Air Contamination Quantification by FTIR Gas Cell

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Wallops Flight Facility

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Why is Gas Composition Important?

Gas quality is of utmost importance when supplied gas is required for breathing

- Firefighters require supplied breathing air in certain circumstances
- Pilots require aviators grade breathing oxygen at certain altitudes and when performing certain maneuvers

Methods of Accreditation

Impurity Requirements for Various Certifications of Air and Oxygen	ABO	ABO	ABO	ABO	Breathing Air	Breathing Air
	MIL-PRF-27210[1]	MIL-PRF-27210[1]	CGA G-4.3[2]	CGA G-4.3[2]	CGA G–7.1[3]	NFPA 1989[4]
	Revision H	Revision H	2015 Edition	2015 Edition	2011 Edition	2013 Edition
	Type I (Gas)	Type II (Liquid)	Type I E (Gas)	Type II D (Liquid)	Grade D	
Oxygen Content	>99.5%	>99.5%	>99.5%	>99.5%	19.5 – 23.5%	19.5 – 23%
Moisture	<6.6ppm / -63.3 °C	<6.6ppm / -63.3 °C	<6.6ppm / -°63.3 C	<6.6 ppm / -°63.3 C	<67 ppm / -°45.6 C	<24 ppm
Nitrogen	Remainder	Remainder	Remainder	Remainder	Remainder	75 - 81%
Rare Gases	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder
Carbon Dioxide	<10 ppm	<5 ppm	<10 ppm	<5 ppm	<1000 ppm	<1000 ± 50 ppm
Carbon Monoxide	N/A	N/A	N/A	N/A	<10 ppm	<5 ± 0.5 ppm
Methane	<50 ppm	<25 ppm	<50 ppm	<25 ppm	N/A	N/A
Acetylene	<0.1 ppm	<0.05 ppm	<0.1 ppm	<0.05 ppm	N/A	N/A
Ethylene	<0.4 ppm	<0.2 ppm	<0.4 ppm	<0.2 ppm	N/A	N/A
Non-methane Hydrocarbons as methane equivalent	N/A	N/A	N/A	N/A	N/A	<25 ± 1 ppm
Non-methane Hydrocarbons as ethane equivalent	<6 ppm	<3 ppm	<6 ppm	<3 ppm	N/A	N/A
Nitrous Oxide	<4 ppm	<2 ppm	<4 ppm	<2 ppm	N/A	N/A
Halogenated Compounds (refrigerant)	<2 ppm	<1 ppm	<2 ppm	<1 ppm	N/A	N/A
Halogenated Compounds (solvents)	<0.2 ppm	<0.1 ppm	<0.2 ppm	<0.1 ppm	N/A	N/A
Other	<0.2 ppm	<0.1 ppm	<0.2 ppm	<0.1 ppm	N/A	N/A
Condensed Hydrocarbons & particulates	N/A	N/A	N/A	N/A	<5 mg/m^3	<2 mg/m^3
Odor	N/A	N/A	N/A	N/A	N/A	No / Slight Odor

Notes: ppm = parts per million; C = Celsius; N/A = Not Applicable; mg/m^3 = milligrams per cubic meter

What is GC?

Gas chromatography

- Separates chemicals by using a carrier gas to carry molecules through a long column
- Chemicals exhibit different retention times based on their physical and chemical properties in relation to a stationary phase

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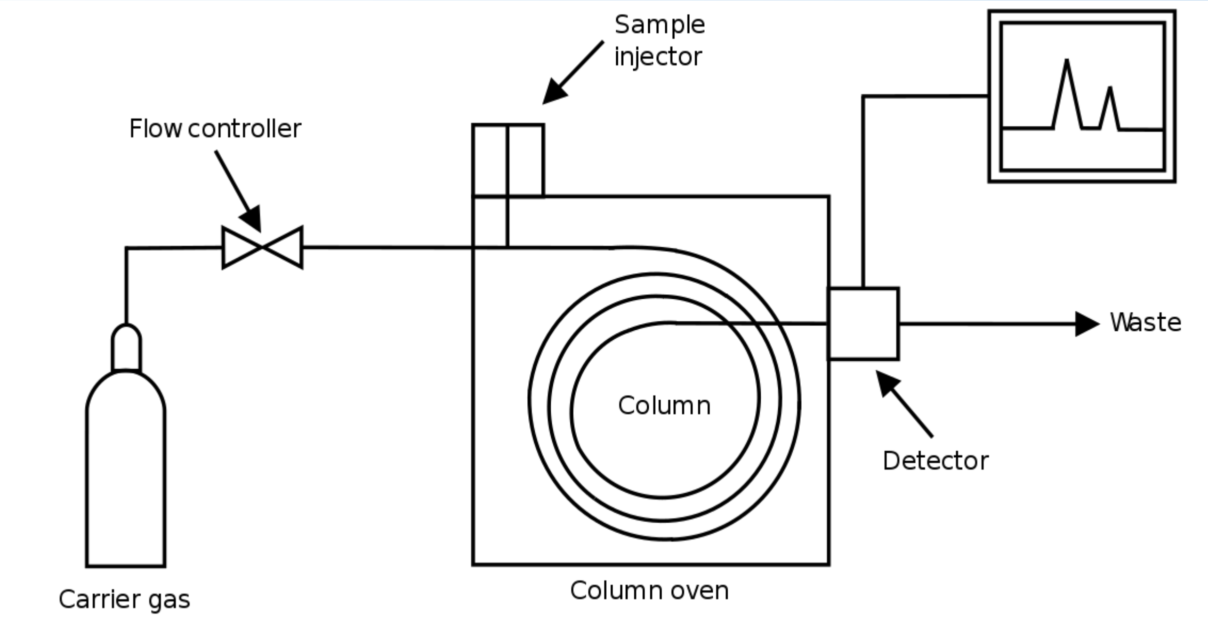


Why Use FTIR Instead of GC?

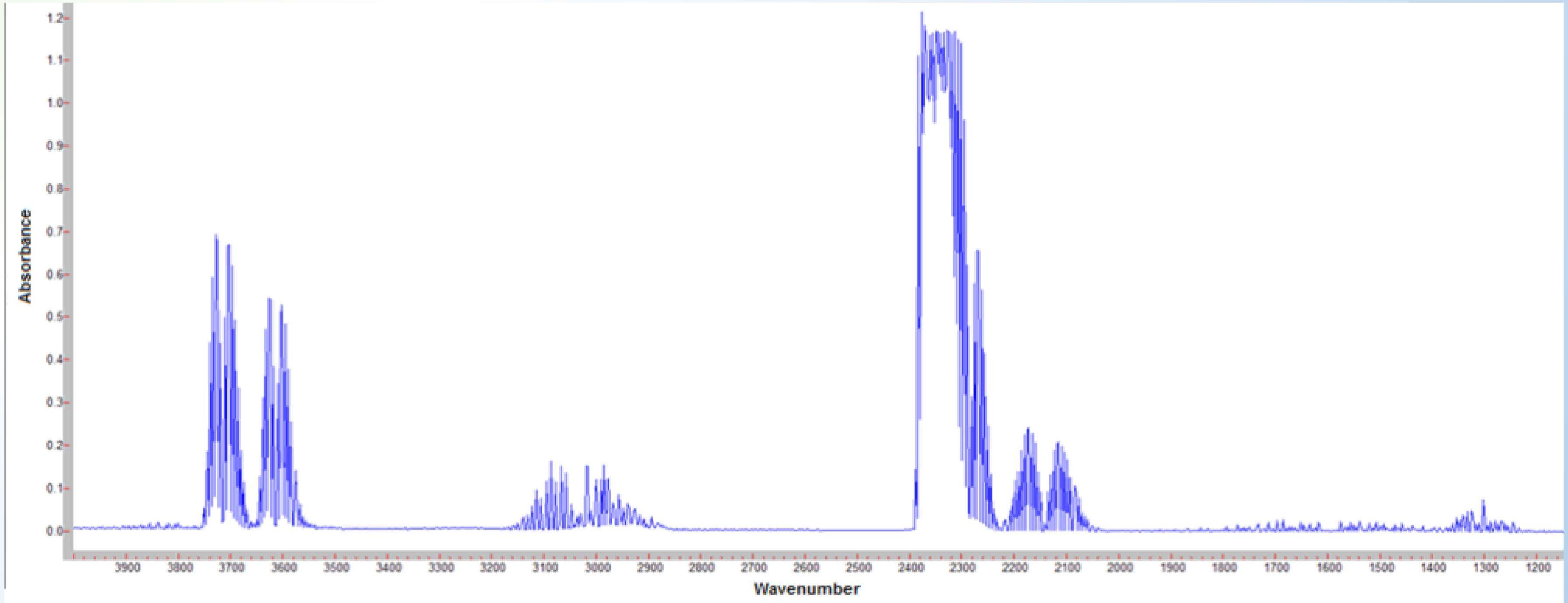
- Calibration time: 15 minutes vs 2-3+ hours
- The requirement of carrier gas and specific columns makes GC more expensive to maintain and operate
- GC is more susceptible to variation from changes in method and conditions such as carrier gas flow rate, column temperature, changes in columns, etc.
- Spectral features associated with FTIR do not vary in location due to changes in external conditions

Infrared Spectroscopy – Brief Overview

- Infrared light is passed through a sample and collected by a detector
- Molecules absorb infrared radiation at resonant frequencies that are characteristic of their structure
- Functional groups display predictable infrared properties that can be used to identify compounds of interest in a sample

Infrared Spectroscopy - Continued

- A spectrum is created with signal response vs. wavelength which acts as a "fingerprint" of the sample
- Only vibrations resulting in a change in dipole moment are detected



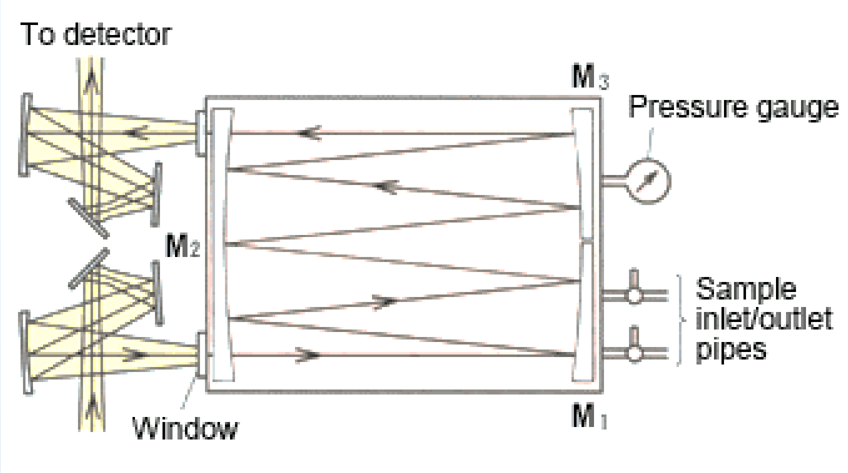
What is FTIR?

- Fourier Transform Infrared Spectroscopy

- FTIR differs from traditional IR spectroscopy in that it allows for the collection of a broad range of wavelengths simultaneously

FTIR Gas Cell

- A common method used with gas cells is the “Least Squares Fit” method
- Works best with pure standards
- Identifies molecules based on their entire spectral fingerprint, as opposed to individual functional group spectral features
- Gas cells allow for high signal throughput by taking advantage of the path length feature of Beer’s Law



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Disadvantages of FTIR

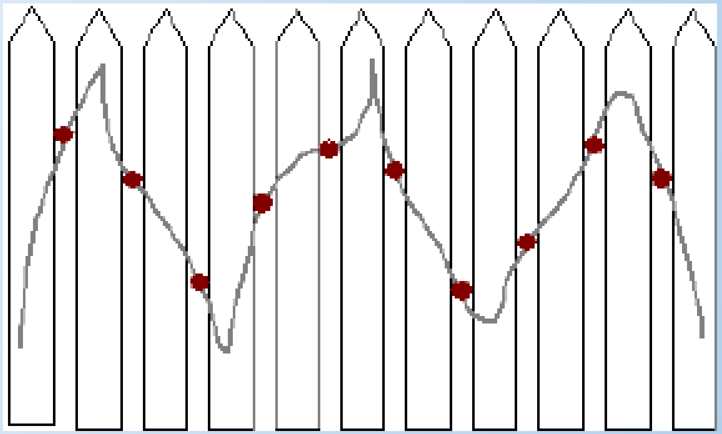
- Infrared radiation has low energy - it can be difficult to obtain high levels of sensitivity
- Noise in one region of a spectrum can spread throughout the spectrum
- Only detects molecular vibrations causing a change in dipole moment - cannot be used for the detection of diatomic molecules

Instrument Set-up

FTIR – Agilent Cary 660

- Software – Resolutions Pro V 5.2.0
- Source – MIR Source
- Beam Splitter – Potassium Bromide (KBr)
- Gas Cell – Mars 2L/10M-SS Multi-Pass Gas Cell
- Detector – Mercury Cadmium Telluride (MCT)
- Resolution – 0.1 cm^{-1}
- Apodization – Happ-Ganzel
- Zero fill – 8

The Picket Fence Effect [7]



MCT Detector

- Mercury Cadmium Telluride
- Only common material that can detect IR radiation in both common atmospheric windows
  - Mid-wave infrared window 3300 cm^{-1} to 2000 cm^{-1}
  - Long-wave infrared window 1250 cm^{-1} to 830 cm^{-1}
- High quantum efficiency gives superior sensitivity
- Requires cooling with liquid nitrogen to reduce noise

Apodization

- The mathematical transformation of raw data used to create spectra
- Common apodization functions include boxcar, triangular, and Happ-Genzel
- Happ-Genzel results in lower resolution but minimizes the ripple effect caused by large peaks

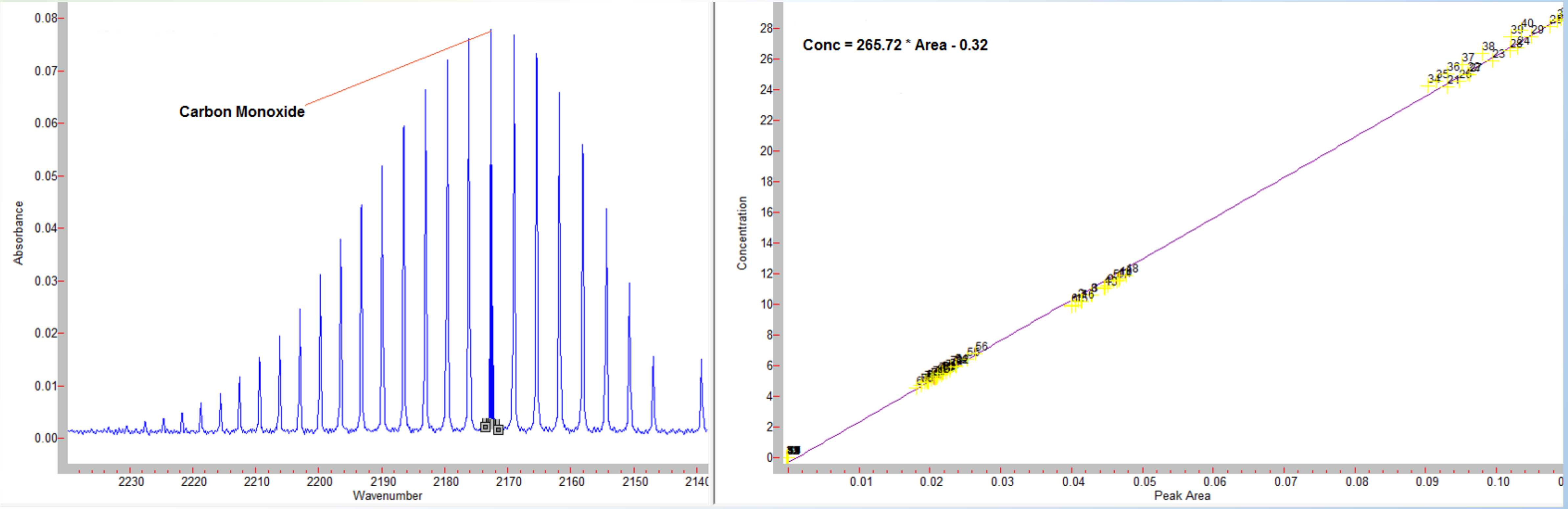
Creating Calibration Curves

- Varying the pressure inside the gas cell can simulate different concentrations

$$C = \frac{PSIg + 14.7}{14.7} * X$$

- Limitations: Any uncertainty in the standards is expanded the further away the pressure in the cell is from 0 PSIg

Carbon Monoxide Curve Example



Using the blank determination method gave us a quantitation limit of 0.37 ppm with an uncertainty of ± 0.09 ppm

Blank Determination Method[8]

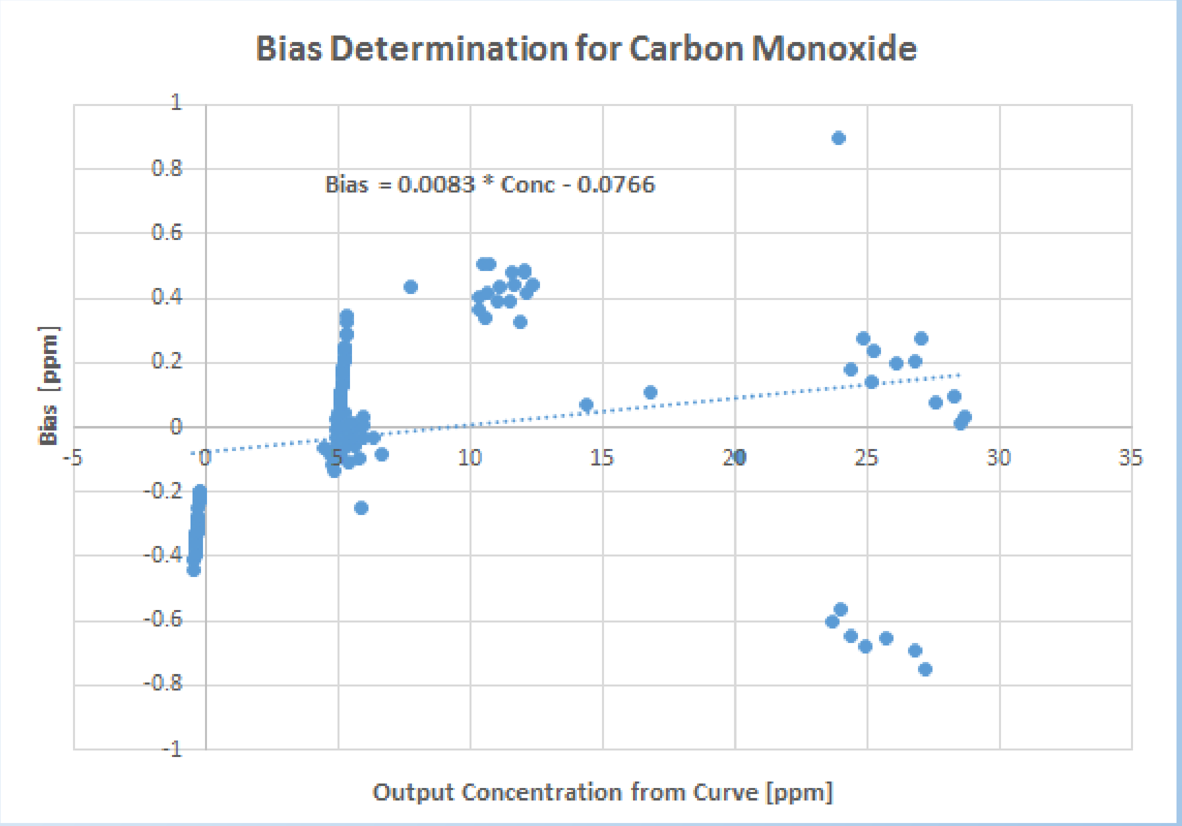
- Detection Limit= $Avg_{Blank} + 3 * Std\ Dev_{Blank}$

- Quantitation Limit= $Avg_{Blank} + 10 * Std\ Dev_{Blank}$

- Used when blank analysis yields results with nonzero standard deviation
- Weakness is that there is no evidence that low concentrations of analyte will actually produce a signal distinguishable from a blank sample

Concentration Dependent Bias[9]

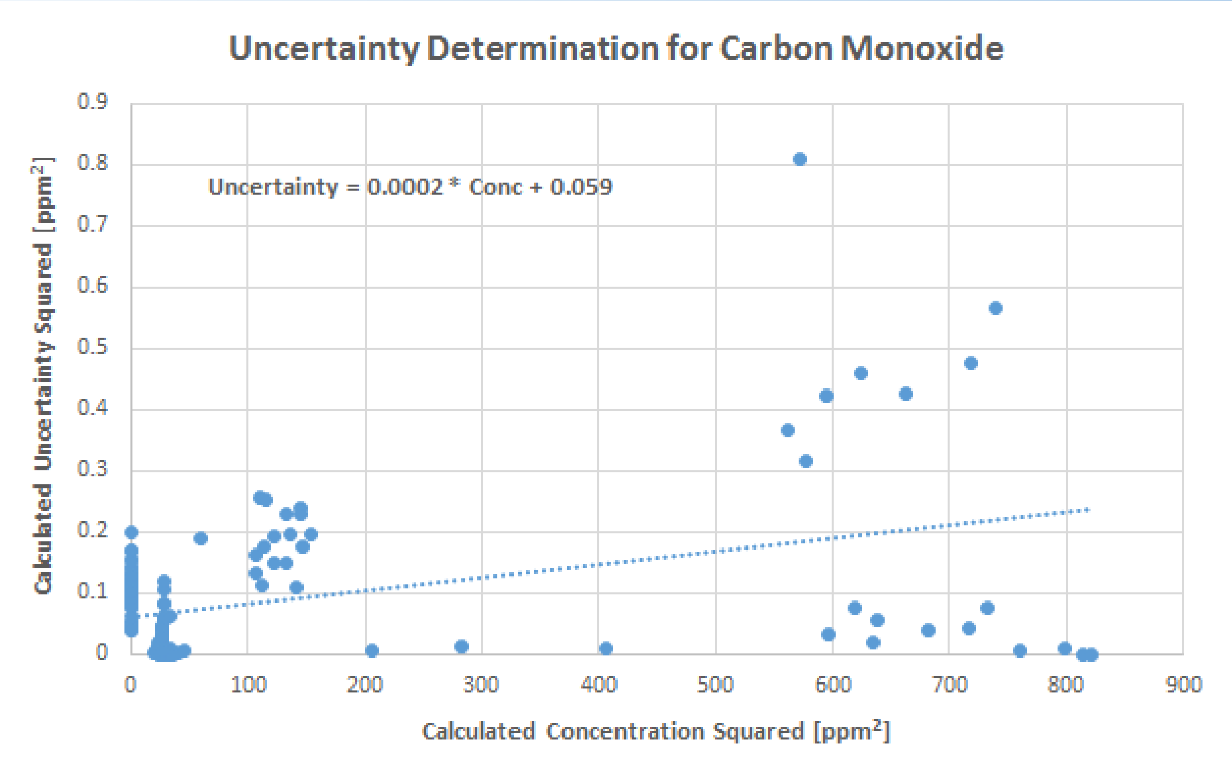
- Bias – Difference between the average of measurements made on the same object and its true value
- Does bias change throughout a curve?
- Eurachem Guide "Quantifying Uncertainty in Analytical Measurement"



Concentration Dependent Uncertainty[9]

- Uncertainty – Estimate of how far an experimental value may be from the true value

- Uncertainty could be overstated or understated based on the concentration used to calculate it

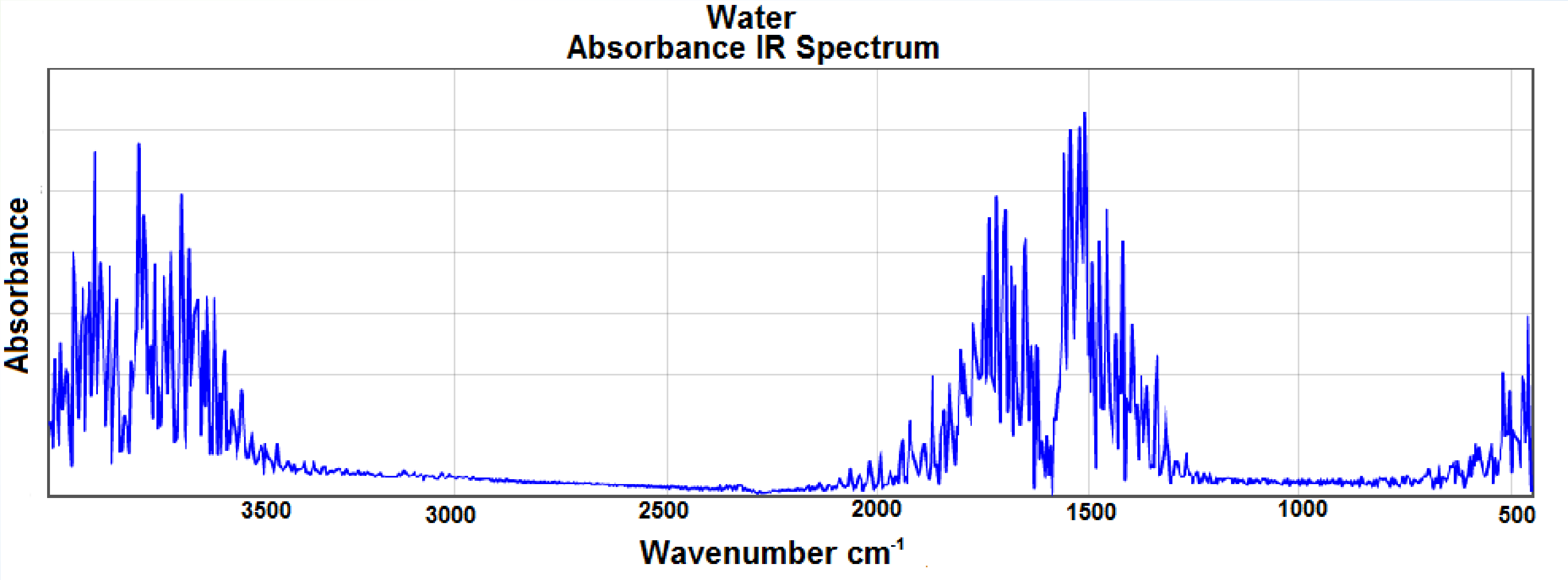


Major Interferences

- Specificity - The extent to which a calibration is specific for a particular molecule
- Care must be taken to ensure specificity of calibration curves before signal to noise can be maximized
- If an interference is found, can use different IR region for identification

Water

- Biggest concern in gas analysis due to overlap of regions
- Water is a strong absorber of IR, combined with the 10 meter path length gives strong signals for small concentrations of water



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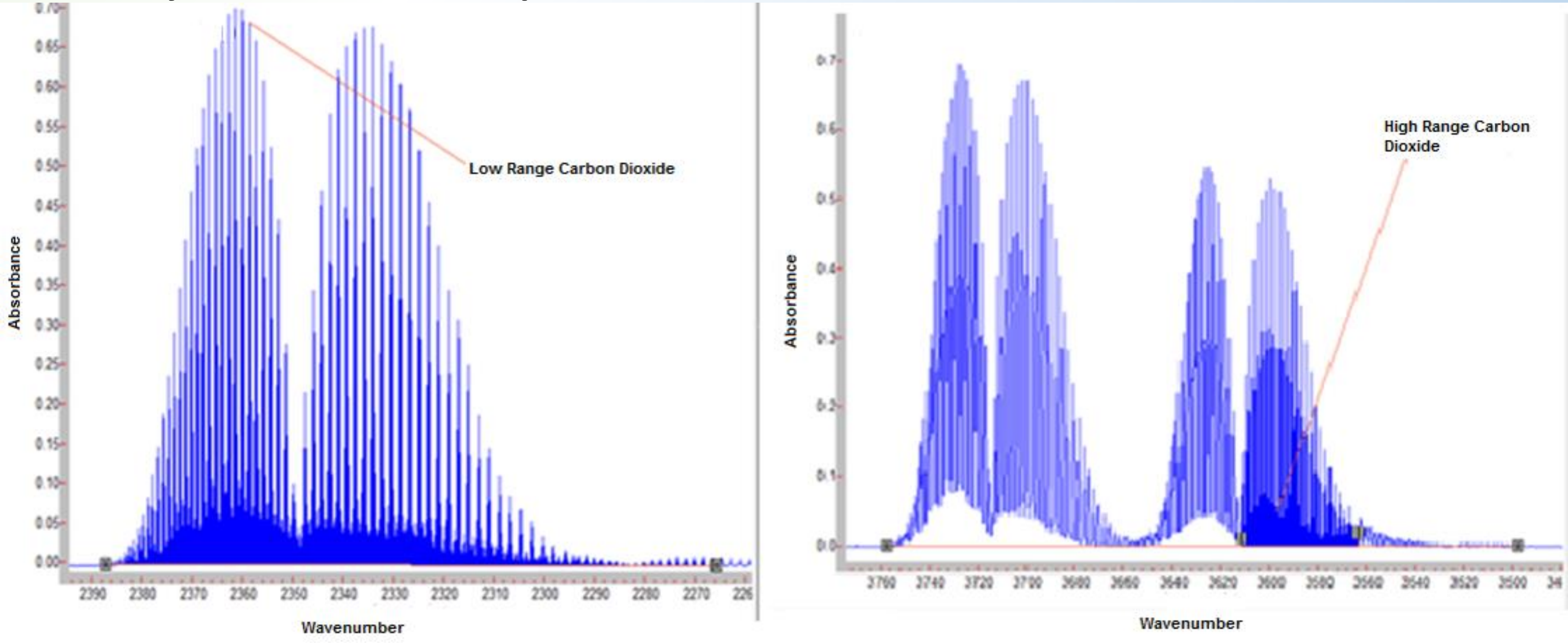
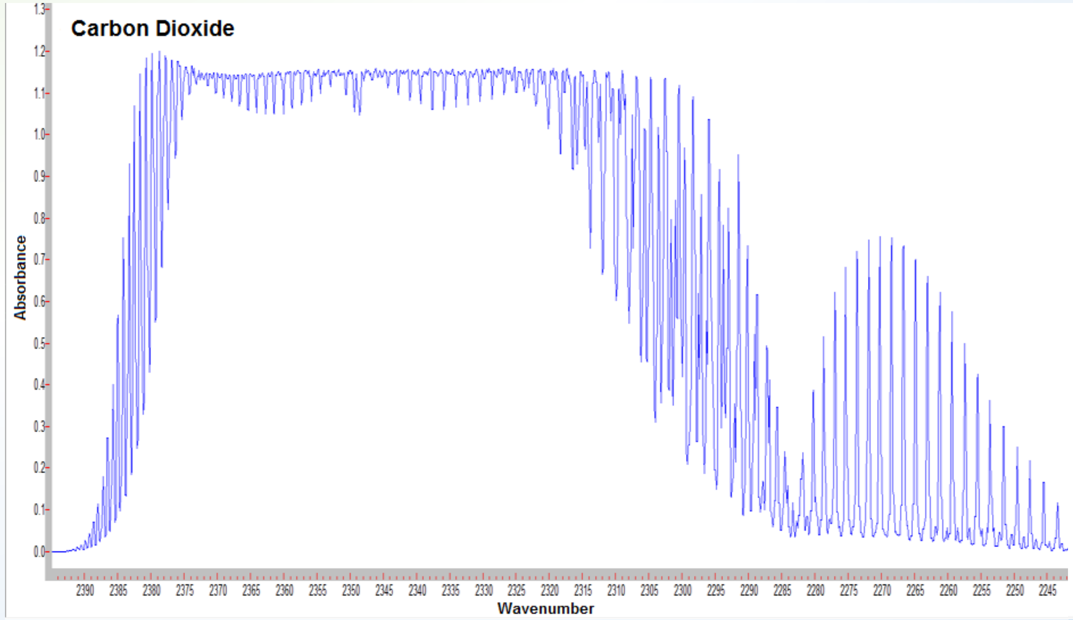
Carbon Dioxide Measurements

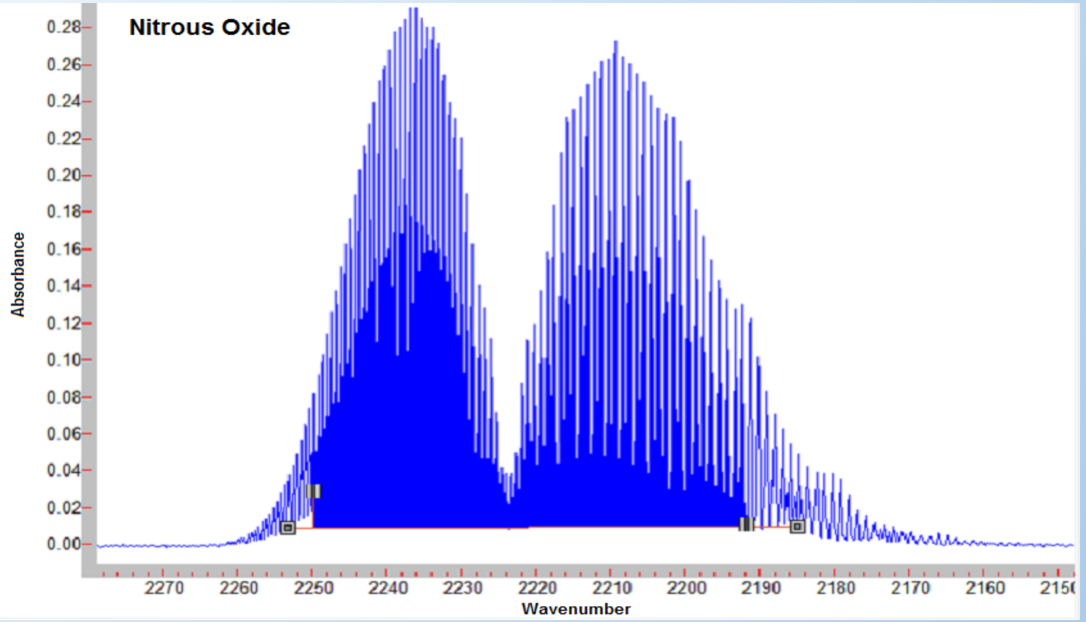
- Carbon Dioxide is present in normal air and most calibration gases
- The most active region for carbon dioxide quantification saturates around 100ppm with my instrument parameters



Nitrous Oxide

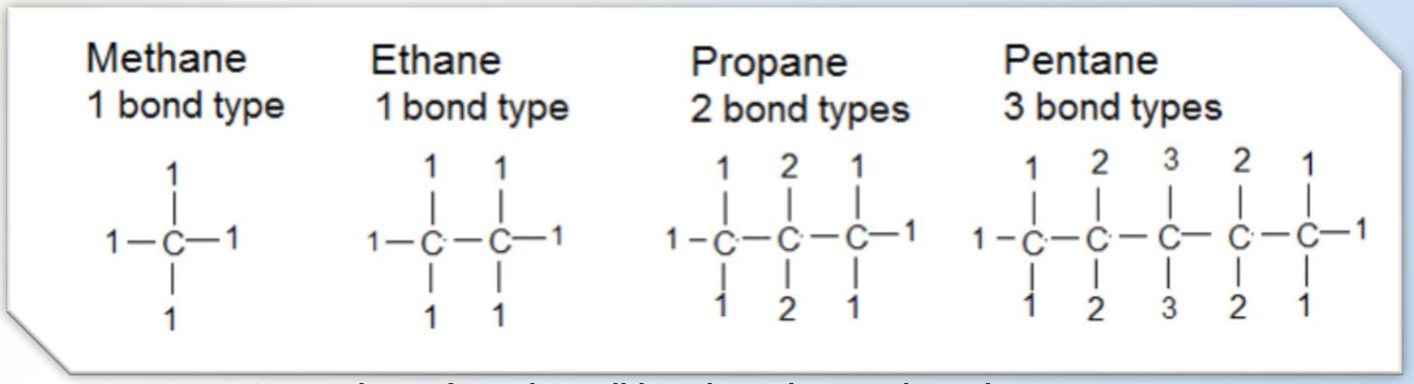
- Nitrous Oxide contains similar functional groups to carbon dioxide and therefore exhibits similar IR modes
- Certifications requiring nitrous oxide measurements contain low concentrations of carbon dioxide





Total Hydrocarbon Determination

- Certifications require grouped quantification of hydrocarbons

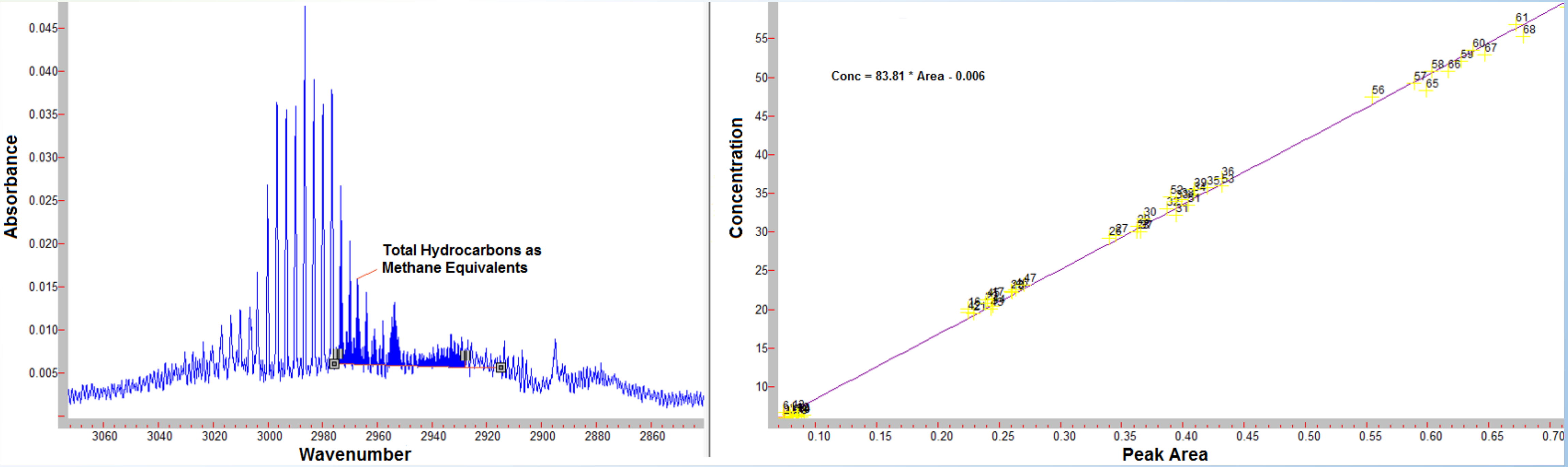


Comparison of Bond Conditions in Various Hydrocarbons

- Methane and ethane have unique IR modes that can be used to distinguish them from other hydrocarbons

Total Hydrocarbon Quantification

- All hydrocarbons exhibit C-H combination bands near 3000 cm^{-1}
- This curve only gives total hydrocarbons as methane equivalents, it cannot be used to distinguish between hydrocarbons such as propane and butane



Results

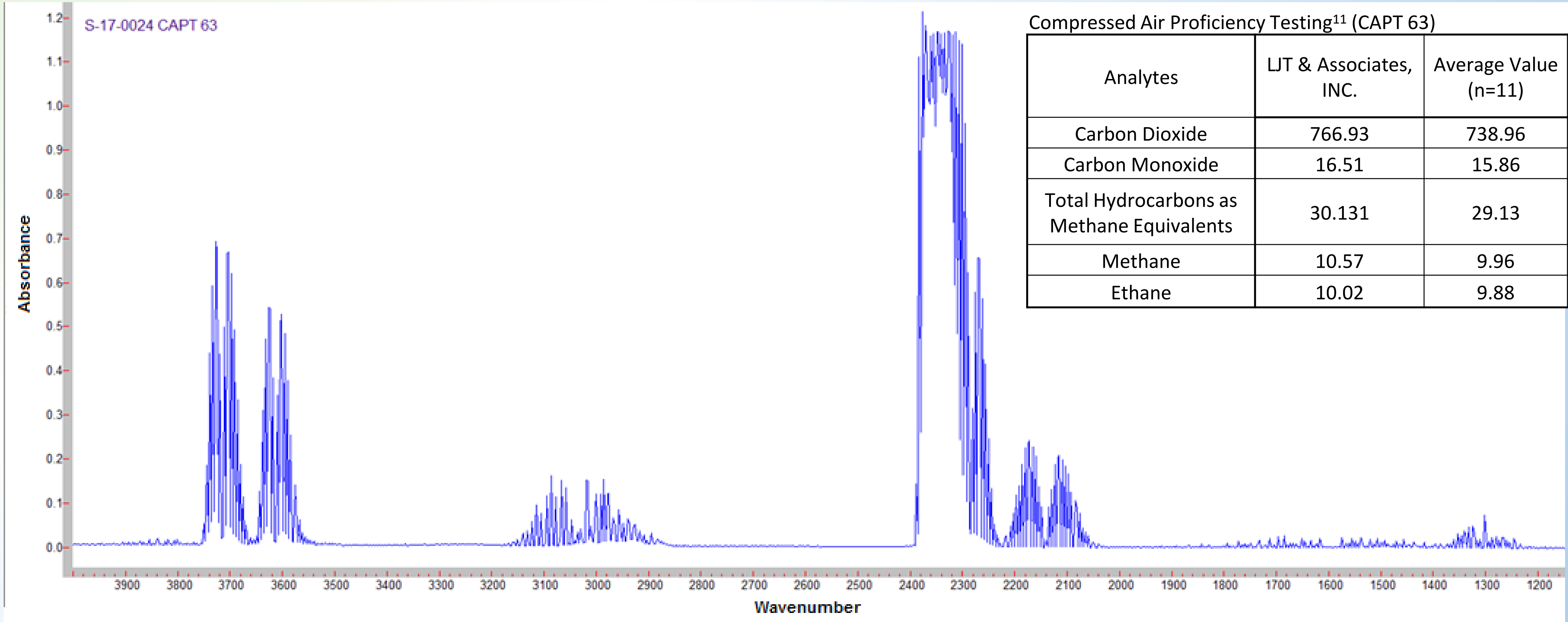
- Results from a comprehensive study of a certified standard at the limits set in NFPA 1989 prove the methods meet the required specifications

Laboratory Control Sample Uncertainty Study (n=43)

Analytes	Average [ppm]	Standard Deviation [ppm]	Expected [ppm]	Bias [ppm]	Expanded Uncertainty (RSD) [%]	Expanded Uncertainty [ppm]
High Range Carbon Dioxide	1024.058	11.635	1038	13.942	2.272	23.27
Carbon Monoxide	5.174	0.077	5.012	-0.162	2.986	0.154
Total Hydrocarbons as Methane Equivalents	26.755	0.751	25.44	-1.315	5.614	1.502
Methane & Ethane as Methane Equivalents	24.955	0.417	25.44	0.485	3.343	0.834
Ethane	13.014	0.142	12.72	-0.294	2.178	0.283

Results

- Five consecutive 100% passing CAPT round robin samples



Compressed Air Proficiency Testing[11] (CAPT 63)

Analytes	LJT & Associates, INC.	Average Value (n=11)	(mean+3σ)	(mean-3σ)
Carbon Dioxide	766.93	738.96	995	528
Carbon Monoxide	16.51	15.86	20.6	10.2
Total Hydrocarbons as Methane Equivalents	30.131	29.13	33	25.2
Methane	10.57	9.96	13.3	7.2
Ethane	10.02	9.88	11.4	8.4

Conclusion

- Very few labs employee FTIR for gas analysis
- The methods created by our lab and discussed here can meet the requirements for gas certifications
- FTIR gas analysis is as or more accurate than GC and is much faster

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