# Dual Function Gas Analyzer For Industrial Monitoring Requirements

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# Discussion Points

- Quick background on IMACC and FTIR
- Needs based assessment
- Brief (very) spectroscopic background Information
  - Fourier Transform Infra-Red
  - Raman
- Instrumental design and data comparison
- Planned events

# Many Applications for FTIR

- •Fence-line Monitoring Programs (Consent Decrees, new California rules, monitoring)
- •Ambient Air Monitoring Stations (part of CDs, replacements)
- •Stack testing firms (technology improvement)
- •Flare Testing (passive, TCEQ and EPA accepted technique!)
- •Flare Composition (alternative to $ GC technology)
- •Fixed FTIR for process control (special applications)
- •Research studies at Universities (volcanology, emissions monitoring, etc.)

IMACC is seeking new technologies and advancing the application of proven technologies.

# IMACC Overview – "Approved" Technologies

EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux

- EPA *accepted* Technology
  - Extractive FTIR testing
  - Open Path FTIR

United States
Environmental Protection
Agency

National Exposure Research Laboratory
Research Triangle Park, NC 27711

Research and Development | EPA/600/R-96/040

April 1996

EPA

**FT-IR OPEN-PATH MONITORING GUIDANCE DOCUMENT**

# So what is the need?

- Continuous flare monitoring (BTU/scf of inlet vent gas.  Calorific value predicts CE)
- Continuous flare “control” – dynamic control of supplemental natural gas (add or remove, when, why)
- Dynamic control of steam/air assist (override potential)
- Emissions calculation – speciation needed for reporting

# Shortcomings with the Current solutions

3 flowmeters and 1 analyzer –

- Flowmeter of choice uses ultrasonic technology – no probe in large diameter pipe, but can't "hear" homonuclear diatomics
- Gas Chromatograph – costly shelter, complicated sampling, calibration drift, calibration gases, limited analytes, response time lag

# Industrial Flares Need
## (minute averaged results)

A compositional analysis in “near real time” to provide -

- nitrogen and hydrogen results for compensation of ultrasonic flowmeters,
- Calorific value - BTU/scf
- MW calculation as qa/qc check of ultrasonics flowmeters
- Wider and fuller speciation of the vent gas
- *Can we apply our strengths to develop a potential solution??*

# Infrared Radiation

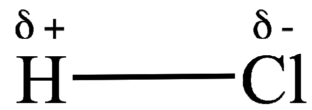
William Herschel (1738 - 1822): a renowned astronomer who discovered the planet Uranus in 1781; also discovered infrared light.

The absorption of IR radiation transfers energy and heats the surface. IR radiation can be felt, but not seen by the human eye.

# Requirements for IR Absorption

**To absorb IR radiation, a molecule must have a net change in dipole moment as a result of vibrational or rotational motion.**

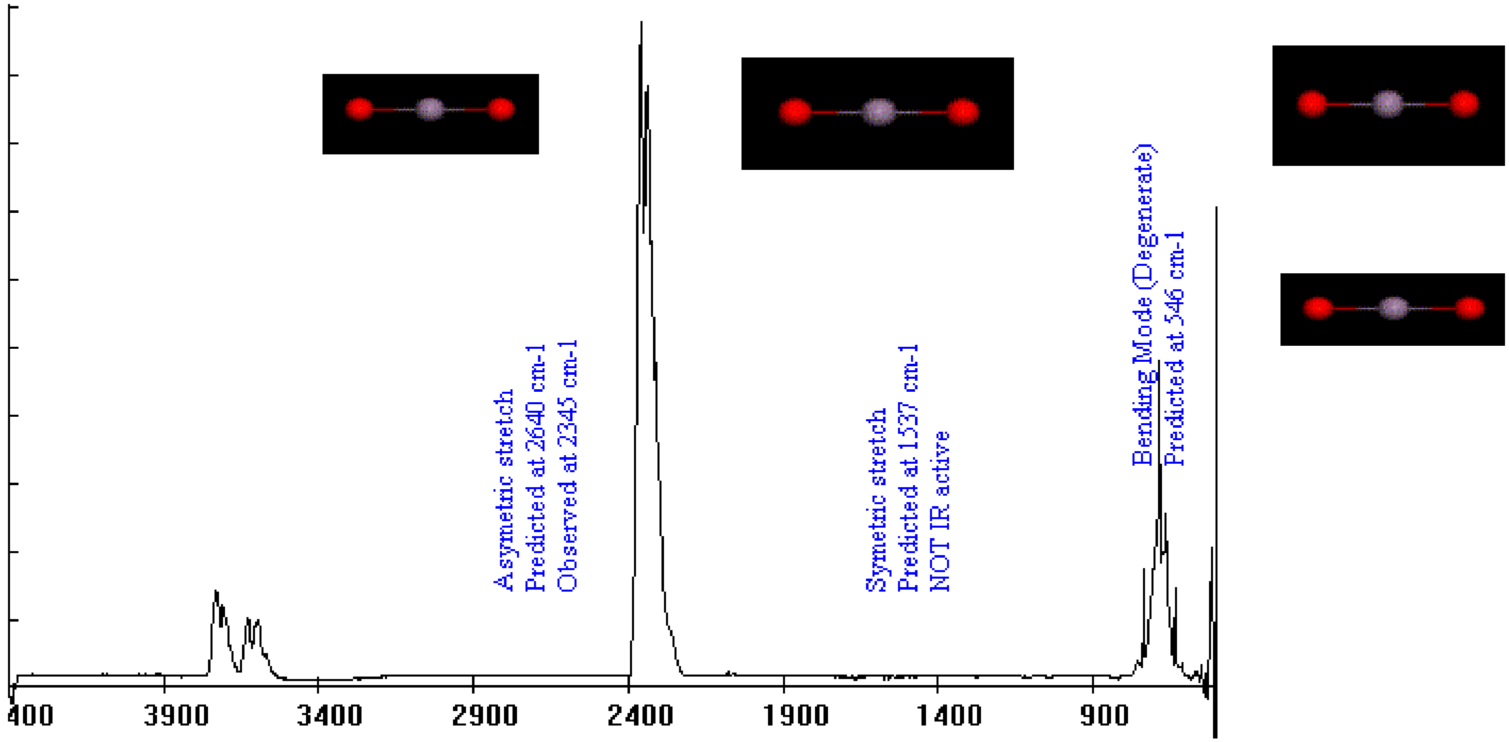
For example,




is a linear molecule. The electron density is distorted toward chlorine (electronegativity of 3.0) in comparison to hydrogen (electronegativity of 2.1).

Molecules have ***dipole moments*** and are termed ***polar*** if their centers of positive and negative charge do not coincide.

# Molecular Vibrations and IR Spectrum for $CO_2$

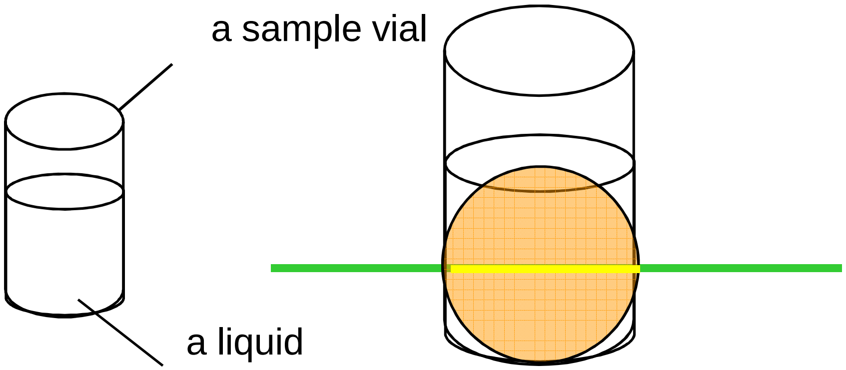



***Homonuclear molecules*** *(e.g., $N_2$, $H_2$ ,$O_2$, $Cl_2$), have no change in dipole during rotation or vibration motion and therefore do not absorb IR radiation…hence the GC providers are doing well !*

# What is "Raman"?

- What it is not..


- What it does/is…
  - Takes advantage of the Light Scattering phenomenon
  - Molecular Spectroscopic Technique
  - Qualitative and Quantitative Information
  - Relatively weak process

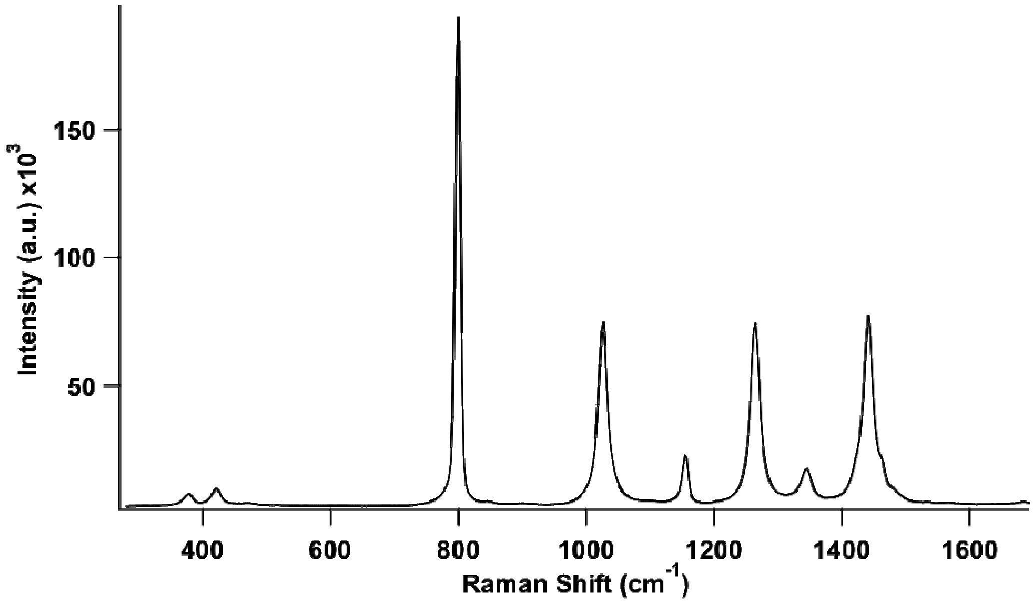


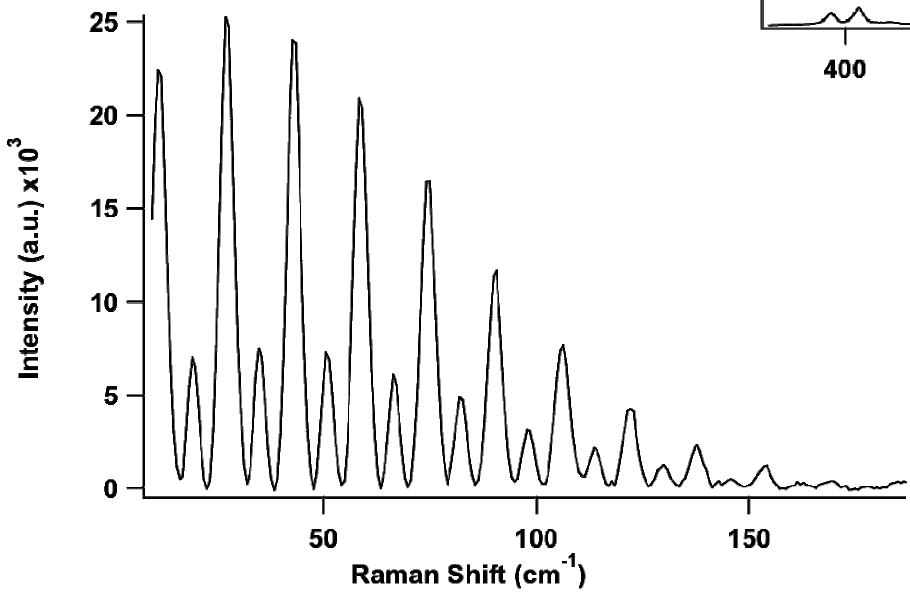

*http://images.43things.com/consuming/00/00/03/946pw800.jpg

# Understanding the Raman Results

## ***Vibrational Spectrum***

• Molecular information
• "finger print"
• Specific vibrations or combinations of vibrations

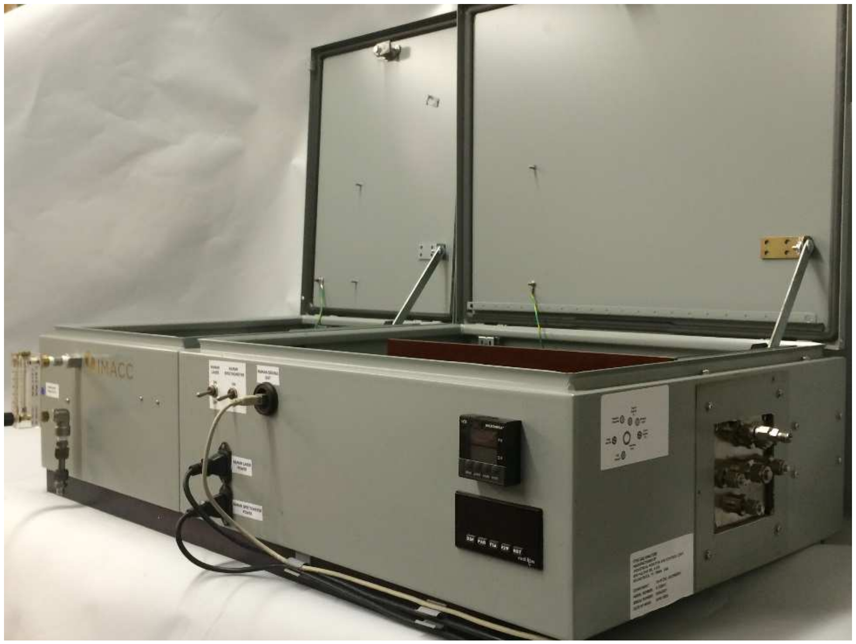



## ***Rotational Spectrum***

• Diatomics and linear molecules
• Sensitive to temperature
• Occurs within a vibrational level

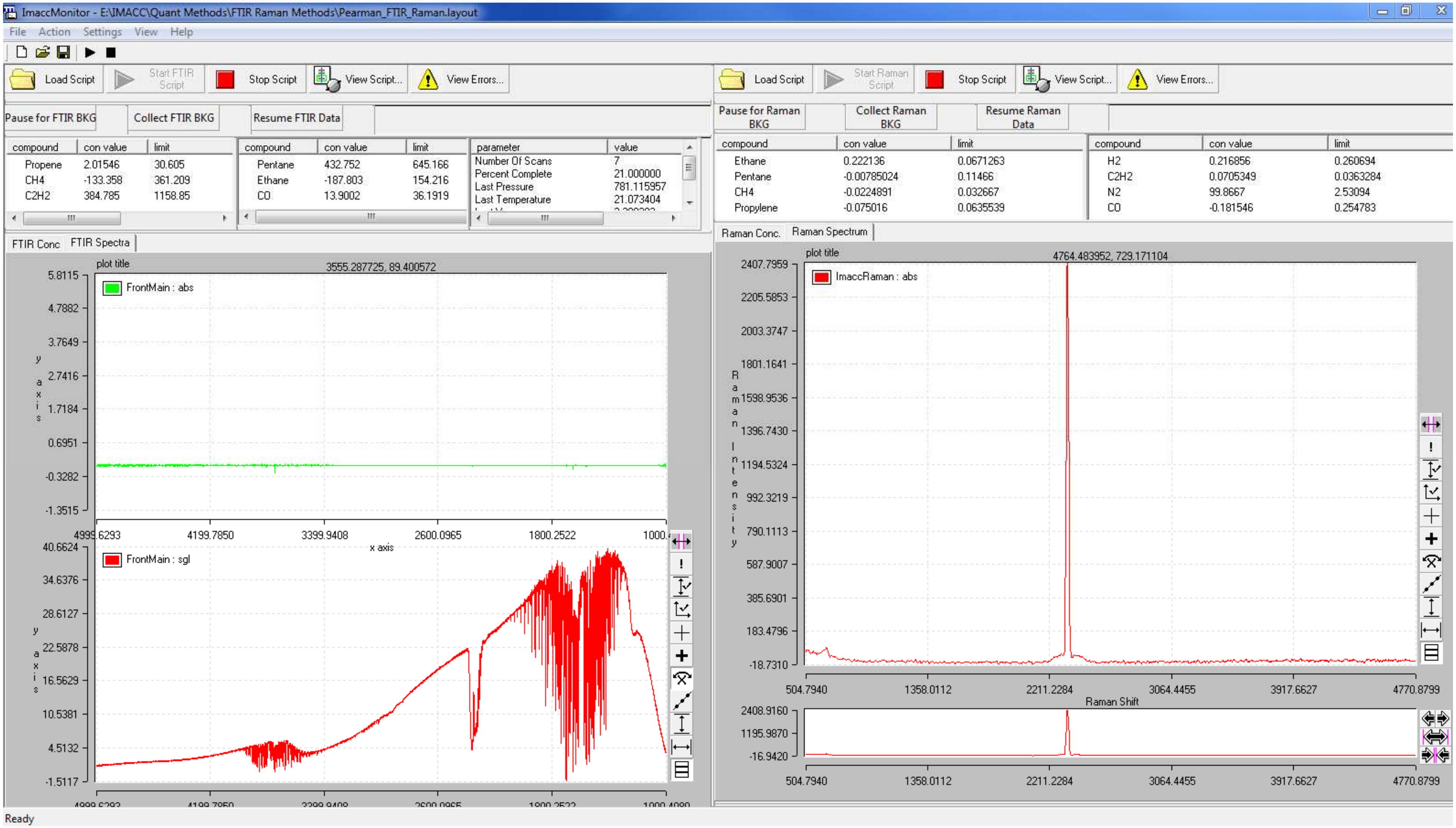
# Current Instrumental Package



- Potential for rack mounting
  - Dimensions:
    - Base Unit
  - 16” (l) x 20” (w) x 8” (h)
    - Accessory Unit
  - 24” (l) x 20” (w) x 8” (h)

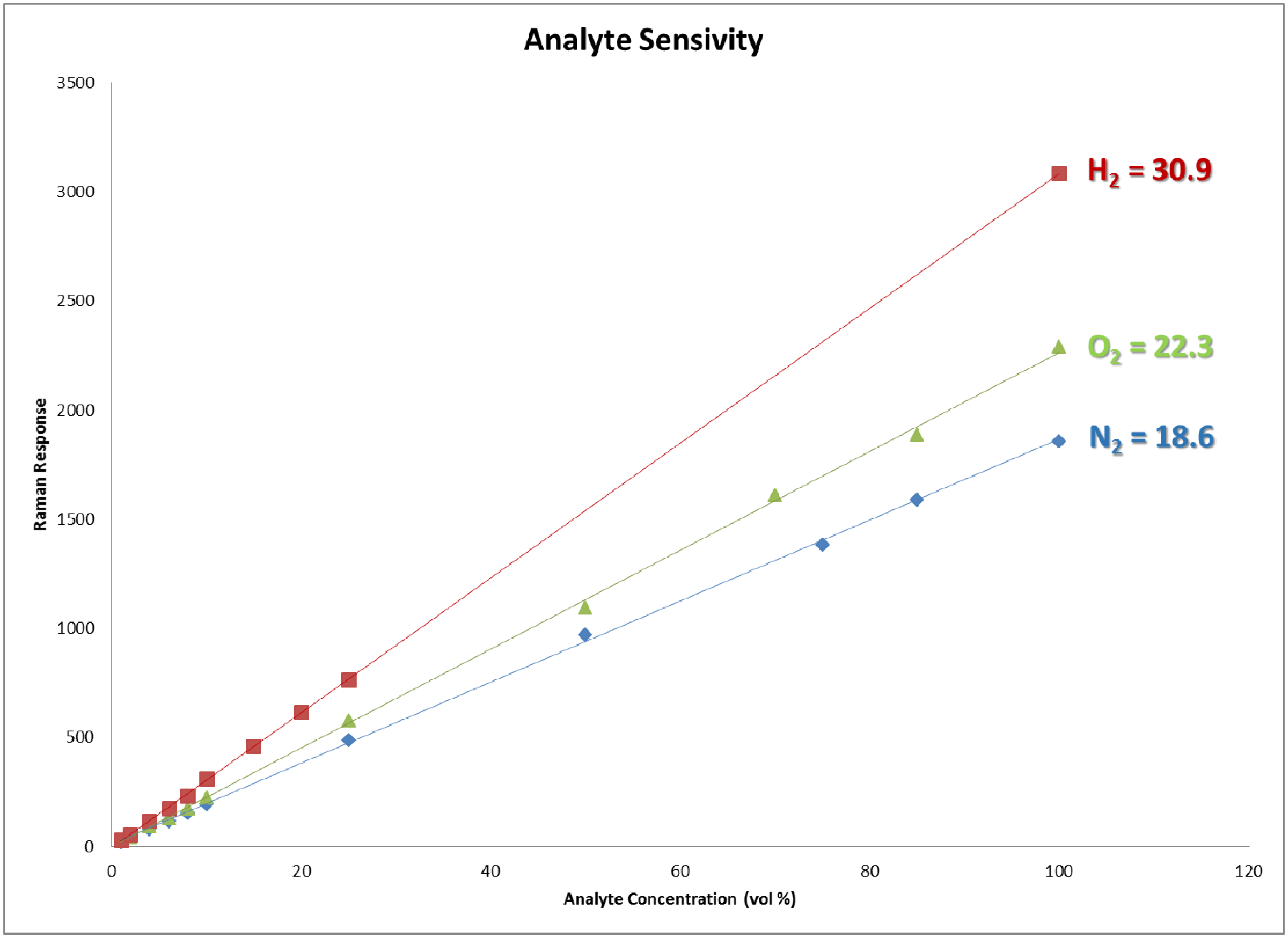
*Accessory Unit:*
*10m Gas Cell with*
*FTIR and Raman*
*Capabilities*

*Base Unit:*
*FTIR Modulator*

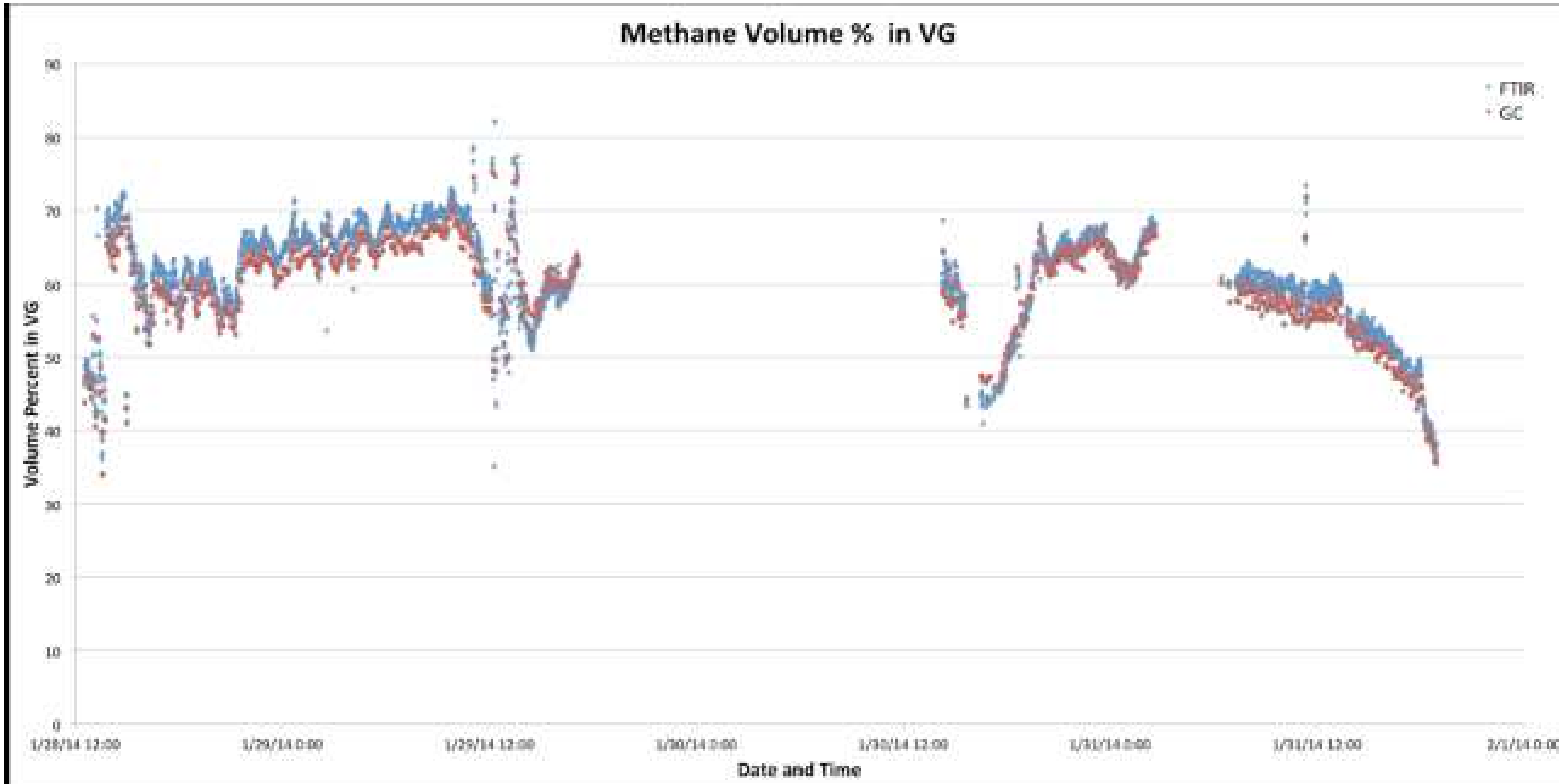

ImaccMonitor - E:\IMACC\Quant Methods\FTIR Raman Methods\Pearman_FTIR_Raman.layout
File Action Settings View Help
Load Script
Start FTIR Script
Stop Script
View Script...
View Errors...
Pause for FTIR BKG
Collect FTIR BKG
Resume FTIR Data
compound con value limit
Propene 2.01546 30.605
CH4 -133.358 361.209
C2H2 384.785 1158.85
compound con value limit
Pentane 432.752 645.166
Ethane -187.803 154.216
CO 13.9002 36.1919
parameter value
Number Of Scans 7
Percent Complete 21.000000
Last Pressure 781.115957
Last Temperature 21.073404
FTIR Conc
FTIR Spectra
plot title
3555.287725, 89.400572
FrontMain : abs
FrontMain : sgl
y axis
x axis
Start Raman Script
Pause for Raman BKG
Collect Raman BKG
Resume Raman Data
compound con value limit
Ethane 0.222136 0.0671263
Pentane -0.00785024 0.11466
CH4 -0.0224891 0.032667
Propylene -0.075016 0.0635539
compound con value limit
H2 0.216856 0.260694
C2H2 0.0705349 0.0363284
N2 99.8667 2.53094
CO -0.181546 0.254783
Raman Conc.
Raman Spectrum
4764.483952, 729.171104
ImaccRaman : abs
Raman Intensity
Raman Shift
Ready


ImaccMonitor - E:\IMACC\Quant Methods\FTIR Raman Methods\Pearman_FTIR_Raman.layout
File Action Settings View Help
Load Script
Start FTIR Script
Stop Script
View Script...
View Errors...
Pause for FTIR BKG
Collect FTIR BKG
Resume FTIR Data
compound con value limit
Propene 725.253 201.471
CH4 18660.2 31822
C2H2 567.846 11777.8
compound con value limit
Pentane -3340.52 2013.41
Ethane -30.4081 4995.21
CO 873.382 1631.97
parameter value
Number Of Scans 0
Percent Complete 0.000000
Last Pressure 781.015054
Last Temperature 21.037634
FTIR Conc
FTIR Spectra
plot title
08:51:40 - 10.08.14, 6113.146100
CO
Pentane
C2H2
Propene
Ethane
CH4
x axis
Start Raman Script
Pause for Raman BKG
Collect Raman BKG
Resume Raman Data
compound con value limit
Ethane 0.190203 0.0775298
Pentane -0.0757633 0.11166
CH4 -0.00557598 0.0267577
Propylene -0.0584076 0.0653428
compound con value limit
H2 0.178614 0.265901
C2H2 0.0839284 0.034018
N2 99.9095 2.5523
CO -0.161559 0.210038
Raman Conc.
Raman Spectrum
08:35:19 - 10.08.14, 507.358530
H2
Ethane
CO
C2H2
Propylene
Pentane
CH4
N2
Ready

# Select Raman Responses

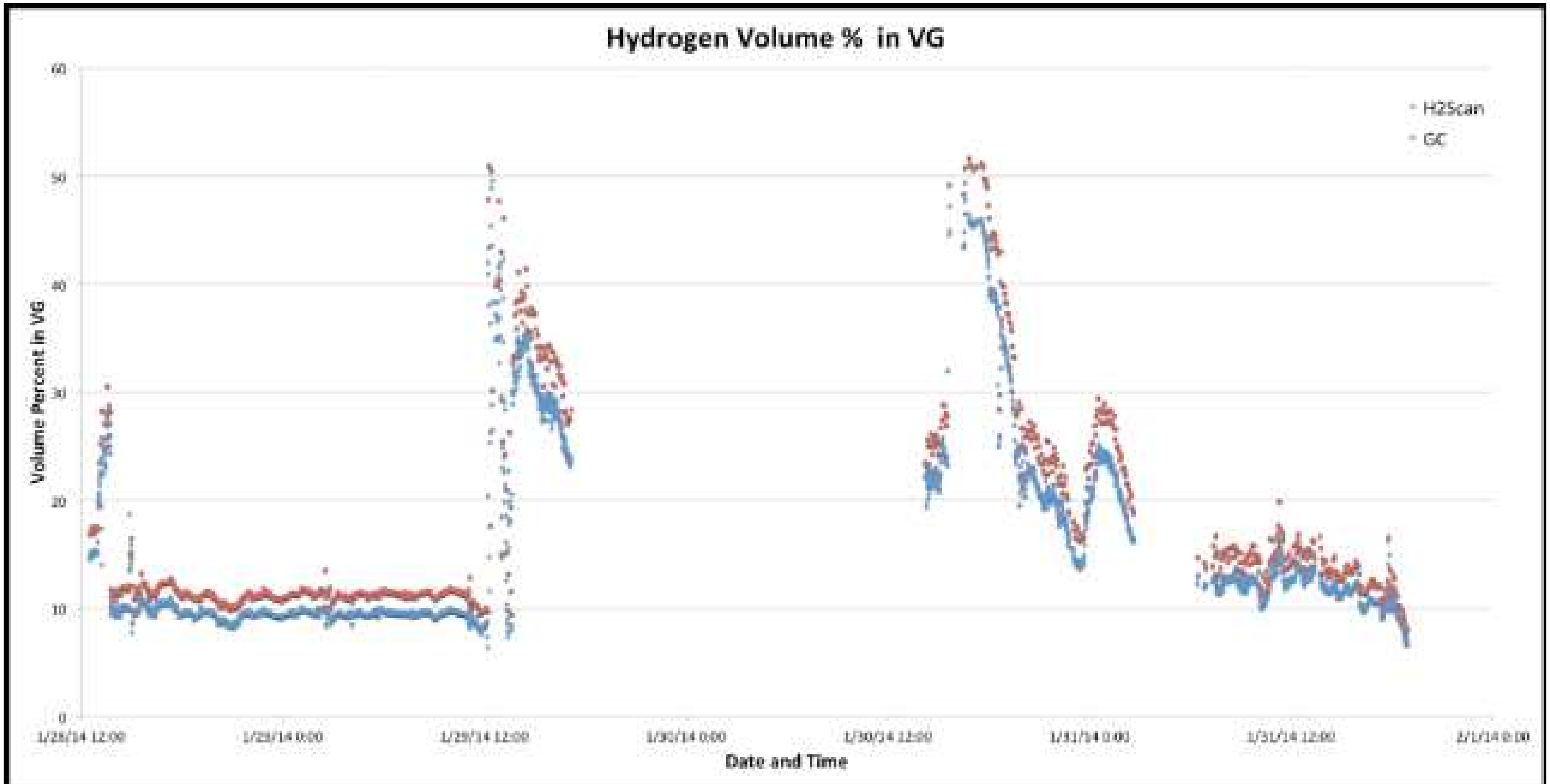


# FTIR Comparison to GC



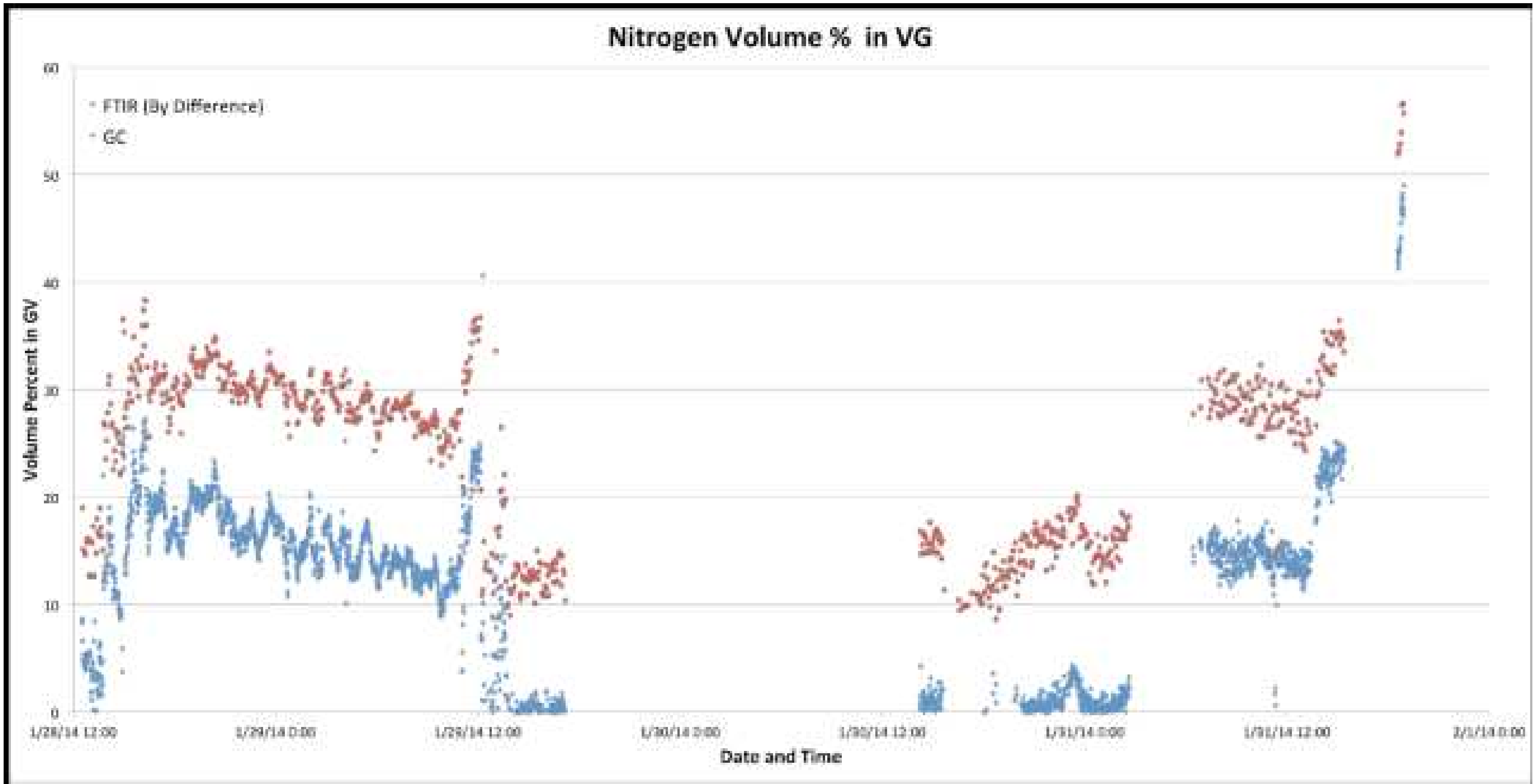

Methane data from the FTIR was very similar to methane data from the GC.

# Hydrogen using separate $H_2$ Analyzer compared to GC




Hydrogen data from the H2Scan was similar to hydrogen data from the GC.

# Nitrogen by Difference compared to GC




Nitrogen concentrations from the GC > Nitrogen concentrations from the FTIR

# Test for Raman Analysis

- Use of certified hydrocarbon gas mixture
- Test consisted of 5 runs varying concentrations of all species
- HovaCAL used to “blend” hydrogen into gas mixture

| ***Analyte*** | ***Bottle Concnetrations (vol %)*** | ***Error ( ± %)*** |
|---|---|---|
| Methane | 19.9 | 2 |
| Carbon monoxide | 5.01 | 2 |
| Acetylene | 3.14 | 2 |
| n-Pentane | 1.52 | 2 |
| Propylene | 5.05 | 2 |
| Ethane | 1.99 | 2 |
| Nitrogen (balance) | 63.39 | 2 |
| | | |
| Hydrogen | 99.99 | 0.01 |

# Results:  HovaCAL to Raman

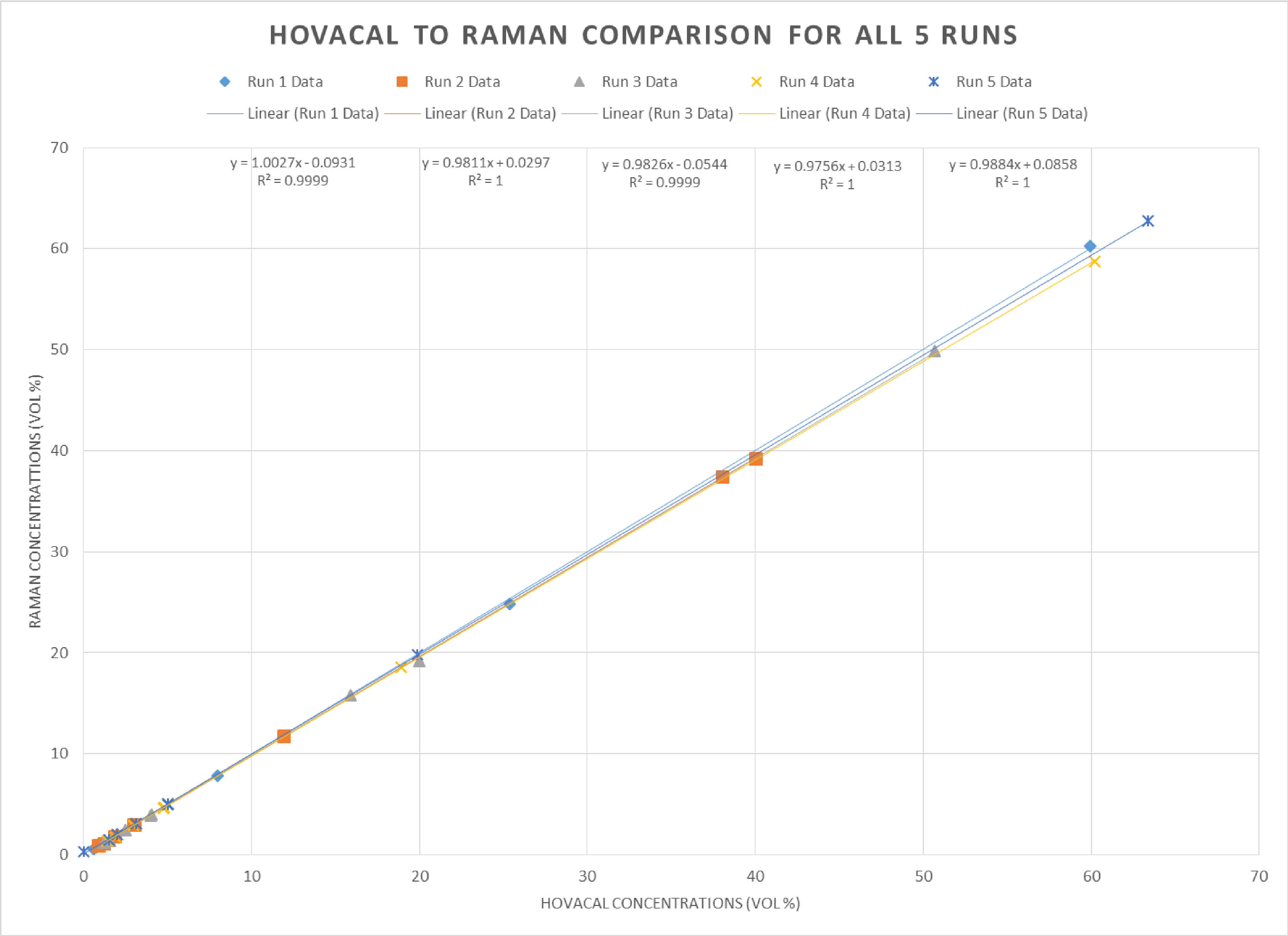
| **Run 1** | | **HovaCAL** | **Raman** |
|---|---|---|---|
| | Methane | 7.97 | 7.84 |
| | Carbon monoxide | 2.01 | 2.03 |
| | Acetylene | 1.26 | 1.22 |
| | Pentane | | |
| | Propylene | | |
| | Ethane | | |
| | Hydrogen | | |
| | Nitrogen | | |

| **Run 2** | | **HovaCAL** | **Raman** |
|---|---|---|---|
| | Methane | 11.94 | 11.80 |
| | Carbon monoxide | 3.01 | 3.01 |
| | Acetylene | 1.88 | 1.84 |
| | | 0.91 | 0.91 |
| | | 3.03 | 3.03 |
| | | 1.19 | 1.15 |
| | | 40 | 39.20 |
| | | 38.03 | 37.40 |

| **Run 5** | | **HovaCAL** | **Raman** |
|---|---|---|---|
| | Methane | 19.9 | 19.85 |
| | Carbon monoxide | 5.01 | 5.04 |
| | Acetylene | 3.14 | 3.12 |
| | Pentane | 1.52 | 1.52 |
| | Propylene | 5.05 | 4.96 |
| | Ethane | 1.99 | 2.00 |
| | Hydrogen | 0 | 0.30 |
| | Nitrogen | 63.39 | 62.72 |

| **Run 3** | | **H** | |
|---|---|---|---|
| | Methane | | |
| | Carbon monoxide | 4.01 | 3.90 |
| | Acetylene | 2.51 | 2.47 |
| | Pentane | 1.22 | 1.21 |
| | Propylene | 4.04 | 3.97 |
| | Ethane | 1.59 | 1.43 |
| | Hydrogen | 20.01 | 19.22 |
| | Nitrogen | 50.71 | 49.86 |

| | | **HovaCAL** | **Raman** |
|---|---|---|---|
| | | 18.9 | 18.59 |
| | Carbon monoxide | 4.76 | 4.65 |
| | Acetylene | 2.98 | 2.92 |
| | Pentane | 1.44 | 1.41 |
| | Propylene | 4.8 | 4.68 |
| | Ethane | 1.89 | 1.77 |
| | Hydrogen | 5.04 | 5.09 |
| | Nitrogen | 60.19 | 58.72 |


HOVACAL TO RAMAN COMPARISON FOR ALL 5 RUNS
Run 1 Data
Run 2 Data
Run 3 Data
Run 4 Data
Run 5 Data
Linear (Run 1 Data)
Linear (Run 2 Data)
Linear (Run 3 Data)
Linear (Run 4 Data)
Linear (Run 5 Data)
y = 1.0027x - 0.0931
R² = 0.9999
y = 0.9811x + 0.0297
R² = 1
y = 0.9826x - 0.0544
R² = 0.9999
y = 0.9756x + 0.0313
R² = 1
y = 0.9884x + 0.0858
R² = 1
RAMAN CONCENTRATTIONS (VOL %)
HOVACAL CONCENTRATIONS (VOL %)
0
10
20
30
40
50
60
70

# Results: Raman to GC (HovaCAL)

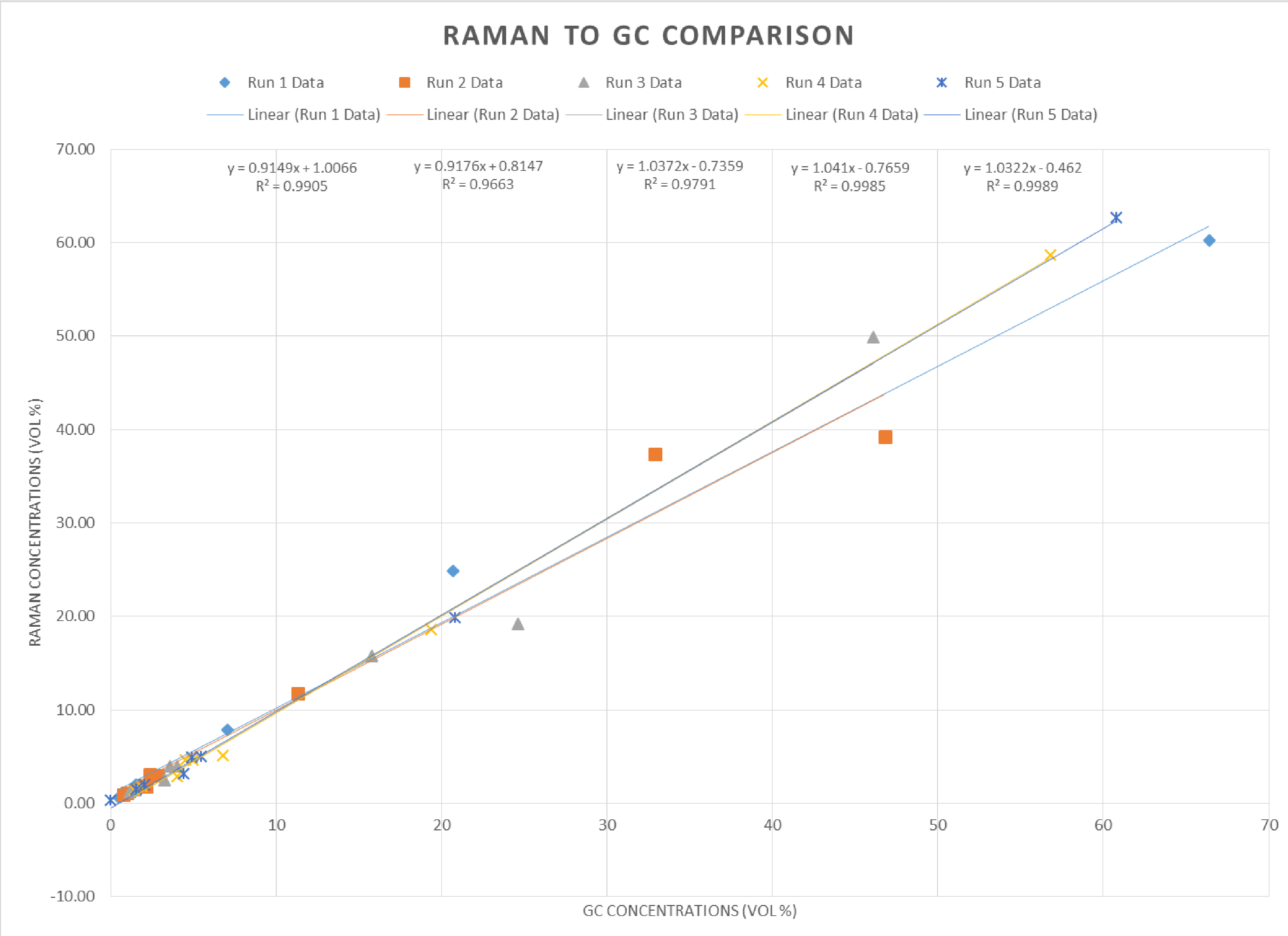
| Run 1 | | GC | Raman |
|---|---|---|---|
| | Methane | 7.08 | 7.84 |
| | Carbon monoxide | 1.77 | 2.03 |
| | Acetylene | [illegible] | [illegible] |
| | Pentane | [illegible] | [illegible] |
| | Propylene | [illegible] | [illegible] |
| | Ethane | [illegible] | [illegible] |
| | Hydrogen | [illegible] | [illegible] |
| | Nitrogen | [illegible] | [illegible] |

| Run 3 | | GC | Raman |
|---|---|---|---|
| | Methane | 15.8 | 15.76 |
| | Carbon monoxide | 4.03 | 3.90 |
| | tylene | 3.23 | 2.47 |
| | tane | 1.15 | 1.21 |
| | pylene | 3.61 | 3.97 |
| | ne | 1.48 | 1.43 |
| | rogen | 24.6 | 19.22 |
| | ogen | 46.1 | 49.86 |

| Run 5 | | GC | Raman |
|---|---|---|---|
| | Methane | 20.8 | 19.85 |
| | Carbon monoxide | 5.45 | 5.04 |
| | Acetylene | 4.42 | 3.12 |
| | Pentane | 1.56 | 1.52 |
| | Propylene | 4.92 | 4.96 |
| | Ethane | 2.05 | 2.00 |
| | Hydrogen | 0 | 0.30 |
| | Nitrogen | 60.8 | 62.72 |

| Run 2 | | GC | Raman |
|---|---|---|---|
| | Methane | [illegible] | [illegible] |
| | Carbon monoxide | 2.85 | 3.01 |
| | Acetylene | 2.13 | 1.84 |
| | Pentane | 0.744 | 0.91 |
| | Propylene | 2.36 | 3.03 |
| | Ethane | 0.98 | 1.15 |
| | Hydrogen | 46.8 | 39.20 |
| | Nitrogen | 32.9 | 37.40 |

| | | GC | Raman |
|---|---|---|---|
| | hane | 19.4 | 18.59 |
| | Carbon monoxide | 4.96 | 4.65 |
| | Acetylene | 4.05 | 2.92 |
| | Pentane | 1.44 | 1.41 |
| | Propylene | 4.53 | 4.68 |
| | Ethane | 1.87 | 1.77 |
| | Hydrogen | 6.8 | 5.09 |
| | Nitrogen | 56.8 | 58.72 |



RAMAN TO GC COMPARISON
Run 1 Data
Run 2 Data
Run 3 Data
Run 4 Data
Run 5 Data
Linear (Run 1 Data)
Linear (Run 2 Data)
Linear (Run 3 Data)
Linear (Run 4 Data)
Linear (Run 5 Data)
y = 0.9149x + 1.0066
R² = 0.9905
y = 0.9176x + 0.8147
R² = 0.9663
y = 1.0372x - 0.7359
R² = 0.9791
y = 1.041x - 0.7659
R² = 0.9985
y = 1.0322x - 0.462
R² = 0.9989
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
RAMAN CONCENTRATIONS (VOL %)
0
10
20
30
40
50
60
70
GC CONCENTRATIONS (VOL %)

# Results: Raman to GC (GC)

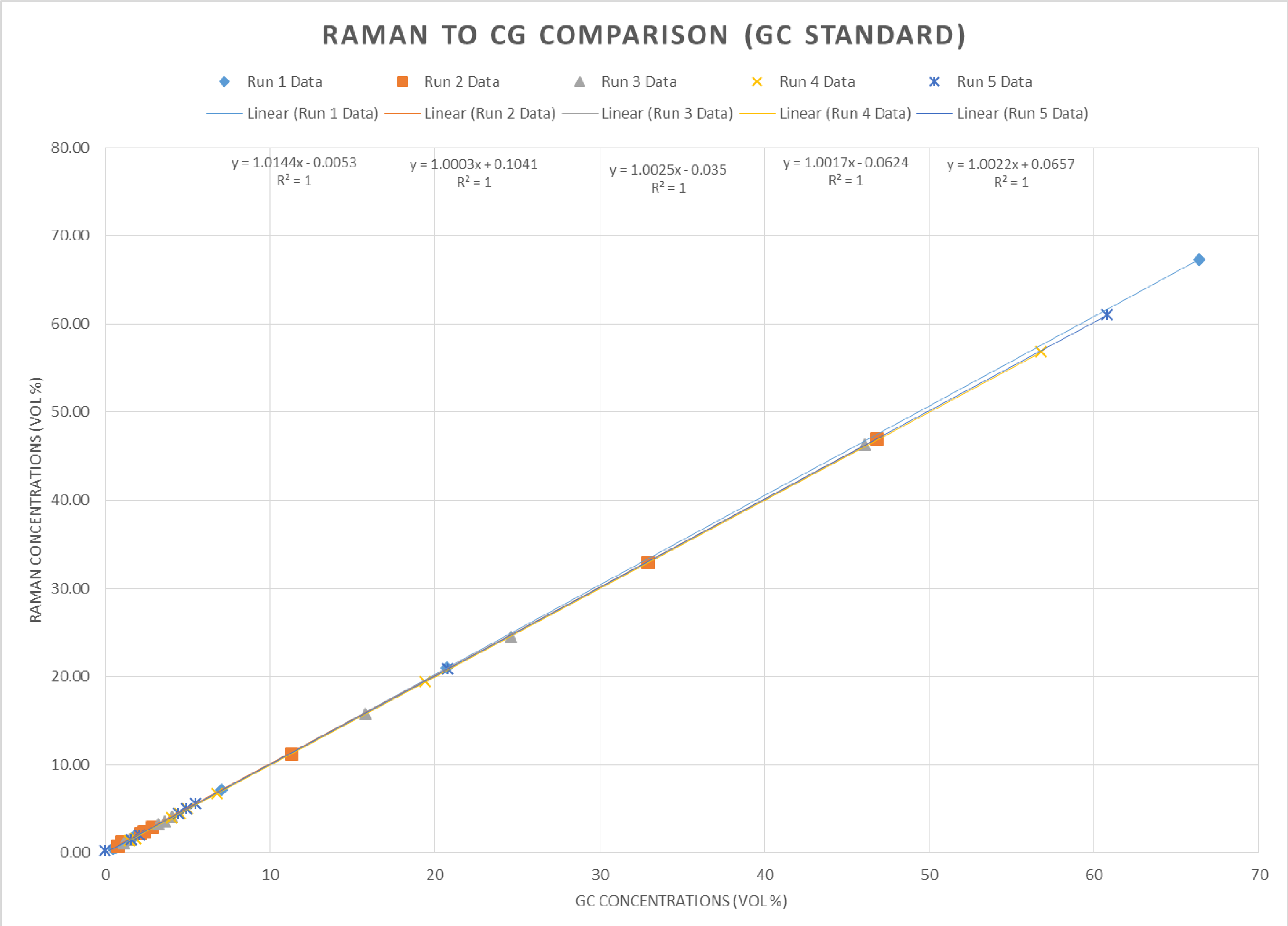
| **Run 1** | | **GC** | **Raman** |
|---|---|---|---|
| | Methane | 7.08 | 7.17 |
| | Carbon monoxide | 1.77 | 1.90 |
| | Acetylene | 1.38 | 1.36 |
| | Pentane | | |
| | Propylene | | |
| | Ethane | | |
| | Hydrogen | | |
| | Nitrogen | | |

| **Run 3** | | **GC** | **Raman** |
|---|---|---|---|
| | Methane | 15.8 | 15.80 |
| | Carbon monoxide | 4.03 | 4.05 |
| | Acetylene | 3.23 | 3.24 |
| | | 1.15 | 1.13 |
| | e | 3.61 | 3.55 |
| | | 1.48 | 1.47 |
| | n | 24.6 | 24.48 |
| | | 46.1 | 46.26 |

| **Run 5** | | **GC** | **Raman** |
|---|---|---|---|
| | Methane | 20.8 | 20.85 |
| | Carbon monoxide | 5.45 | 5.63 |
| | Acetylene | 4.42 | 4.45 |
| | Pentane | 1.56 | 1.56 |
| | Propylene | 4.92 | 4.96 |
| | Ethane | 2.05 | 2.00 |
| | Hydrogen | 0 | 0.27 |
| | Nitrogen | 60.8 | 61.02 |

| **Run 2** | | **GC** | **Raman** |
|---|---|---|---|
| | Methane | | |
| | Carbon monoxi | | |
| | Acetylene | 2.13 | 2.23 |
| | Pentane | 0.744 | 0.78 |
| | Propylene | 2.36 | 2.48 |
| | Ethane | 0.98 | 1.30 |
| | Hydrogen | 46.8 | 46.99 |
| | Nitrogen | 32.9 | 32.95 |

| | | **GC** | **Raman** |
|---|---|---|---|
| | | 19.4 | 19.45 |
| | onoxide | 4.96 | 5.00 |
| | Acetylene | 4.05 | 4.02 |
| | Pentane | 1.44 | 1.41 |
| | Propylene | 4.53 | 4.50 |
| | Ethane | 1.87 | 1.61 |
| | Hydrogen | 6.8 | 6.71 |
| | Nitrogen | 56.8 | 56.80 |


RAMAN TO CG COMPARISON (GC STANDARD)
Run 1 Data
Run 2 Data
Run 3 Data
Run 4 Data
Run 5 Data
Linear (Run 1 Data)
Linear (Run 2 Data)
Linear (Run 3 Data)
Linear (Run 4 Data)
Linear (Run 5 Data)
y = 1.0144x - 0.0053
R² = 1
y = 1.0003x + 0.1041
R² = 1
y = 1.0025x - 0.035
R² = 1
y = 1.0017x - 0.0624
R² = 1
y = 1.0022x + 0.0657
R² = 1
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
10
20
30
40
50
60
70
RAMAN CONCENTRATIONS (VOL %)
GC CONCENTRATIONS (VOL %)

# Conclusion

IMACC has identified an industrial need and has a new viable solution (patent-pending!)

- Theoretical Design
- Proof of Concept – bench tests successful
- Local and remote location
- Field Demo – 3 planned before end of year

IMACC device yields minute resolved results

- Continuous BTU monitoring
- Improves dynamic control of supplemental gas and steam or air assist
- Continuous emissions monitoring

# Contact Information

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Thank You for your attendance!!