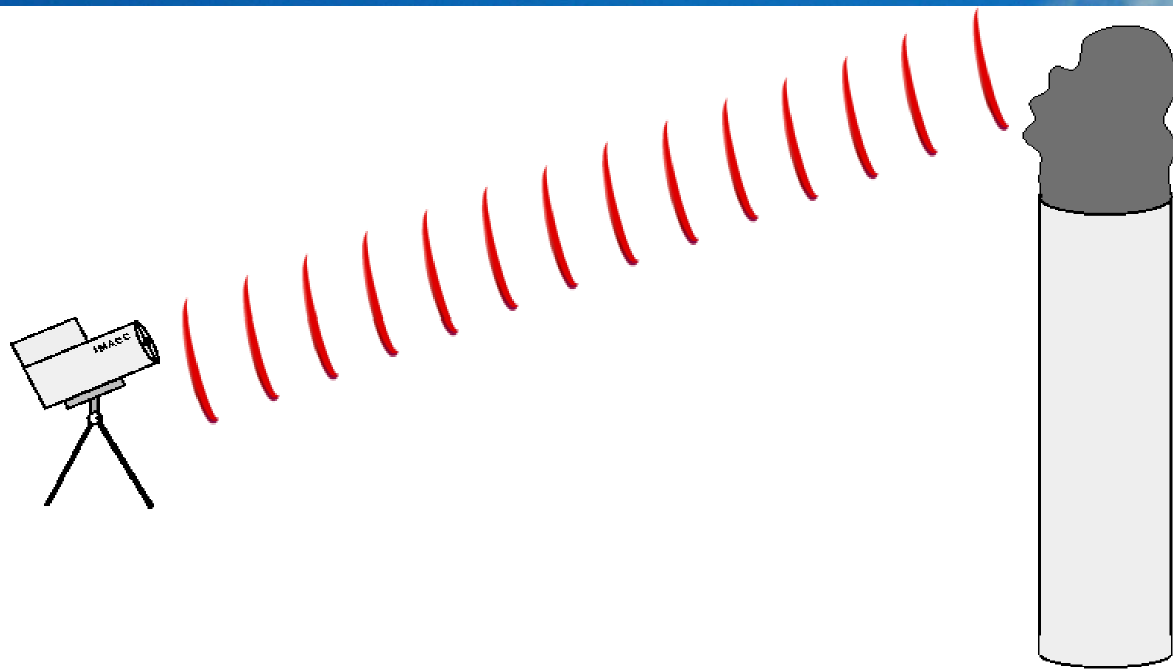
Lower-Level FTIR Modulator

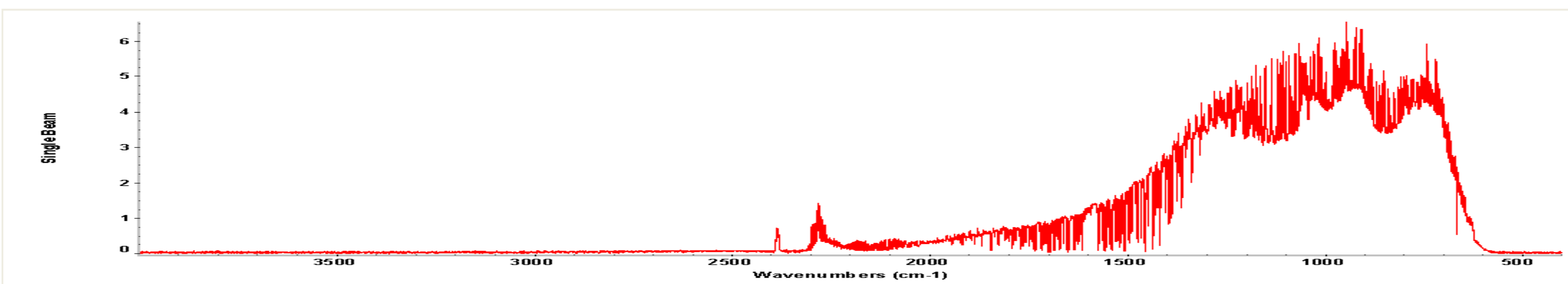


Upper-Level Cell and Detector

Passive FTIR Operation

Passive FTIR Radiometer

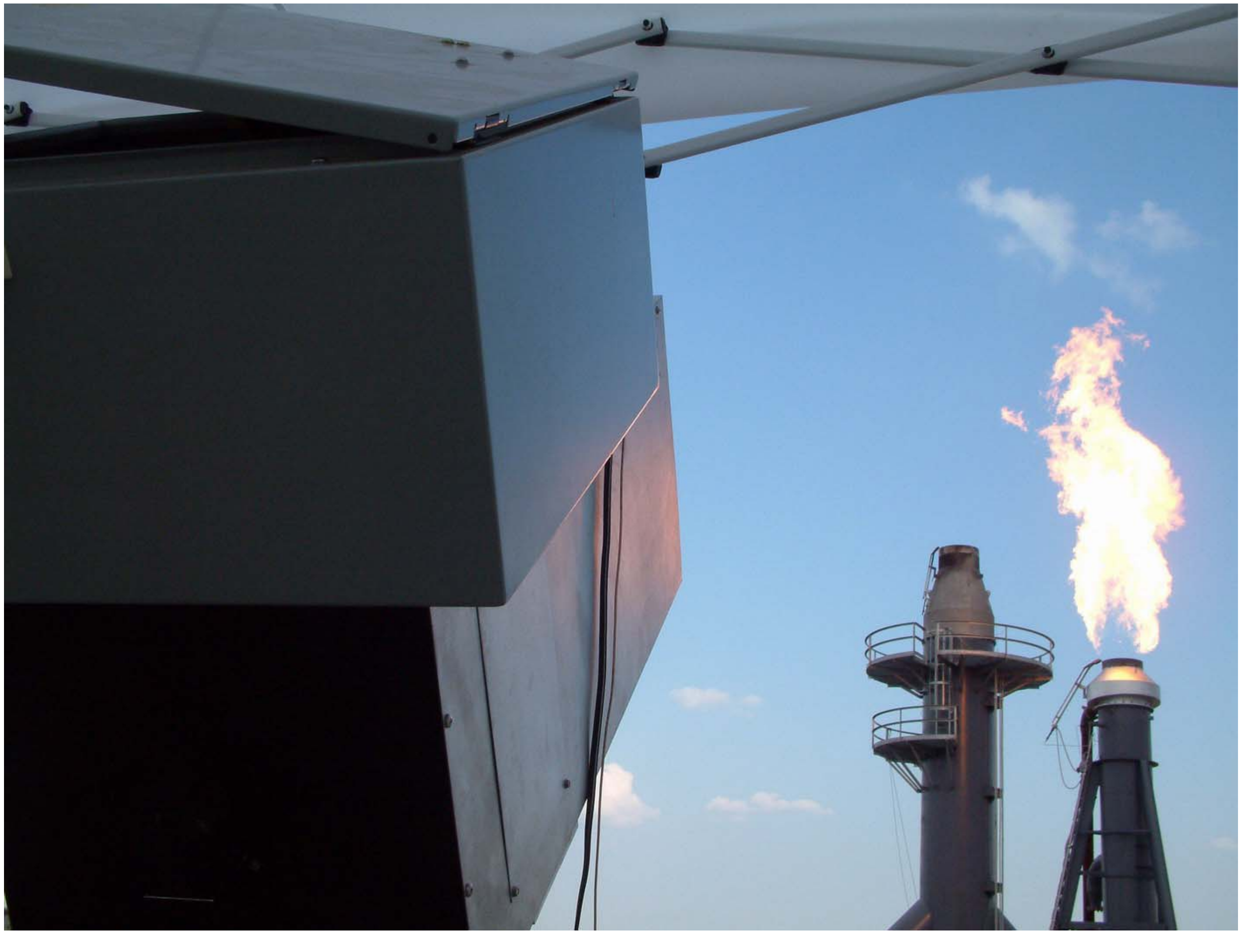




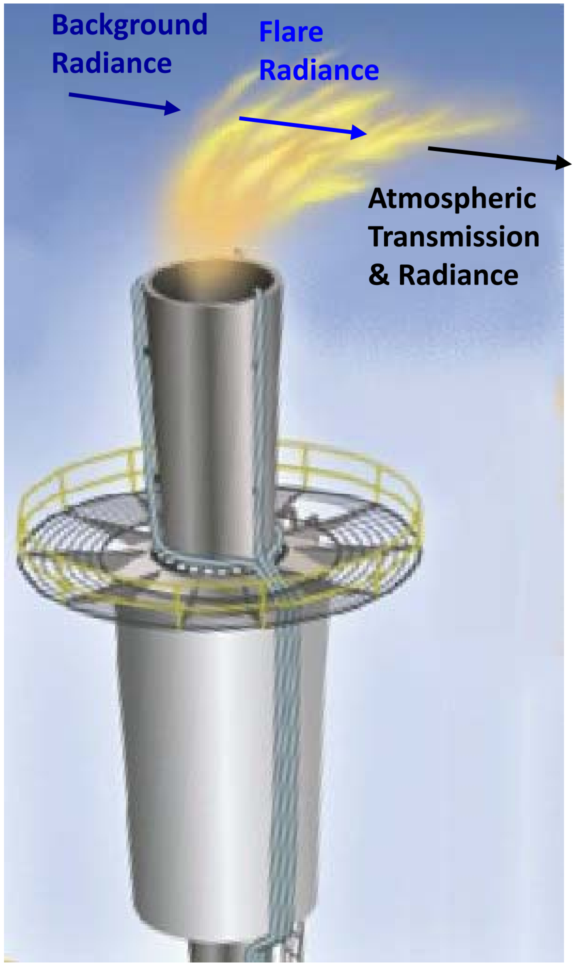
Passive Open-Path Signatures

- Any hot gas emits infrared with exactly the same pattern that it has in absorption
- Therefore species in emission spectra can be identified and quantitated in the same manner as they are in absorption spectroscopy
- However
- The strength of emission is proportional to concentration as it is in absorption spectra but also to the temperature of the gas.

Hardware - Passive FTIR At Flare Test



The Signal Observed



The FTIR Signal arises from Four elements:

- Background radiance
- Flare radiance
- Atmospheric Transmission and Radiance

- **The Total FTIR Signal M_p is then:**

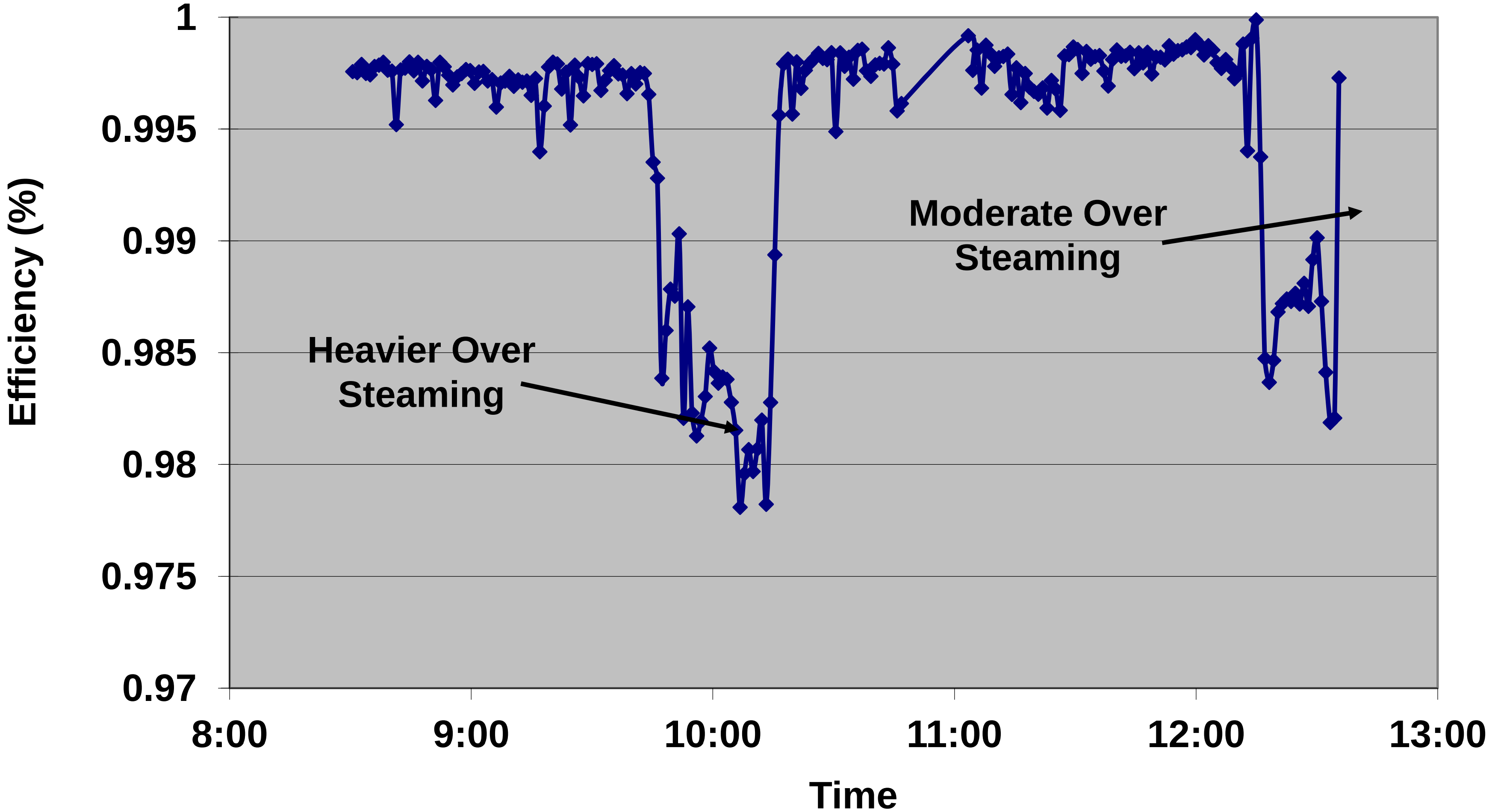
$$R_b * \tau_{plume}\, \tau_{atm} + R_p * \tau_{atm} + R_{atm} + R_{ftir}$$

The FTIR signal can be reduced to:

$$R_p = \frac{(M_p - M_b) * Cal}{\tau_{air} - \frac{(M_b - M_n) * Cal}{L_{bb}^{p}}}$$

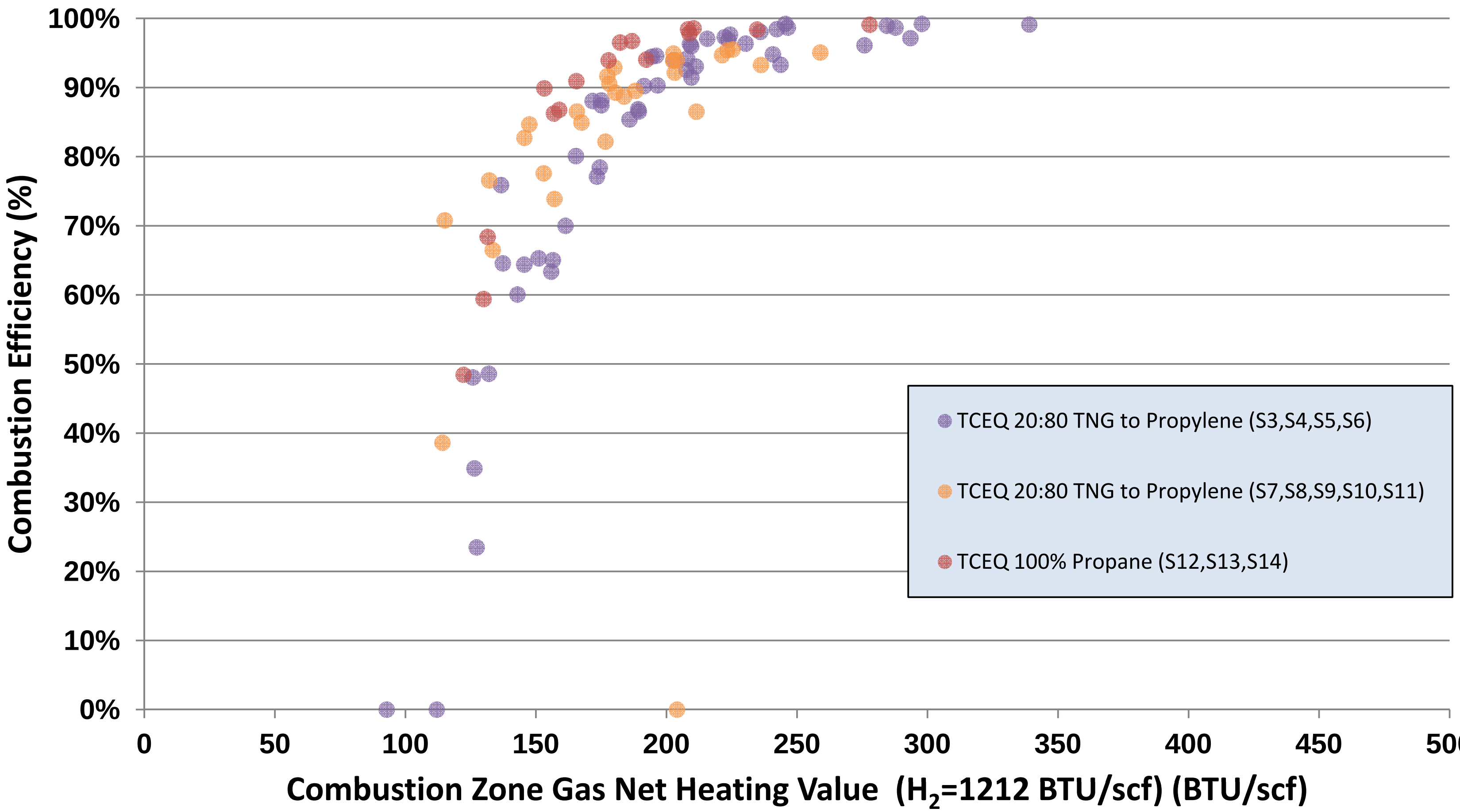
M_p = The measured plume radiance
M_b = The measured background radiance
Mn = The measured cold source background
L^p_{bb} = The Planck function at temperature of plume
Cal = The system calibration function
τ_{air} = Air Transmission

Flare Efficiency

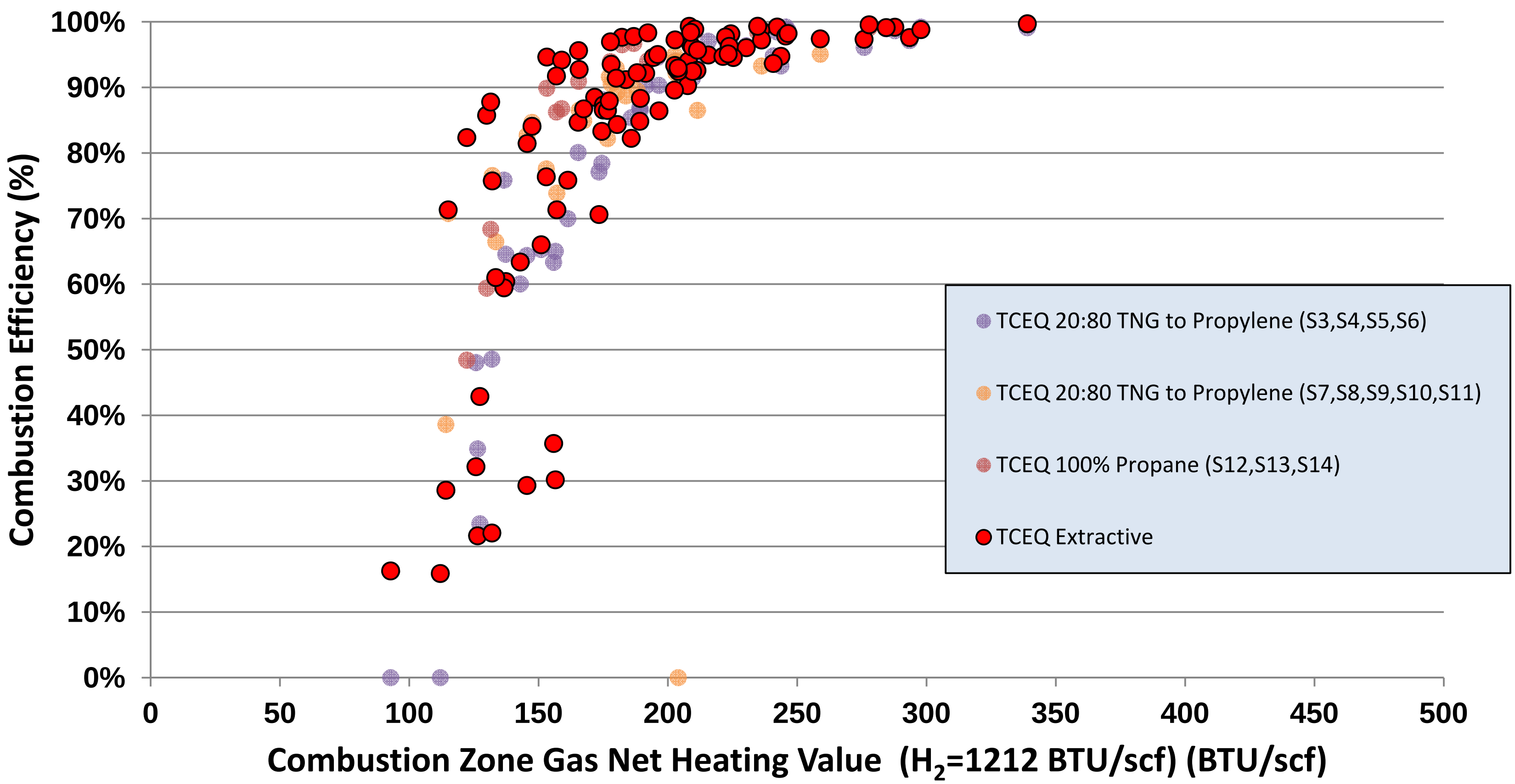


Extractive Probe Used in TCEQ Flare Validation Test

CE vs. CZG NHV - All TCEQ Steam



CE vs. CZG NHV - All TCEQ Steam




"That's all Folks!"