Certification Methods Errors in the Analysis of NMHC and VOCs in CNG-Based Engine Emissions

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Technology for Productivity

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Which is Best for CNG Fueled Engine NMHC or VOCs Emissions?

FID

FTIR

GC

EPA Proposed Changes to 40 CFR Subpart JJJJ

- Rule as proposed has Method 25A along with EPA part 1065 for NMC providing VOCs
  - (v.) Not correct – NMC only provides CH4, **NOT** Ethane gives NMHC not VOCs

Current Regulation since 2008

You must	Using	According to the following requirements
v. Measure VOC at the exhaust of the stationary internal combustion engine	(5) Methods 25A and 18 of 40 CFR part 60, appendix A, Method 25A with the use of a methane cutter as described in 40 CFR 1065.265, Method 18 or 40 CFR part 60, appendix A[c d], Method 320 of 40 CFR part 63, appendix A, or ASTM D 6348–03 (incorporated by reference, *see* §60.17).	(d) Results of this test consist of the average of the three 1-hour or longer runs.

Proposed Changes

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v. Measure VOC at the exhaust of the stationary internal combustion engine; if using a control device, the sampling site must be located at the outlet of the control device.	(5) Method 25A of 40 CFR part 60, appendix A–7 or Method 25A with the use of a methane cutter as described in 40 CFR 1065.265.	(d) Results of this test consist of the average of the three 1-hour or longer runs.
vi. If necessary, measure methane and/or ethane at the exhaust of the stationary internal combustion engine; if using a control device, the sampling site must be located at the outlet of the control device.	(6) Method 18 of 40 CFR part 60, appendix A–6, Method 320 of 40 CFR part 63, appendix A, or ASTM Method D 6348–03[c].	(e) Measurements to determine methane and/or ethane must be made at the same time as the measurement for VOC concentration.

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  - (v.) Not correct – NMC only provides CH4, **NOT** Ethane gives NMHC not VOCs
  - (vi.) Not correct – Methane and Ethane **ARE** needed for VOCs
  - EPA clarified - M320/ASTM D6348 and Method 18 are required for VOCs but proposed language is written incorrectly.

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EPA Proposed Changes to 40 CFR Subpart JJJJ

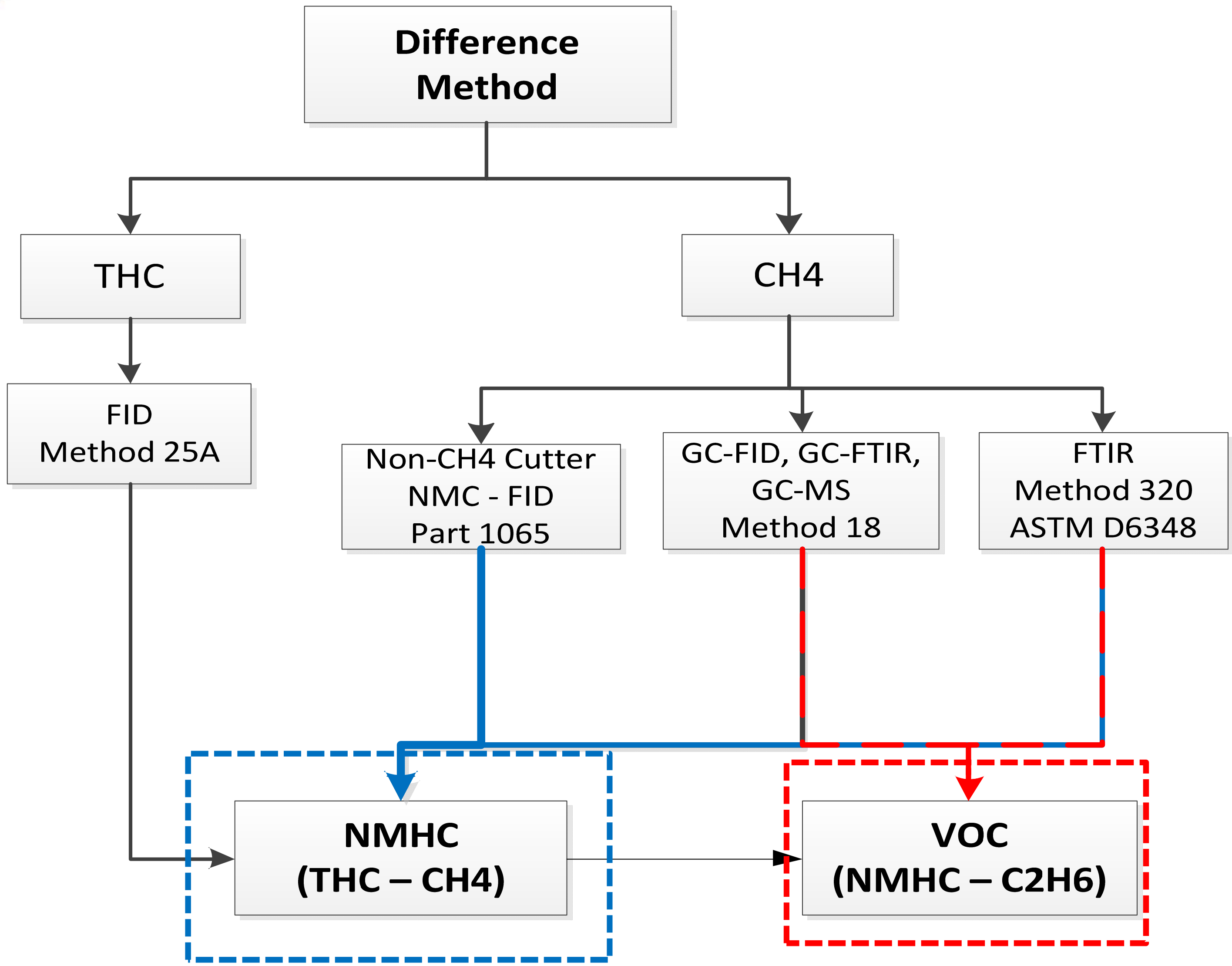
"EPA clarification comments on Sept 28 explaining why this step is being considered has many flaws"

- A speciated list of gaseous components that are always present in these types of engines is available with validation provided.
  - The community of stack testers and vehicle and engine manufactures have numerous data sets comparing speciated FTIR methods to Method 25A
  - Numerous published data sets on LD Vehicles comparing different fuel types to THC-FIDs are also available
  - 3 - 7 components account for more than 95% of the VOCs in Lean burn, Rich burn and 2-stroke engines

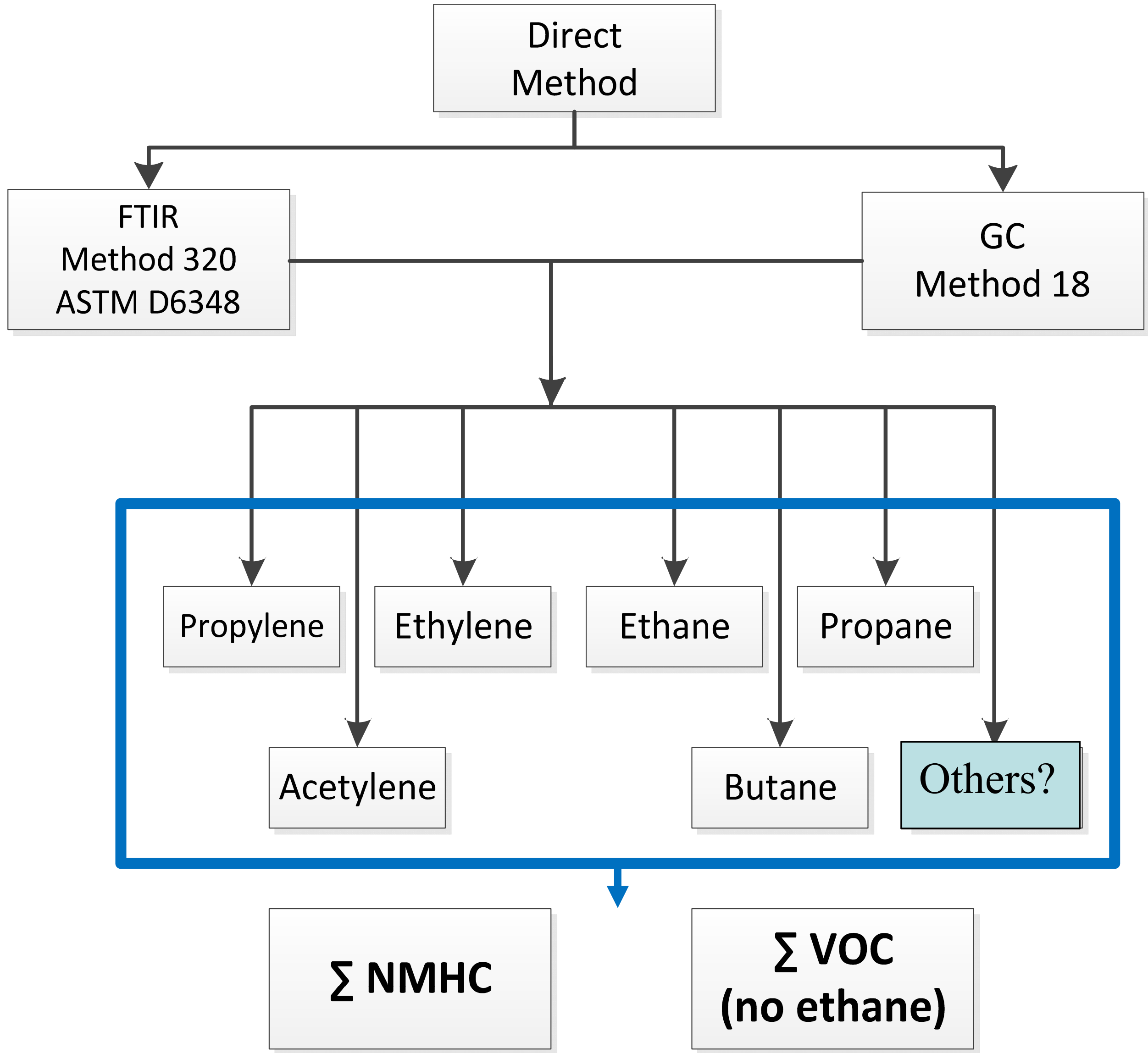
20 JJJJ Data Sets		Methane	Ethane	Propane	Butane	Ethylene	Propylene	Acetylene	Formaldehyde	Acetaldehyde	Methanol	Formic Acid	m-xylene	1,3-butadiene
Average for Specie		1035.44	55.72	6.75	2.96	7.39	1.10	0.22	13.01	0.21	0.51	0.15	0.20	0.26
Median For Specie		871.00	59.76	4.32	2.66	6.37	0.74	0.00	8.46	0.00	0.20	0.09	0.00	0.16

- FTIR methods VOC ARE robust enough for Total VOCs
  - QA/QC checks are spelled out in M320 and D6348 checking interference
  - Error of the Difference method for high methane emissions **greatly** exceeds that of any speciated method
- There a numerous training opportunities on the use of FTIR that have been offered (and taken up) by state regulators and EPA

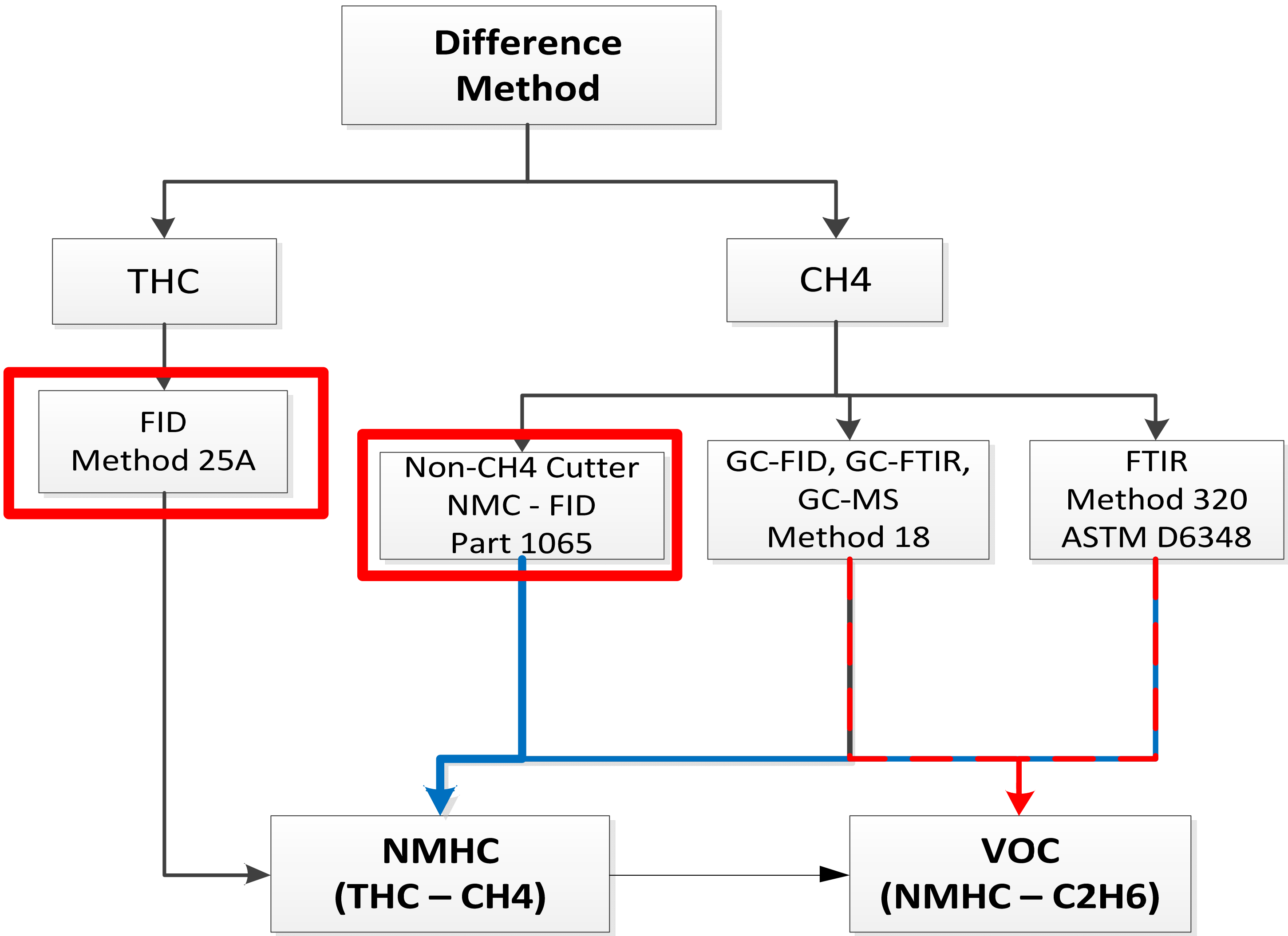
Difference Method for NMHC (or VOC)



Direct Method VOC (or NMHC)



Let's Examine the Various Methods

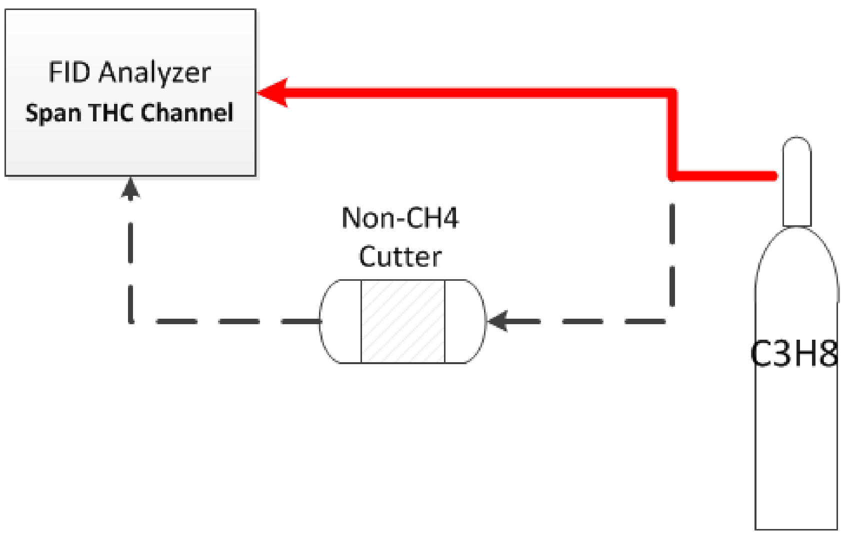


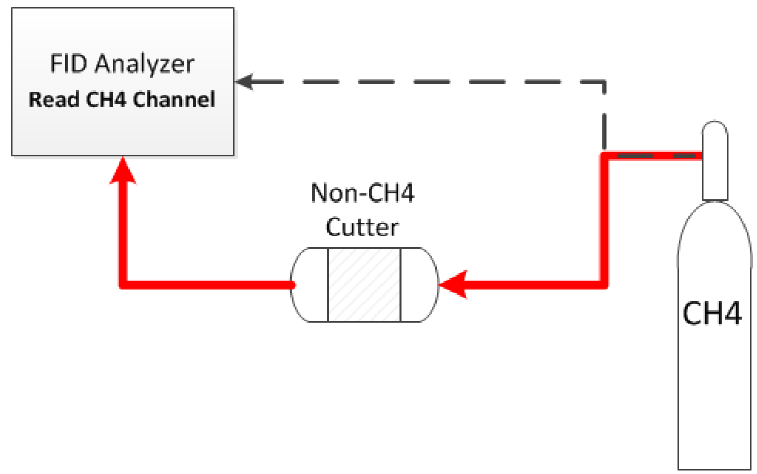
Method 25A
THC Analysis

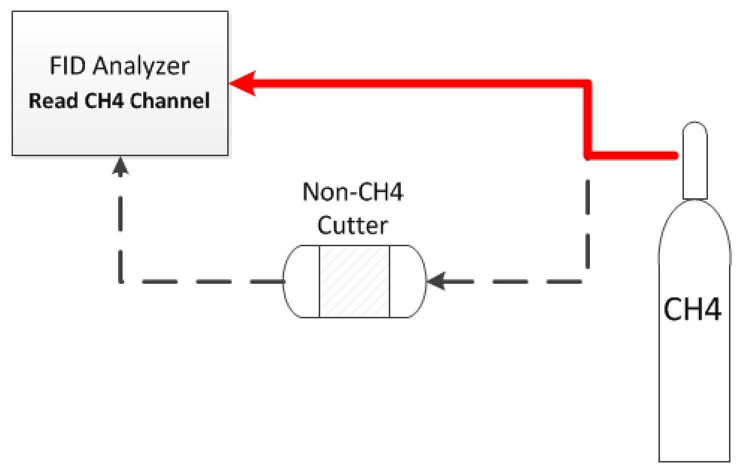
- Gas sample extracted from source through heated sample line and glass fiber filter and sent to a flame ionization analyzer (FIA)
  - Sampling components to FIA shall be heated ≥ 110°C
  - FIA shall be heated ≥ 120°C
  - **Heavy HCs must be heated to 190°C to not condense**
- Calibration of FIA
  - Use Certified Gases which were certified by the EPA Protocol method - Should use 2% or better accuracy
  - SPAN the analyzer using highest span gas (85-90% FIA range)
    - Check response of mid and low range gas cylinder
    - Must be <5% of calibration gas value
  - Zero Drift
    - Must be ±3% of Span value

Method 25A Using Single FID with NMC for NMHC

EPA Part 1065.365 (e) or (f)



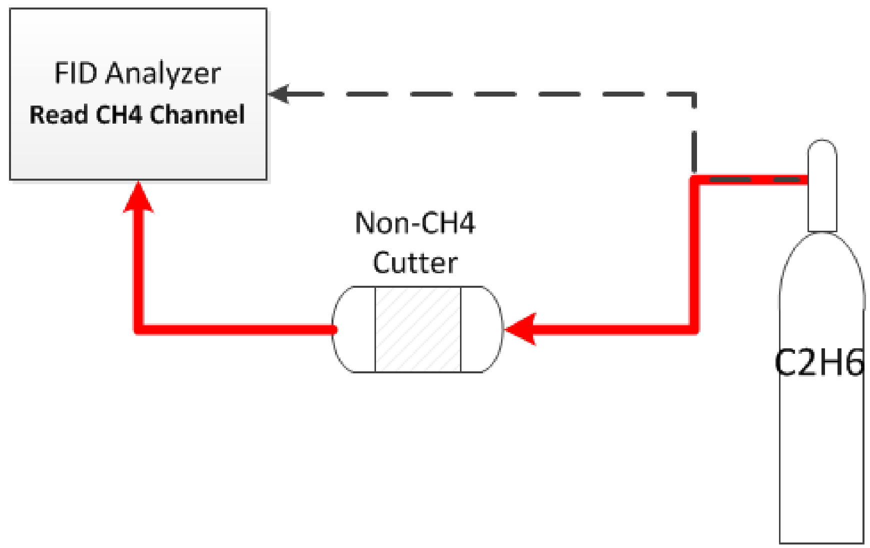




- **Span FID THC to C_3H_8 on C1 basis**
- **Run CH4 through Bypass NMC then NMC**
  - **Max C1 Range concentration**
  - **$PF_{CH4[NMC\text{-}FID]} = CH_{4NMC}/CH_{4Bypass}$**

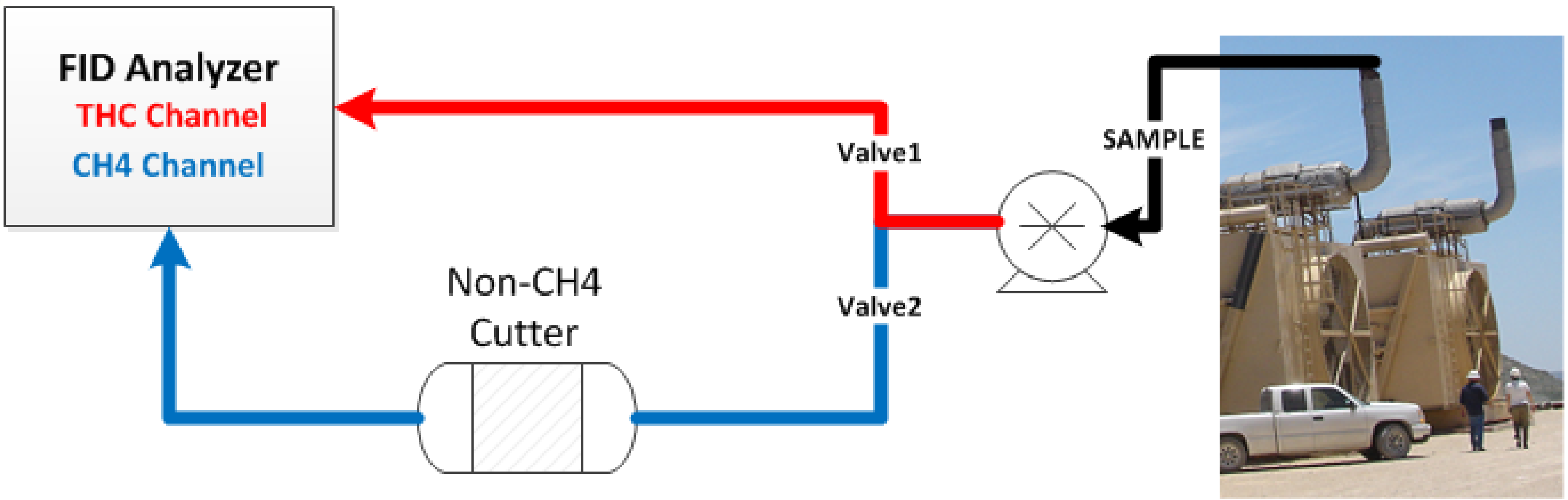
Method 25A Using Single FID with NMC for NMHC

EPA Part 1065.365 (e) or (f)



- **Run Ethane through NMC and Bypass**
  - **Expected NMHC max**
  - **$PF_{C2H6[NMC\text{-}FID]} = C_2H_{6NMC}/C_2H_{6Bypass}$**

Field Sampling



- **Sample is switched from going straight to FID (Valve1) to going through the NMC (Valve2)**
- **Depending on how you calibrate and use the FID with NMC the NMHC Equations are different**

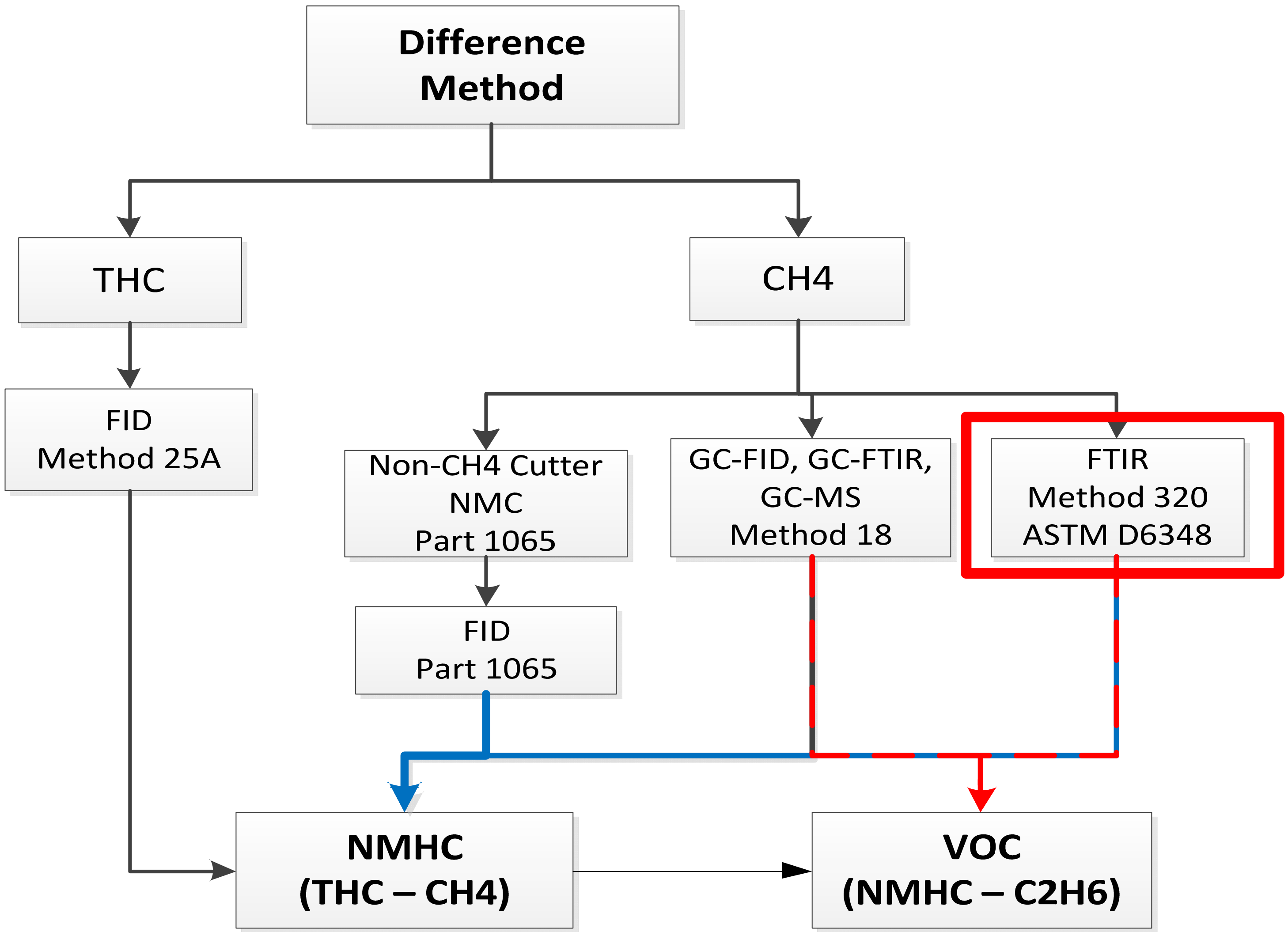
Example Calculation of NMHC Part 1065.660(b)(2)(ii)

$$x_{NMHC} = \frac{x_{THC[THC\text{-}FID]cor} \cdot PF_{CH4[NMC\text{-}FID]} - x_{THC[NMC\text{-}FID]cor}}{PF_{CH4[NMC\text{-}FID]} - PF_{C2H6[NMC\text{-}FID]}}$$

- x_{NMHC} — NMHC concentration
- $x_{THC[THC\text{-}FID]cor}$ — Sample THC corrected to dry on THC-FID
- $PF_{CH4[NMC\text{-}FID]}$ — NMC CH4 penetration fraction
- $x_{THC[NMC\text{-}FID]cor}$ — Sample THC corrected to dry on THC-FID through NMC
- $PF_{C2H6[NMC\text{-}FID]}$ — NMC Ethane penetration fraction

(1) Large number THC-FID (THC) minus another Large number NMC-FID (CH4)
(2) Plus Tester do not do this calculation – they use the numbers from the Analyzer for NMHC – NOT corrected for the penetration factors

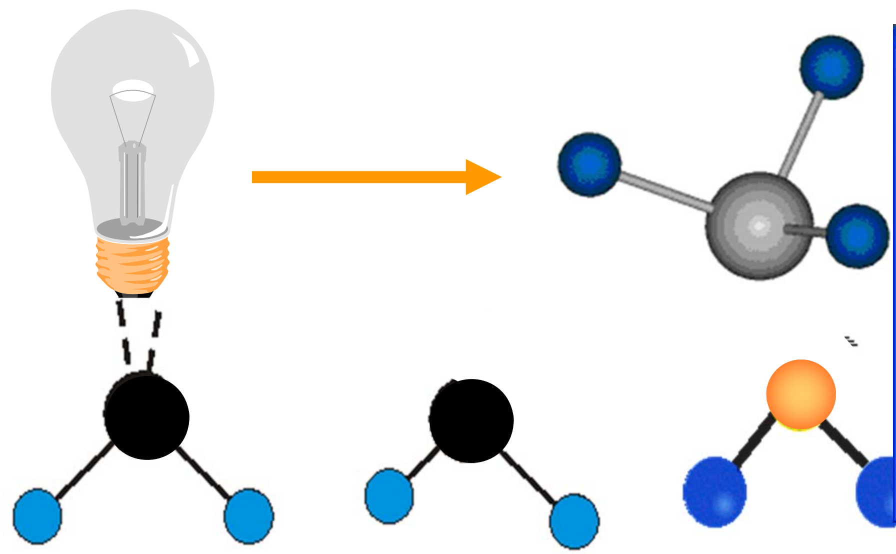
So Does the FTIR Work?



Method 320 or D6348

Fourier Transform Infrared (FTIR) Spectroscopy

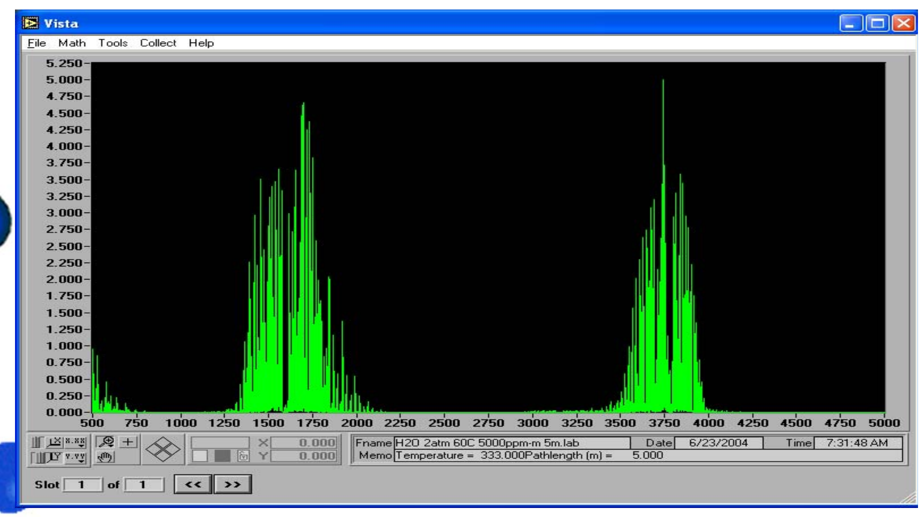
- Based on IR light absorption
  - Energy (IR radiation) heats the gas molecule - vibrates and rotates
  - The result is a pattern and peak height which correlates to the gas molecule and concentration
  - Gas molecule must have a dipole moment
    - O_2, H_2, N_2, Ar, He do NOT have a dipole moment



symmetric stretch ν_s

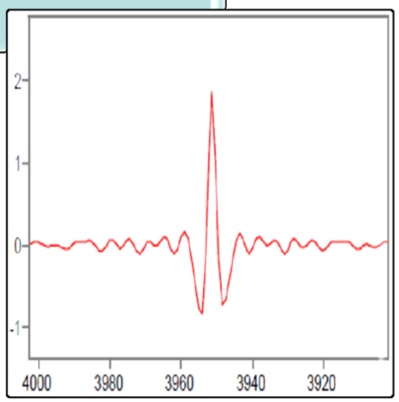
asymmetric stretch ν_{as}

bend δ



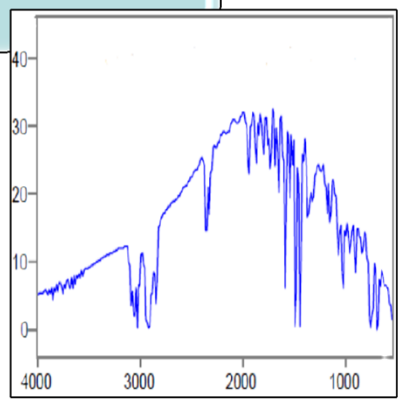
Interferogram to Gas Concentration Pathway

Interferogram



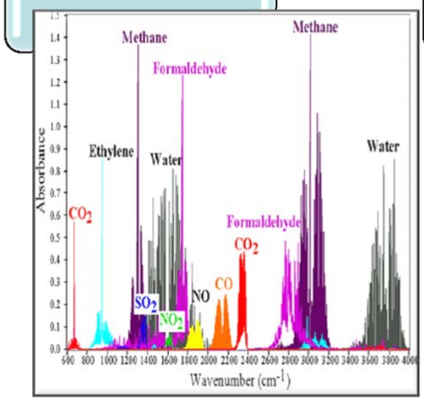
f(time)

Single Beam



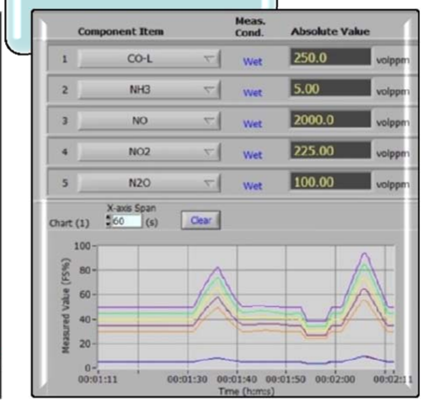
f(frequency)

Absorbance Spectrum



f(concentration)

Method Analysis



Fourier Transform Algorithm

$$I(\tilde{v}) = \int_{-\infty}^{+\infty} I(x)D(\tilde{v})\exp(2\pi\tilde{v}x)\,dx$$

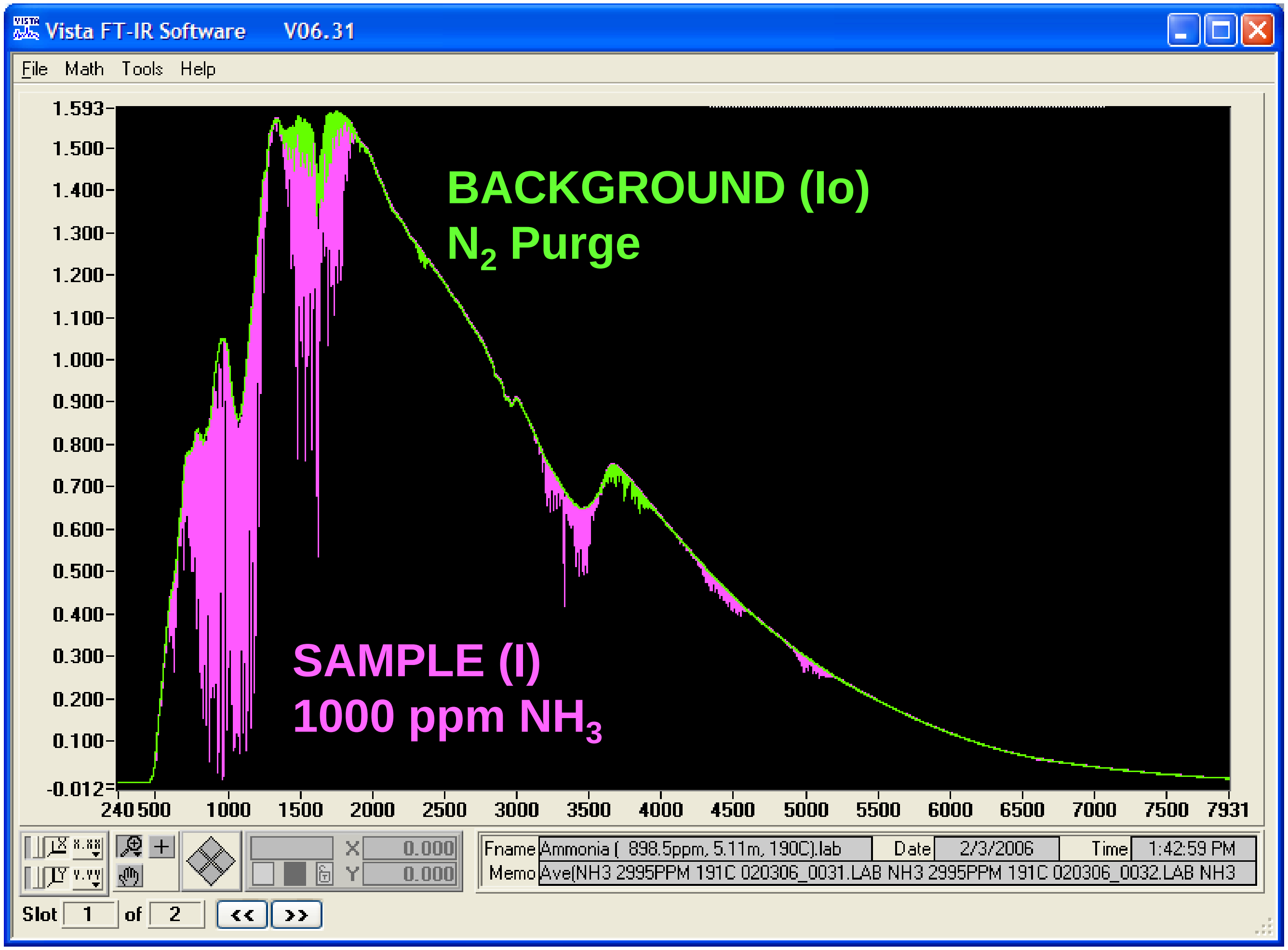
Remove Background

$$A = -\mathrm{Log}(I/Io)$$

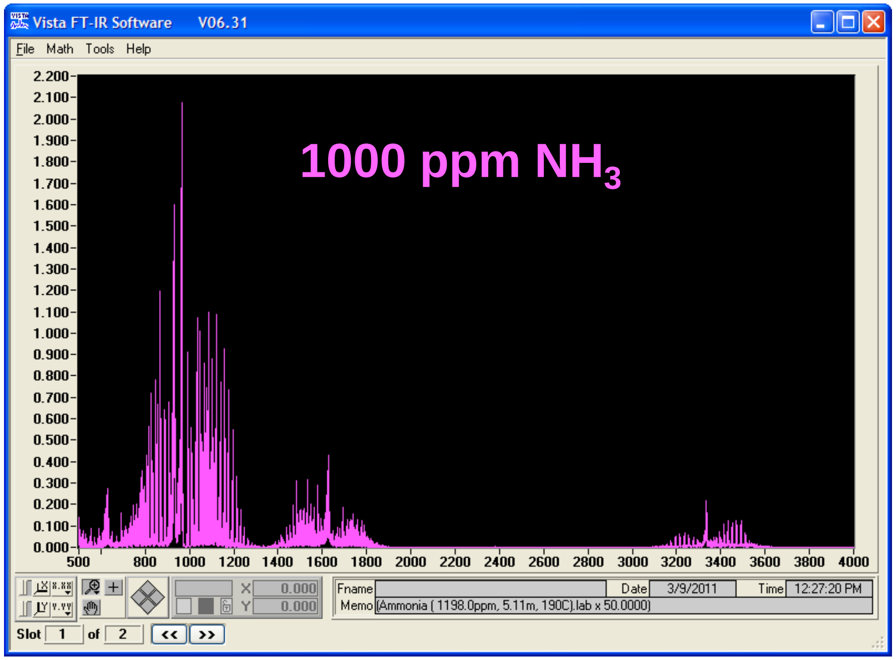
Spectrum Analysis

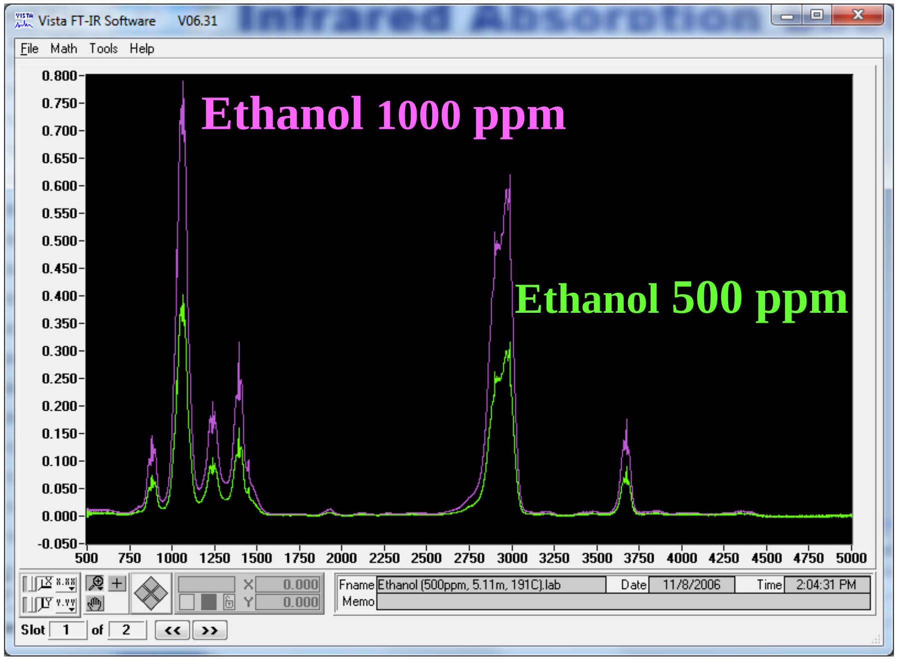
- Method Determination (Gas, Diesel, CNG, Etc.)
- Analysis of absorption regions
- Speciation of gases

Background and Sample Single Beam Spectra

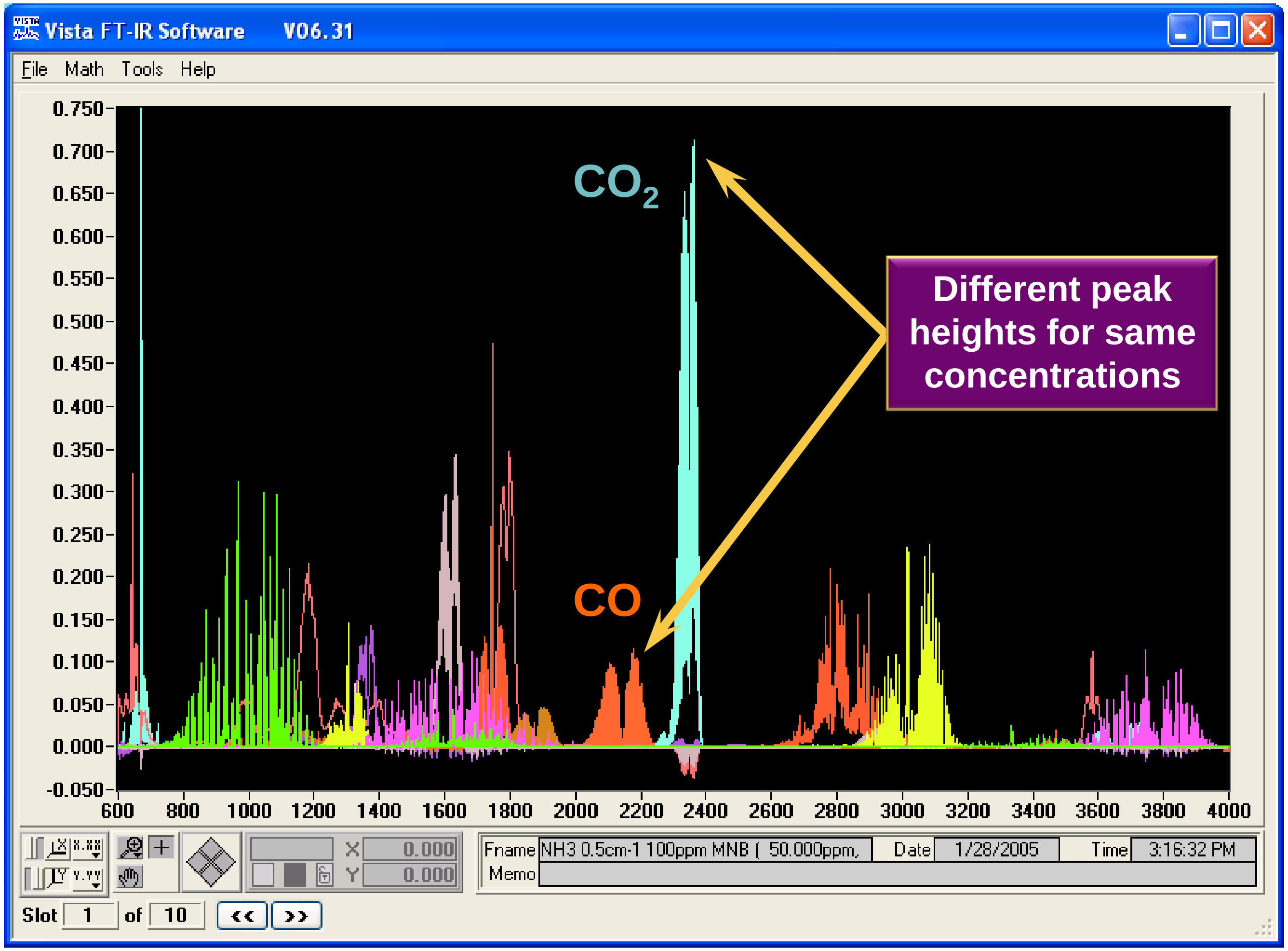


Final Absorbance Spectrum Proportional to Concentration

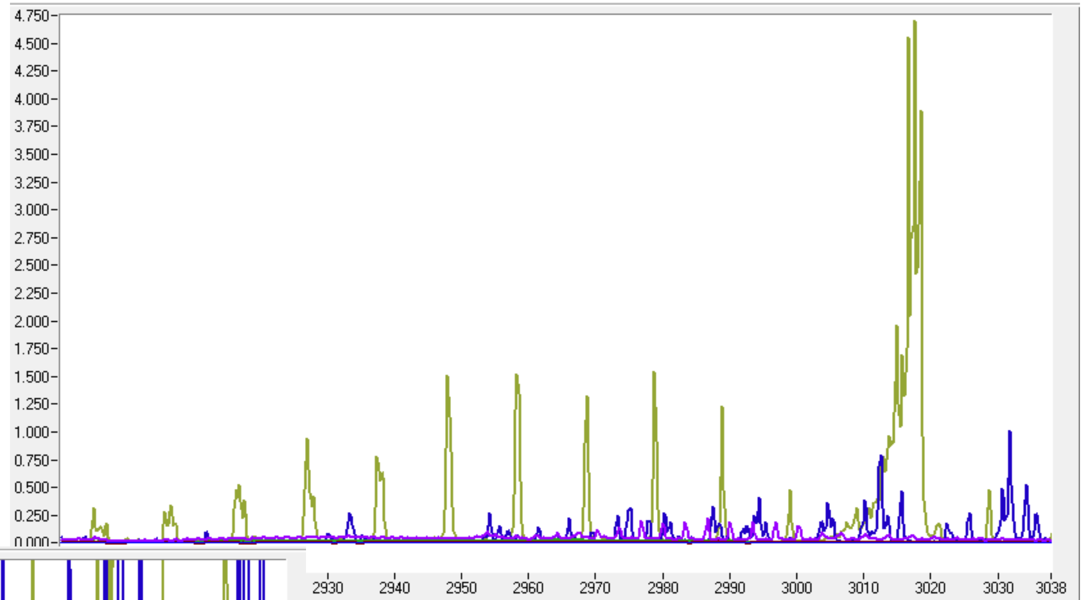


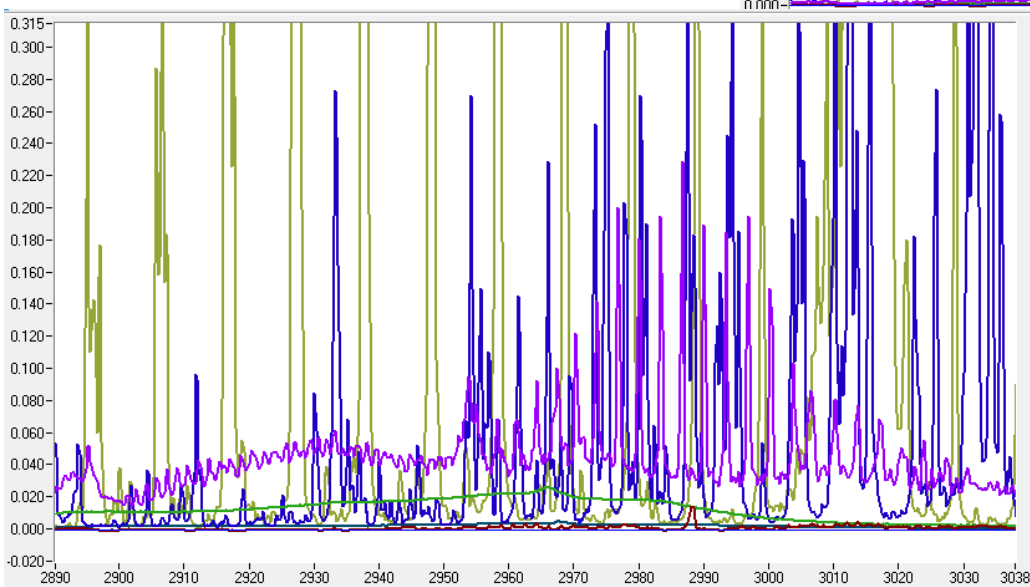


10 Typical Components (50 ppm-v Conc)



CNG Emission Spectrum ~10% H_2O, 1000 ppm CH_4





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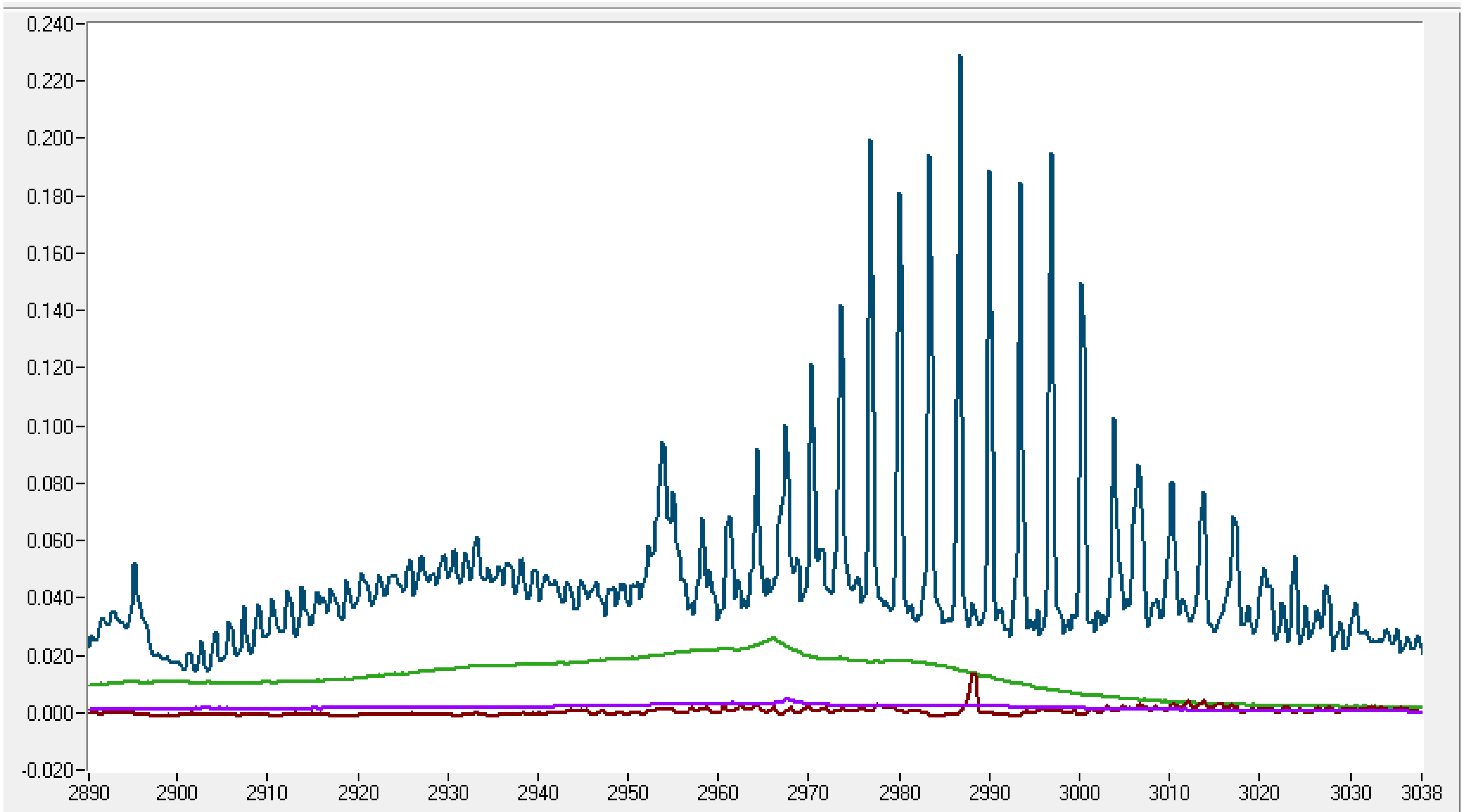
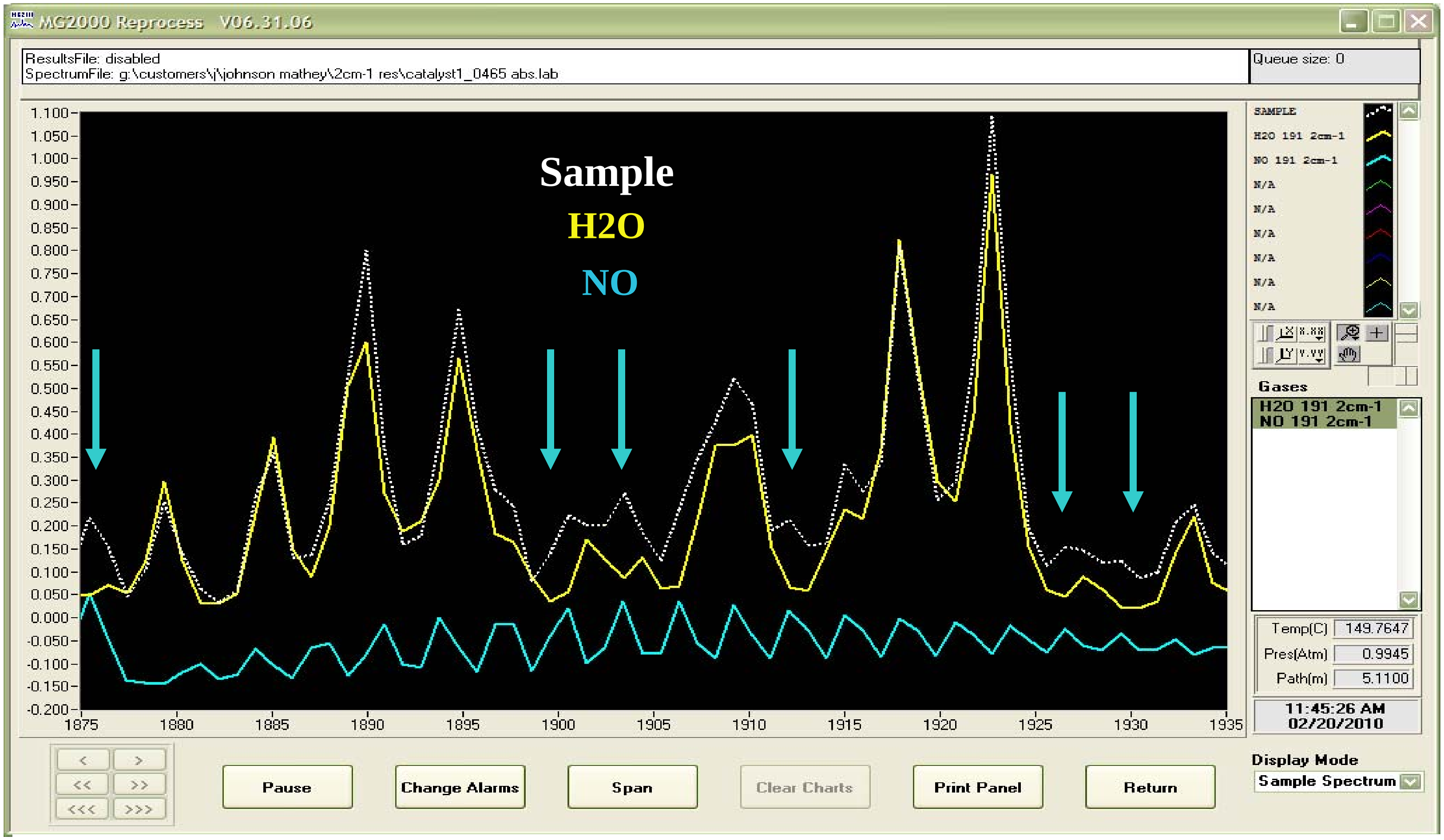


Resolution

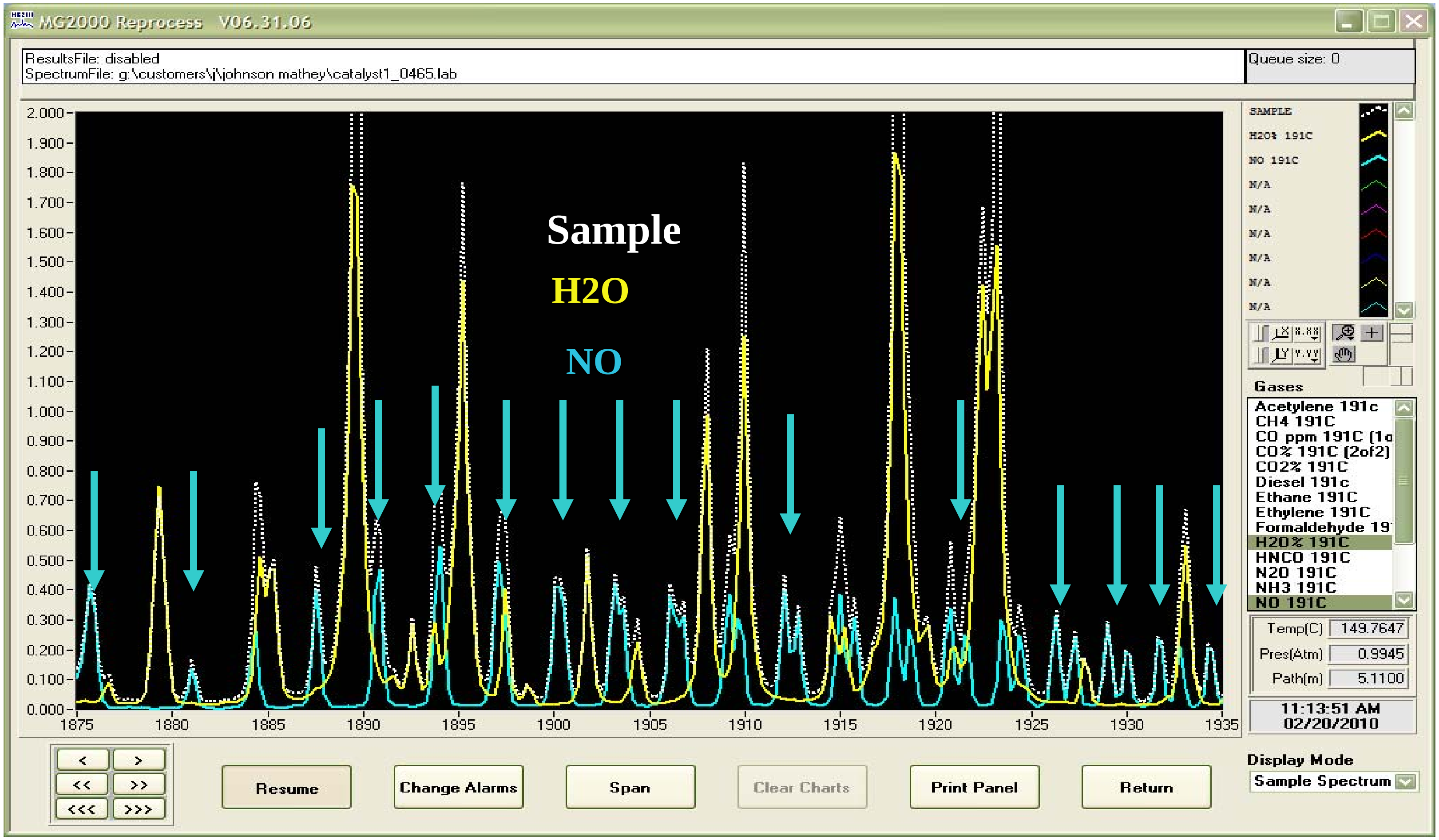
Low Resolution (2.0 cm^{-1})



Example of catalyst performance evaluation

Figure used with permission from Johnson Matthey plc, Wayne, PA

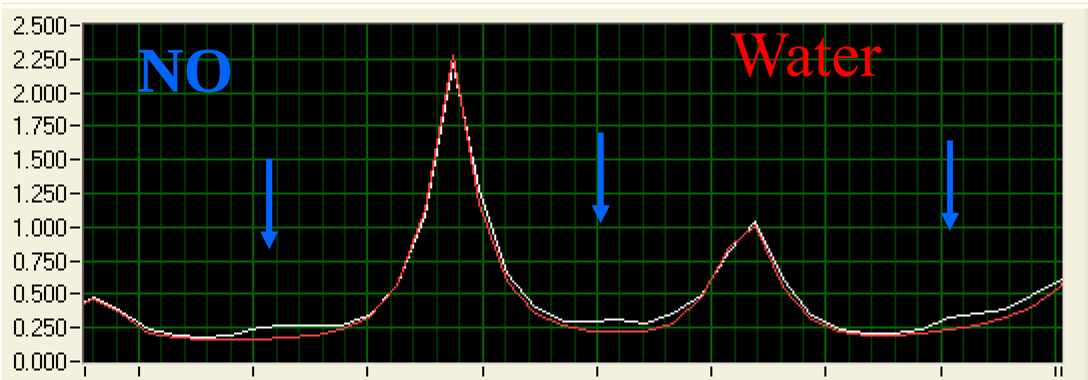
Resolution
High Resolution (0.5 cm^{-1})



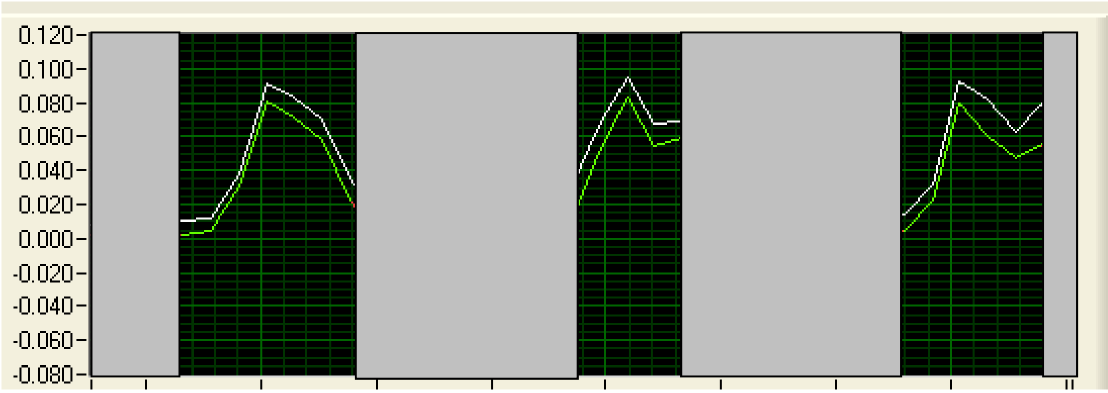
Example of catalyst performance evaluation
Figure used with permission from Johnson Matthey plc, Wayne, PA

Interference Removal

Masking and Removing H_2O Interference

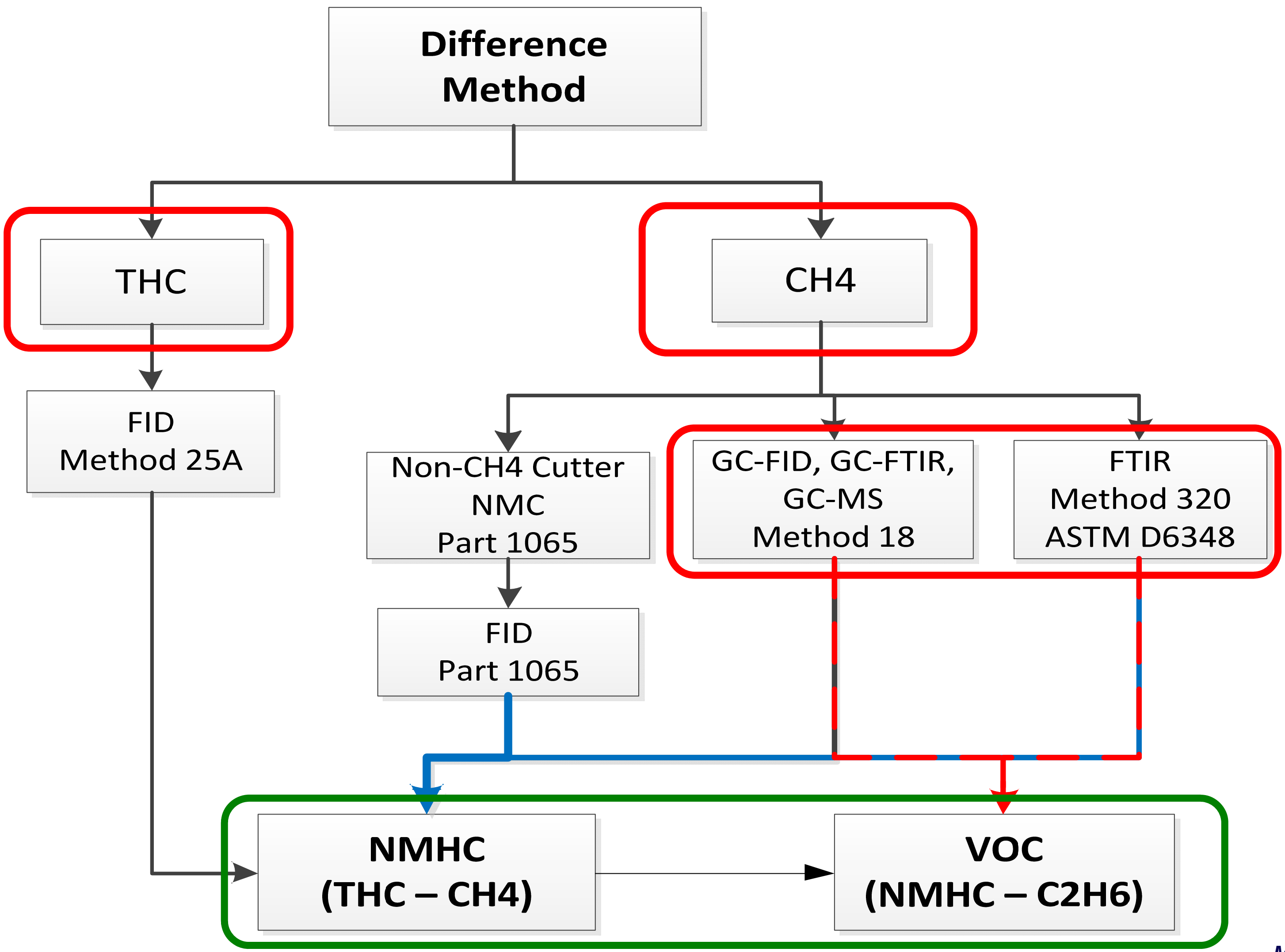


WHITE: Sample spectrum (~150ppm NO)
RED: 35% H_2O calibration spectrum



WHITE: Sample spectrum (minus H2O)
GREEN: 150ppm NO calibration spectrum

Review of Difference Method Errors



FID and FTIR Comparison of THC and CH4 values

THC %Error

	THC FID	THC FTIR	%Error
Engine1 Mode 1	847.0	805.0	5.0
Engine1 Mode 2	1407.9	1328.4	5.6
Engine1 Mode 3	1795.3	1757.2	2.1
Engine1 Mode 4	2079.9	2073.0	0.3
Engine1 Mode 5	2700.5	2679.1	0.8

	THC FID	THC FTIR	%Error
Engine2 Fuel 1	4420.90	4466.104	1.0
Engine2 Fuel 2	3297.00	3263.163	1.0
Engine2 Fuel 3	955.56	924.8726	3.2
Engine2 Fuel 4	648.53	625.2356	3.6

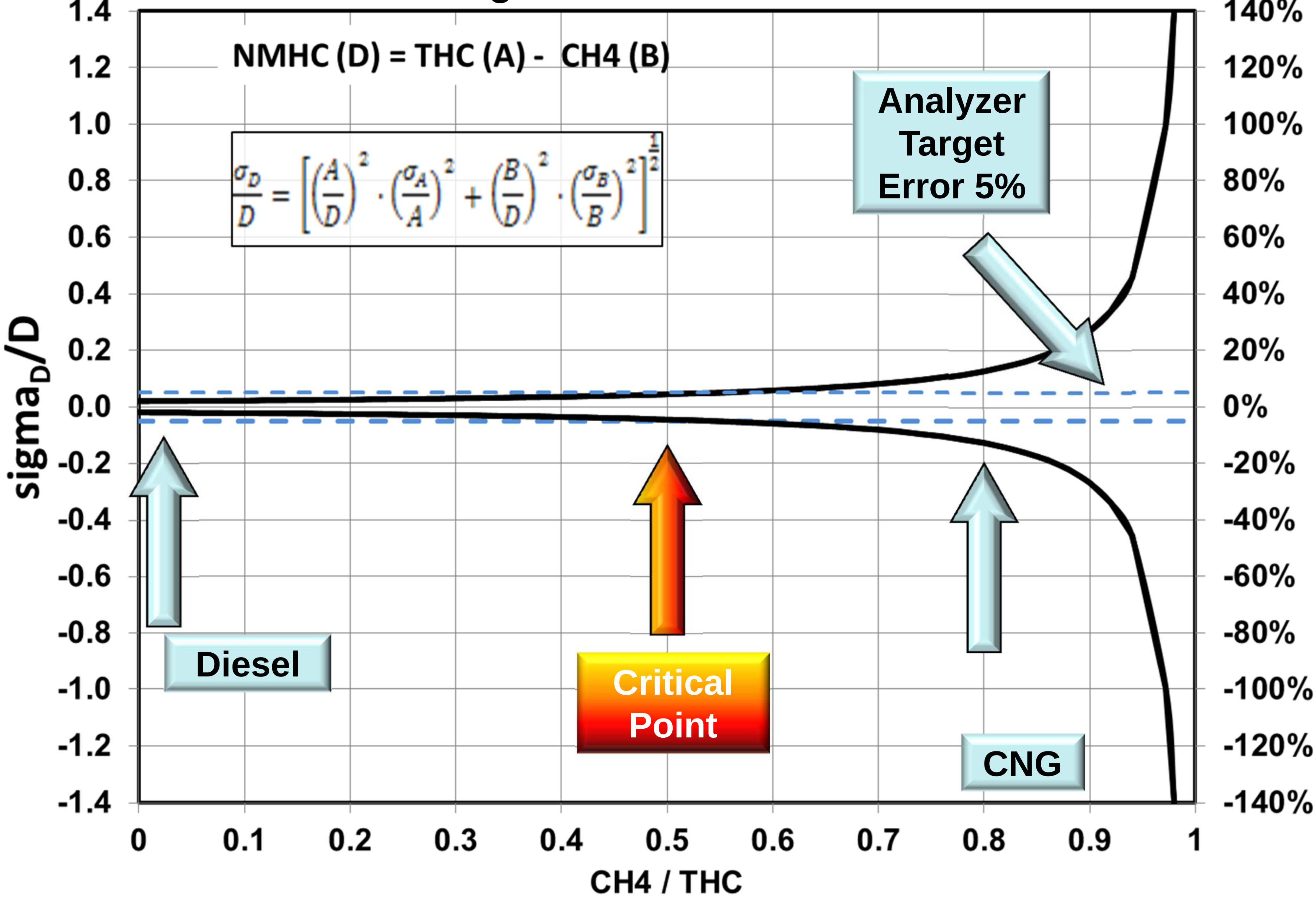
CH4 %Error

CH4 NMC FID	CH4 FTIR	%Error
688.6	687.6	0.1
1181.0	1181.5	0.0
1521.0	1581.9	4.0
1774.7	1888.2	6.4
2320.4	2452.7	5.7

CH4 NMC FID	CH4 FTIR	%Error
4157.90	4337.702	4.3
3102.60	3180.318	2.5
539.19	551.6467	2.3
400.10	409.8761	2.4

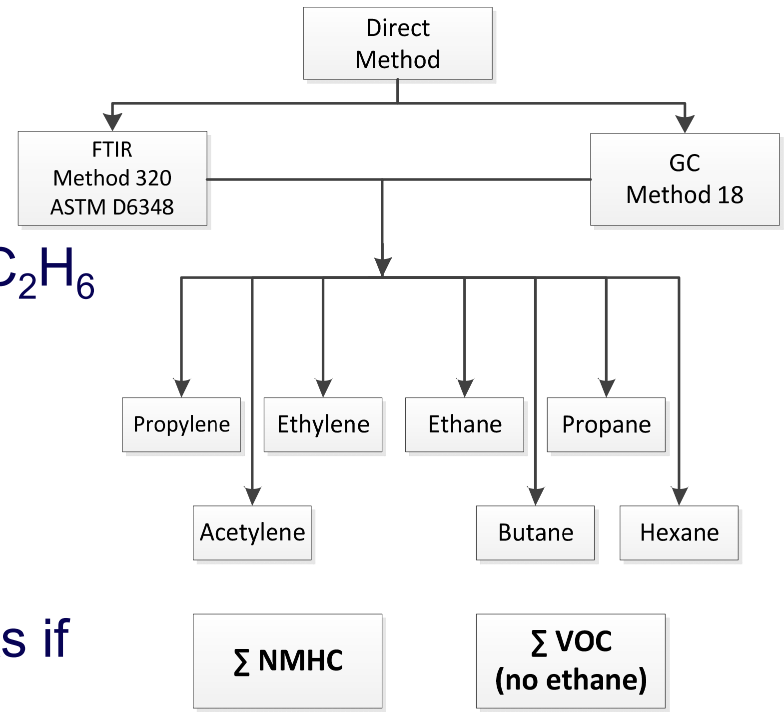
All FTIR values are well within 10% of the FID values

Growth of the Random Error using the Difference Method



Difference versus Direct

- Difference Method
  - Uses FID for THC
  - FTIR for CH_4 and C_2H_6
  - Errors are compounded as CH_4 and C_2H_6 reach ~50% of THC
- Direct or Speciated Method
  - Uses FTIR only for calculating VOCs
  - Uses fixed list of components in CNG emissions
  - Can add or subtract other components if present
  - Errors are much lower and due to analyzer DLs
  - Validation of Method
    - Test for VOC interference biases by running 15% H2O, 10% CO2, 3000 ppm CH4 and 100 ppm Ethane through Method



Speciated CNG Engine Exhaust Emissions

	LEAN		RICH			
	Engine #1	Engine #2	Engine #3	Engine #4	Engine #5	Engine #6
H_2O%	9.6	10.2	19.2	18.8	18.5	19.2
CO	25.3	14.7	118	223	120	78.9
CO_2%	4.7	4.7	9.9	9.8	10.1	9.7
CH_4	1618	1851	116	279	277	353
ETHANE	20.3	10.5	0.7	13.3	13.1	4.46
ETHYLENE	3.5	4.45	0.77	1.36	1.22	0.83
ACETYLENE	0.22	0.32	0.09	0	0.33	0
PROPANE	0	0	0	1.96	1.09	0
PROPYLENE	0.2	0.1	0	2.65	0	0
BUTANE	0	0	0.52	0	1.62	1.41
FORMALDEHYDE	14.2	17.6	0	0	0	0
FORMIC ACID	0.16	0.12	0	0	0	0
ACETALDEHYDE	3.26	2.15	2.06	3.19	5.25	4.96

The oxygenates are greater than the alkanes – they need to be added

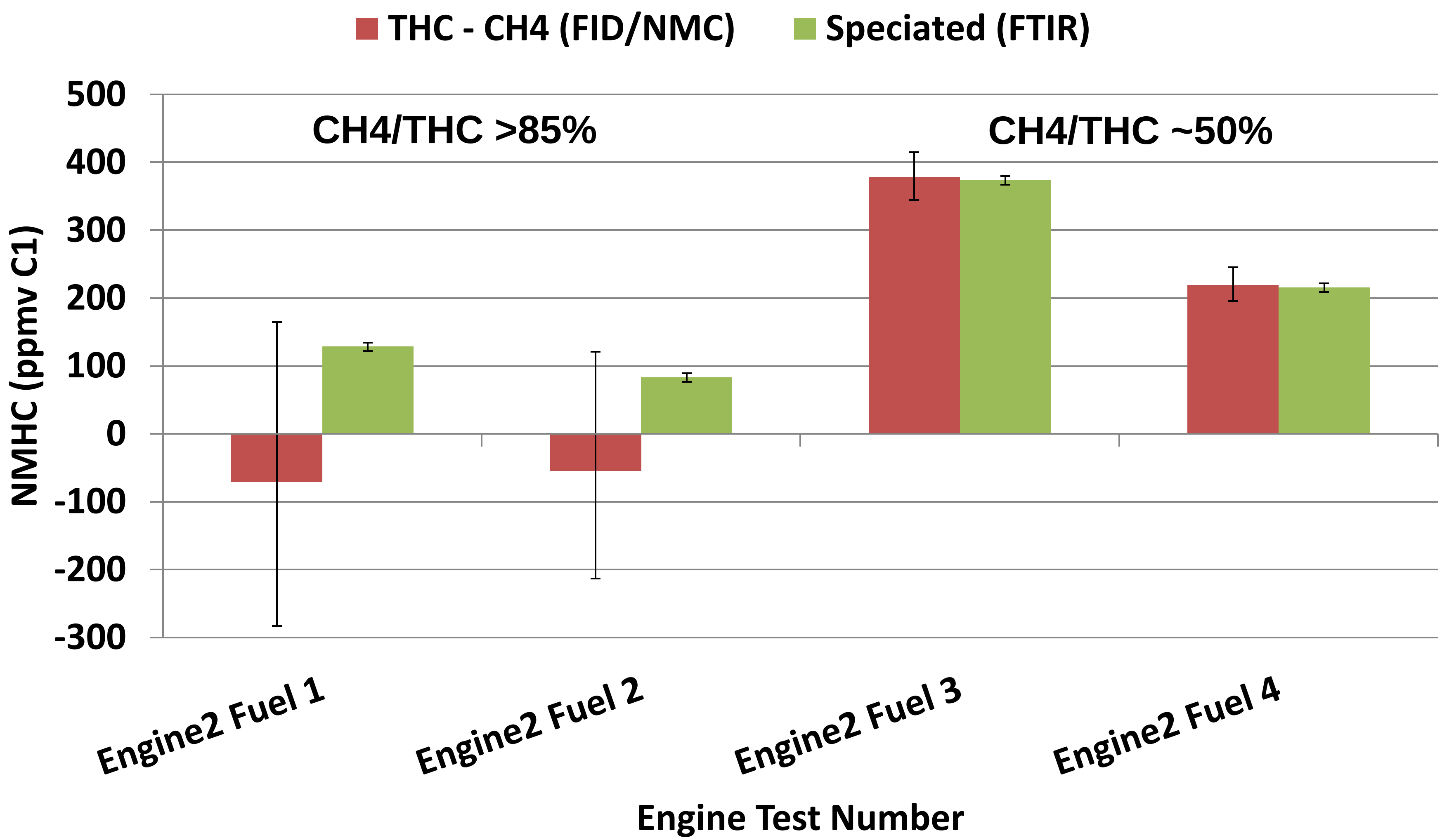
Difference FID Method for NMHC Error Estimate

	Typical Conc	5% Overall Error (C1)
THC	1575 ppm C1	78.9 ppm C1
CH4	1500 ppm C1	75.0 ppm C1
NMHC	**75 ppm C1**	$\sqrt{(78.9^2+75^2)}$ **± 108.9 ppm(C1)** **Rel Error = 145%**

Direct FTIR Method for NMHC Error Estimate

	Typical Conc	5% Error	Instrument Error
Ethane	30.0 ppm C1	1.5 ppm C1	1 ppm C1
Ethylene	10.0 ppm C1	0.5 ppm C1	1 ppm C1
Acetylene	1.0 ppm C1	0.05 ppm C1	1 ppm C1
Propylene	1.5 ppm C1	0.08 ppm C1	3 ppm C1
Propane	3.0 ppm C1	0.15 ppm C1	3 ppm C1
Butane (C4+ Surrogate)	2.5 ppm C1	0.13 ppm C1	4 ppm C1
NMHC	**48 ppm C1**	$\sqrt{(1.5^2 + 0.5^2 + 0.05^2 + 0.08^2 + 0.15^2 + 0.13^2)}$ **± 1.59 ppm (C1)**	$\sqrt{(1^2 + 1^2 + 1^2 + 3^2 + 3^2 + 4^2)}$ **± 5.9 ppm (C1)** **Rel Error = 12%**

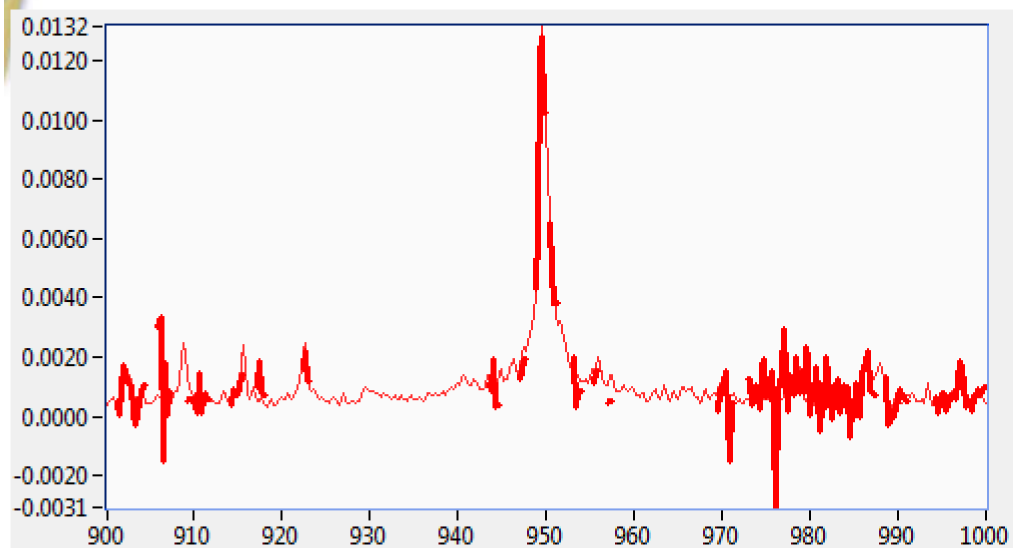
Difference vs Direct / Speciated Method Comparing Uncertainties



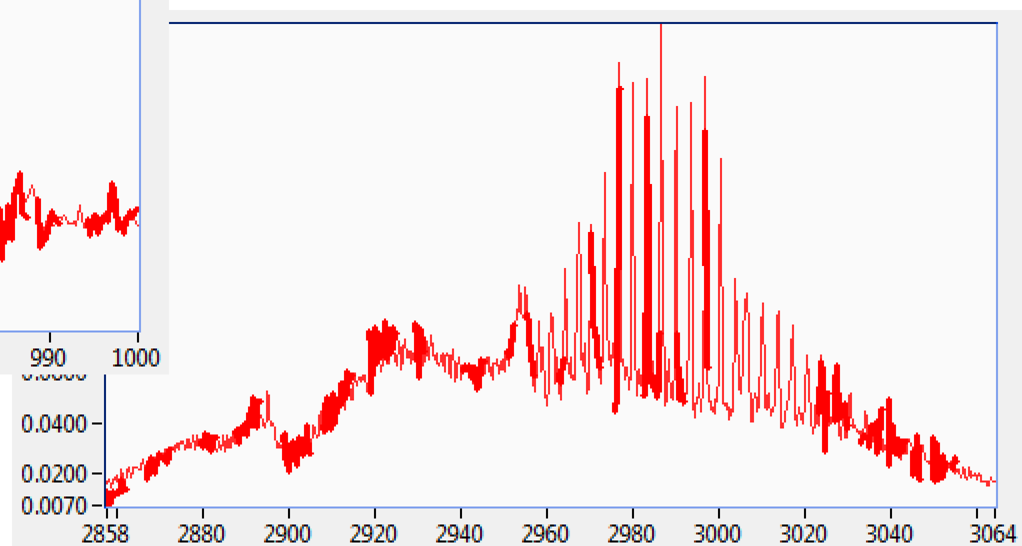
FTIR Can SEE What is in the Emissions for NMHC

Engine2 Fuel1

~5ppmC1 Ethylene



~120ppmC1 Ethane

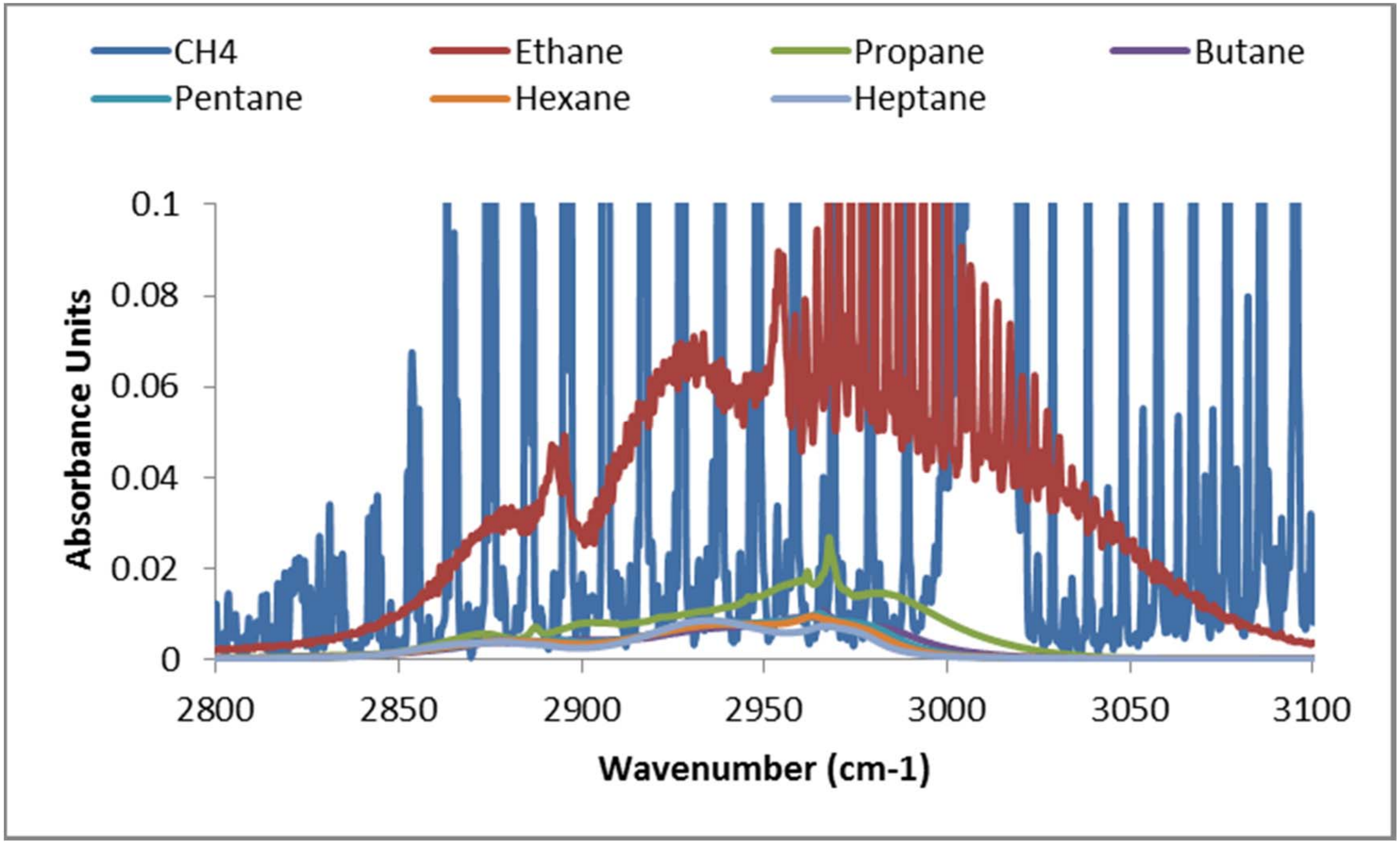


Stationary Engine Test Example
40 CFR Part 60 JJJJ

MAIN COMPONENTS	Engine 1	Engine 2
CH4	1374 ppm	1618 ppm
Ethane	24.8 ppm	21.8 ppm
Ethylene	11.1 ppm	0.3 ppm
Propane	~ 0 ppm	~ 0 ppm
VOC (M320)	10.5 ± 2 ppm (C3)	0.3 ± 2 ppm (C3)
VOC (M25A - M320)	2.6 ± 11ppm (C3)	0.8 ± 12 ppm (C3)

Typical State VOC Permit Limits range from 10 – 75 ppm (C3)

FTIR Surrogates



Comparison with and without the use of surrogates

- Synthetic Spectra
- Mixture of propane, butane, pentane, hexane
- Typical relative concentrations in NG gas
- Only propane and butane used in analysis model

Nominal Total Alkanes	Measured Total Alkanes
22 ppm (C3)	21.6 ppm (C3)
17 ppm (C3)	19.2 ppm (C3)
11.7 ppm (C3)	12.6 ppm (C3)

→ Low error on Alkanes total contribution

Speciated Method Using FTIR

- Produces more accurate NMHC and VOC values compared to the Difference method
- Speciated Method has much lower overall error in the analysis
  - The Relative Error of the Speciated Method was ~12% compared to >143% for the Direct FID Method example here
  - Even if you were off by 50% of the concentration of higher HCs using a surrogate for C4 and above you would still have a NMHC (or VOC) value that is more representative of what is present with a much lower overall error.
  - The Spectra are all saved and they can be validate post test
- There are many published comparisons showing the validity of using FTIR for NMHC and VOC analysis as compared to the FID-based Methods

Summary

- The Problem is not with FID Analyzers that are used for NMHC or VOC but with the Difference Method itself.
  - The FTIR THC and CH_4 values have been shown to be well within 10% of the FID–based values
  - There is an inherent error in the Difference method that propagates exponentially and when CH_4 (and/or Ethane) ≥ ~50% of the THC concentration
  - You **must** use another method such as Speciated Methods like FTIR or GC for CNG type fueled engine emissions for accurate VOCs
- For Quad J and Quad Z the only way to get closer to the true value with overall lower uncertainty for NMHC and VOC values is by using a speciated method.
- MKS Offers Free Training on FTIR to Regulators
  - April 2016 ASTM D6348 Hands On Method Training at MKS Office in Austin, TX
  - 2015 presented two webinars on how to validate MKS FTIR data in the field and a review of FTIR in general. Presentations available upon request.
  - Willing to host more hands on training and webinars – just say the word.

Sample of References on FTIR vs FID Study Comparisons

- SAE TECHNICAL - PAPER SERIES 2000-01-1142, “Measurement of Ambient Roadway and Vehicle “Exhaust Emissions – An Assessment of Instrument Capability and Initial On-Road Test Results with an Advanced Low Emission Vehicle” by Truex et.al.
- “Catalytic and Engine Exhaust Characterization Utilizing Gas Phase FTIR for Real Time Feedback” poster presented at the 2012 North American Catalysis Society Meeting by Barbara Marshik, Sylvie Bosch-Charpenay, MKS Instruments and Christine Gierczak, Ford Motor Company
- "Time-Resolved FTIR Measurements of Non-Methane Organic Gases (NMOG) in Vehicle Exhaust Gas" poster presentation by Christine A. Gierczak, Ford at the 23rd CRC Real World Workshop; "The Effect of Analytical Errors on NMHC Analysis from CNG based Fuel Emissions" presentation by Barbara Marshik, MKS at the 24th CRC Real World Workshop.
- "Catalytic and Engine Exhaust Characterization Utilizing Gas Phase FTIR for Real Time Feedback", MKS Application Note 07/15 - 4/15
- "NMHC and VOC Analysis via FTIR and Comparison to FID and GC Based Techniques" presented at the 39th Source Evaluation Society workshop April 2015, B. Marshik, S. Bosch-Charpenay, R. Bosco, P. Zemek, L. McDermott.