



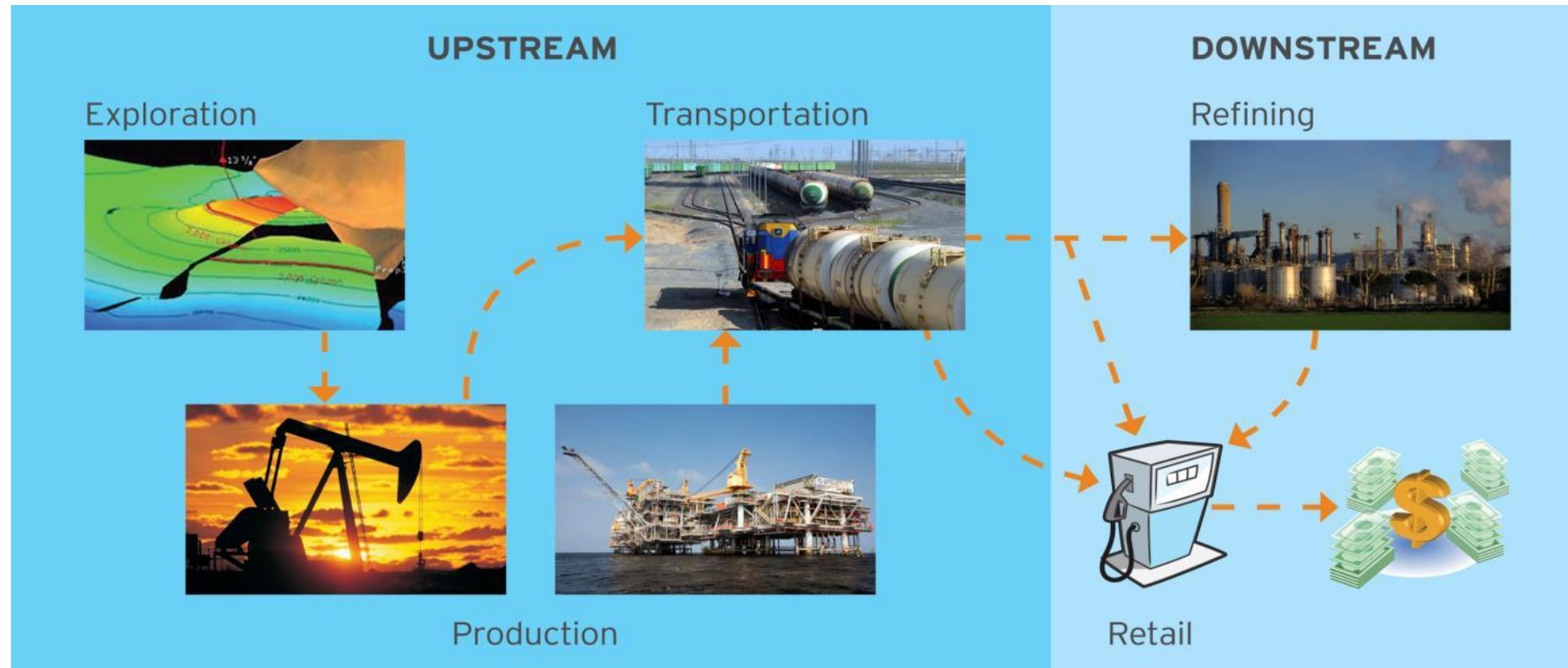
# ***Fast Process Gas Chromatography Implementations in Refining and Petrochemical Plants***

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CRechsteiner Consulting, LLC



# Gas Chromatography in the Oil Business

- GC widely used in the oil, gas, refining, petrochemical and chemicals business



Falcon Analytical  
makers of the . . .

**CALIDUS**  
micro GAS CHROMATOGRAPH

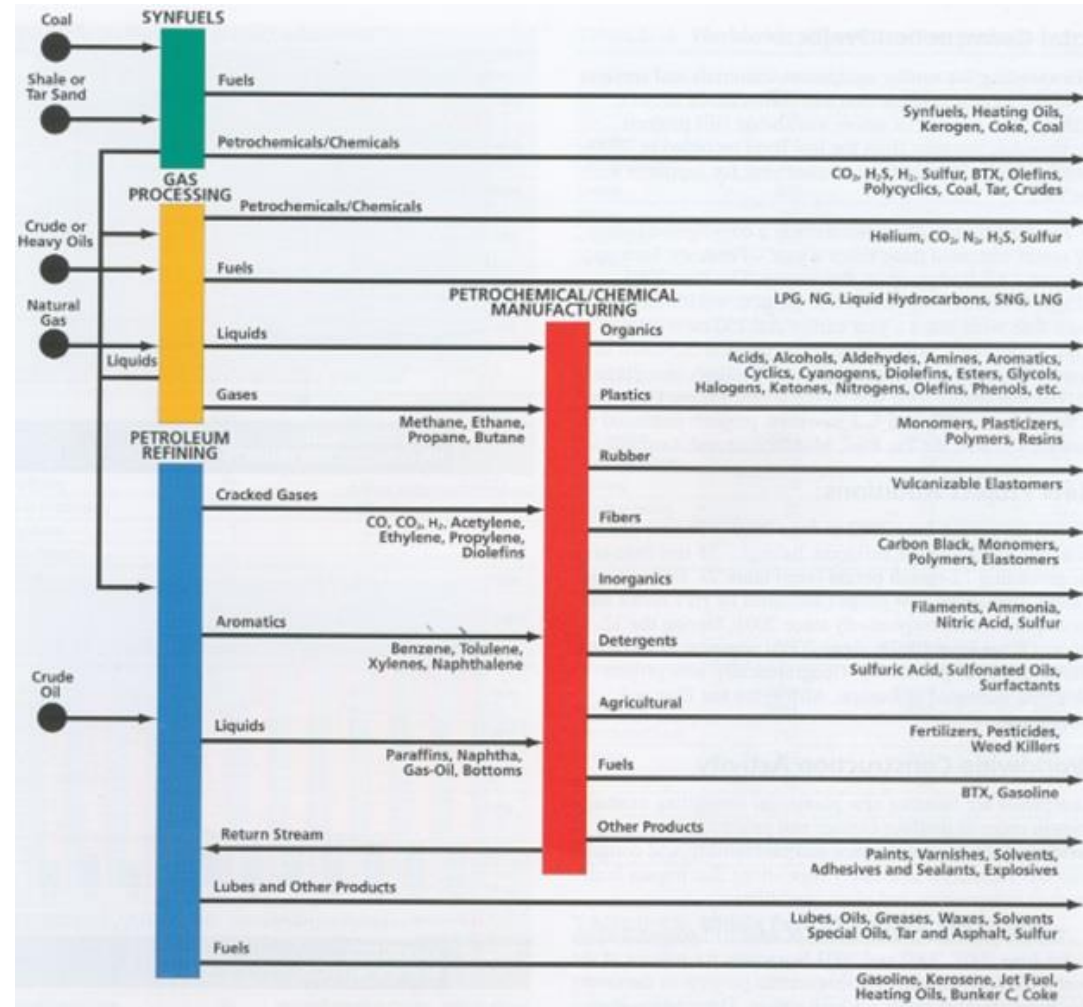
in the lab...

in the process...

in the field.



# Importance of the Oil Business to Our Economy



From "Hydrocarbon Processing"

# Four Example Oil Business Applications

## 1. Upstream

*Onsite oil & gas evaluations*

## 2. Downstream

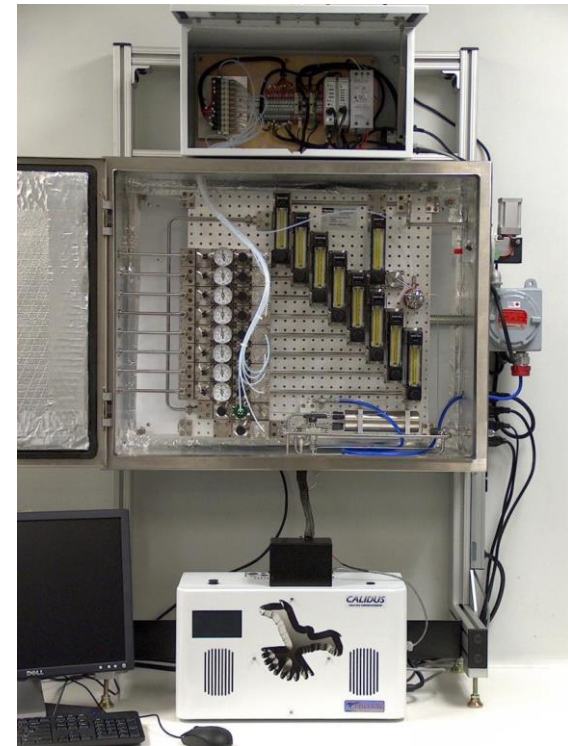
*Gasoline Blender Control*

## 3. Chemical/Petrochemical

*Polymers (dimer, trimer and tetramer product process control)*

## 4. Petrochemical

*Monomer Product Purity*



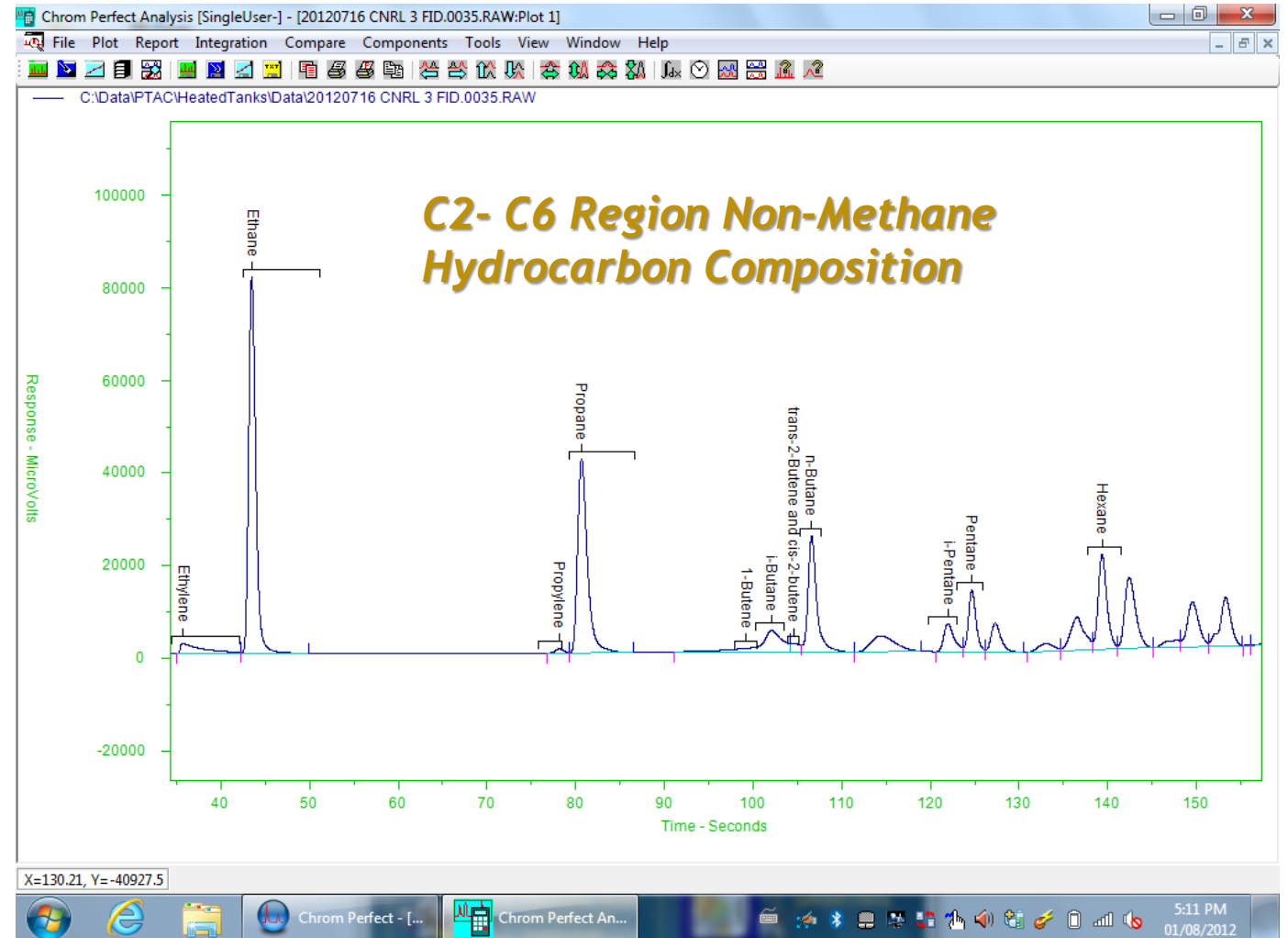
# 1. Onsite Oil & Gas Evaluations

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- **Composition evaluations at the wellhead are important diagnostics for the geochemist**
  - **Offgas from drilling mud and cuttings (pay or no pay zone evaluations)**
  - **Production testing**
    - Gas composition leading to energy content (BTU)
    - Crude characterization, chemical fossil screening and ratio analysis (pristane/phytane)
- **Fugitive Emissions, Fence line Testing, Green House Gas, Offgas from the Mud Pits**
  - **Key questions - What are the levels of regulated emissions (typically trace components)? Are there leaks in plants, piping, tanks?**



# Typical Natural Gas Sample: Calidus CS FID Signal

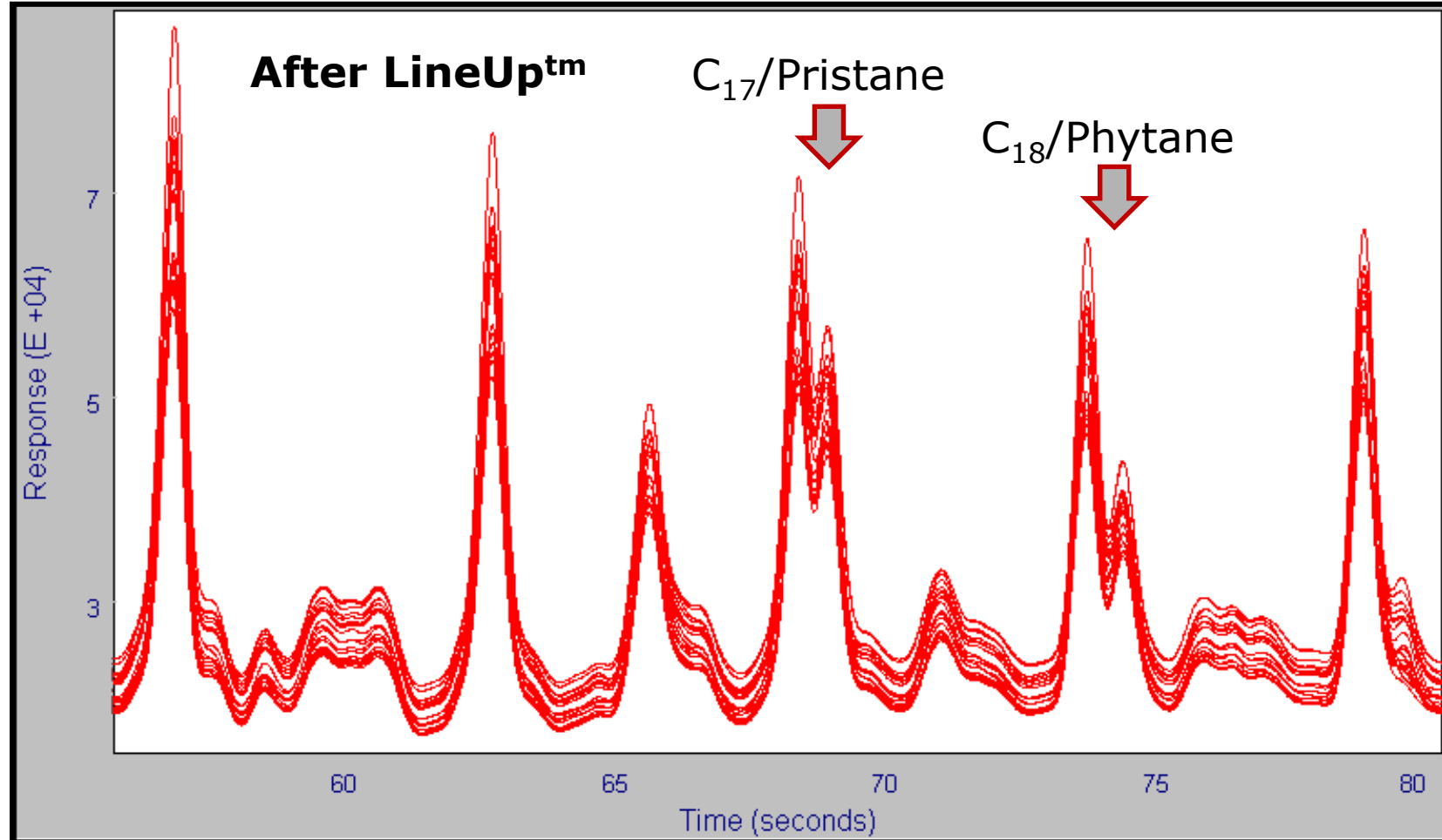
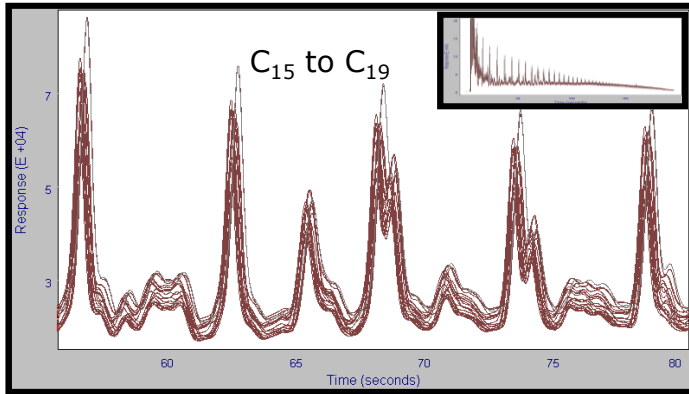


# Typical Crude Oil Characterization



Ratios of these components are important geochemical markers.

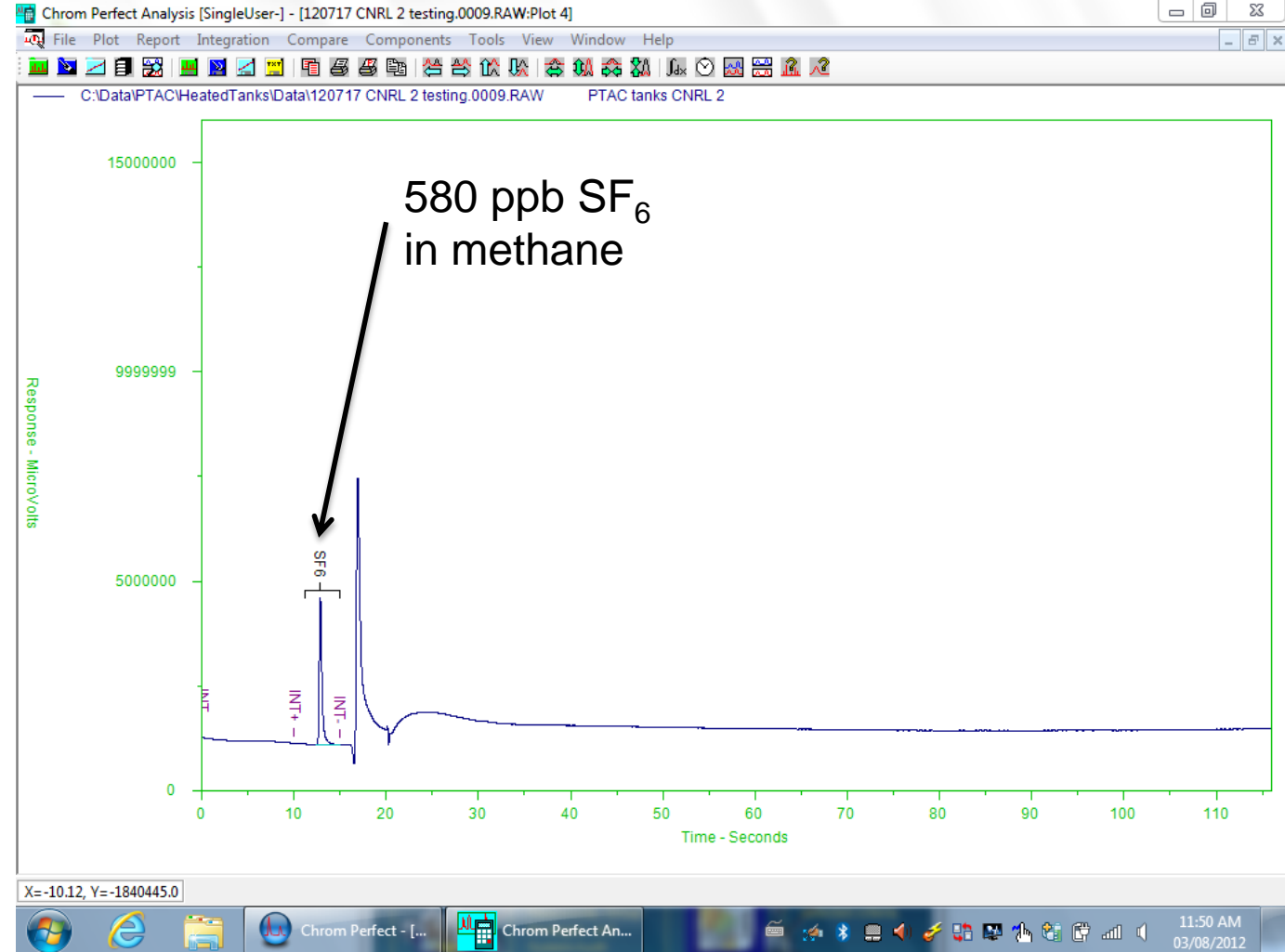
## Before LineUp™



# SF<sub>6</sub> Tracer in Natural Gas & Boiler Plumes



- **Tracer is added to methane fuel**
  - **Amount is verified by GC**
  - **The gas is used to fire boilers**
- **Then the boiler plume is tracked in the environment**
  - **SF<sub>6</sub> survives the combustion**
  - **Indicates direction of emissions**



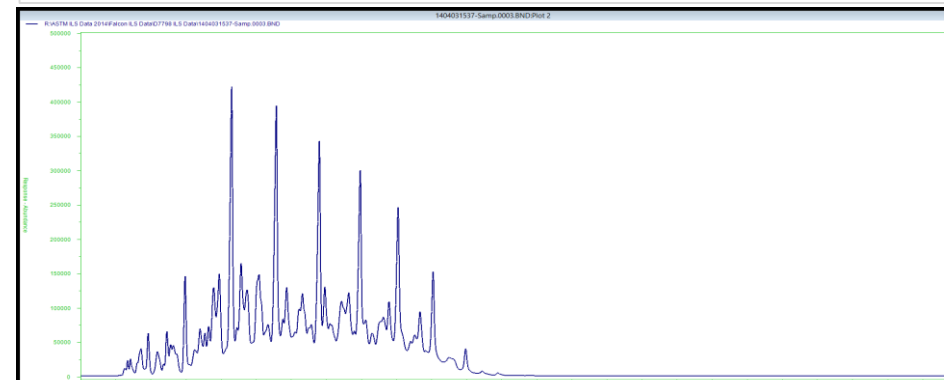
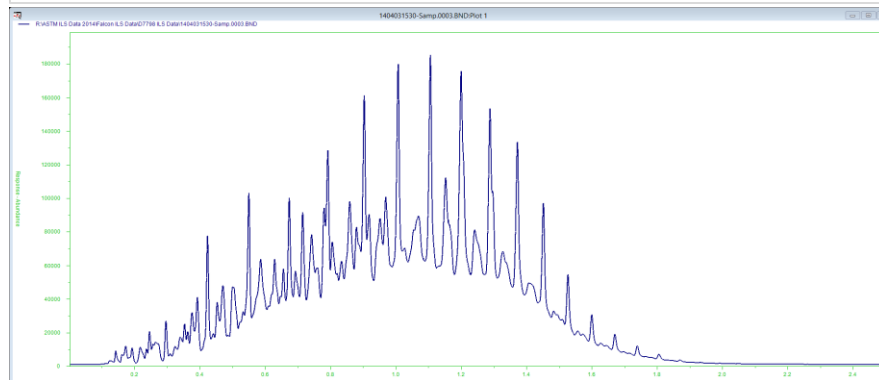
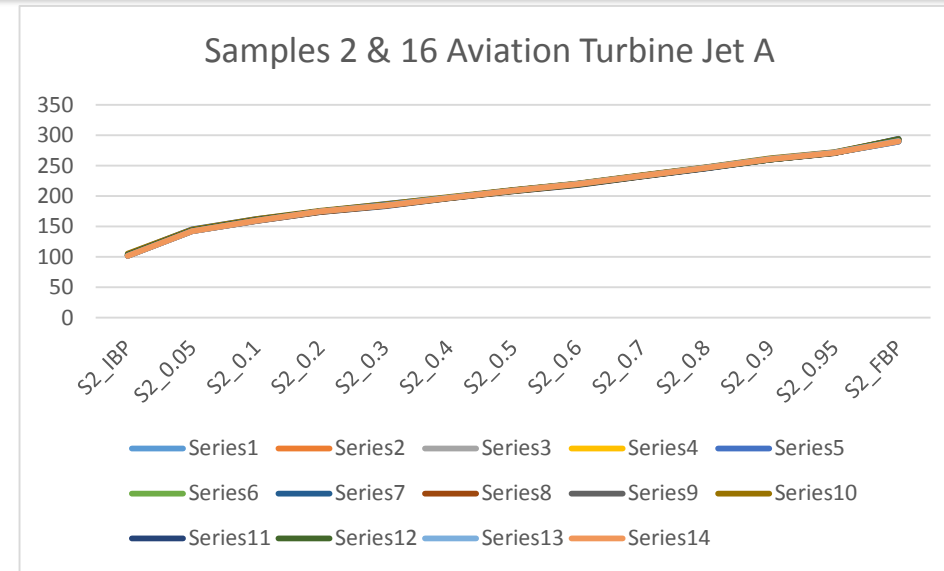
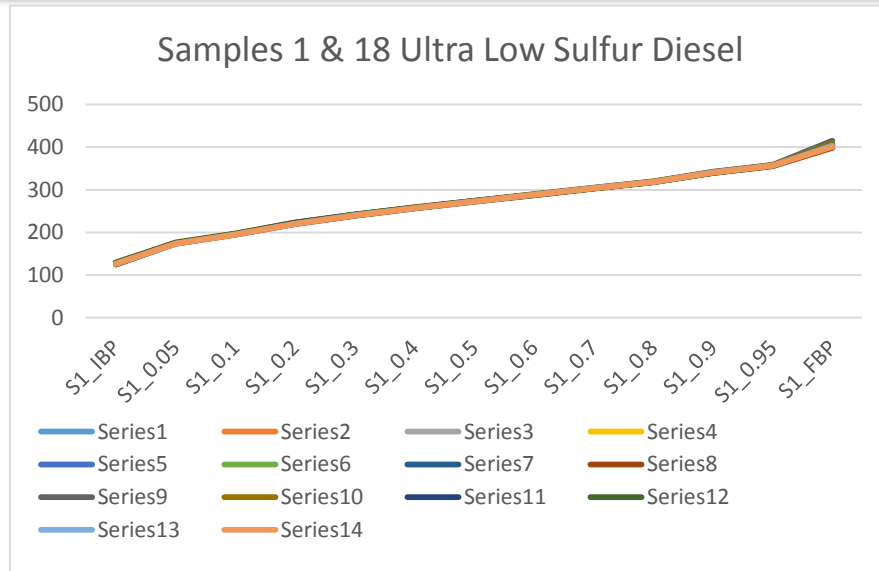


## 2. Los Angeles Refinery - Gasoline Blender Application

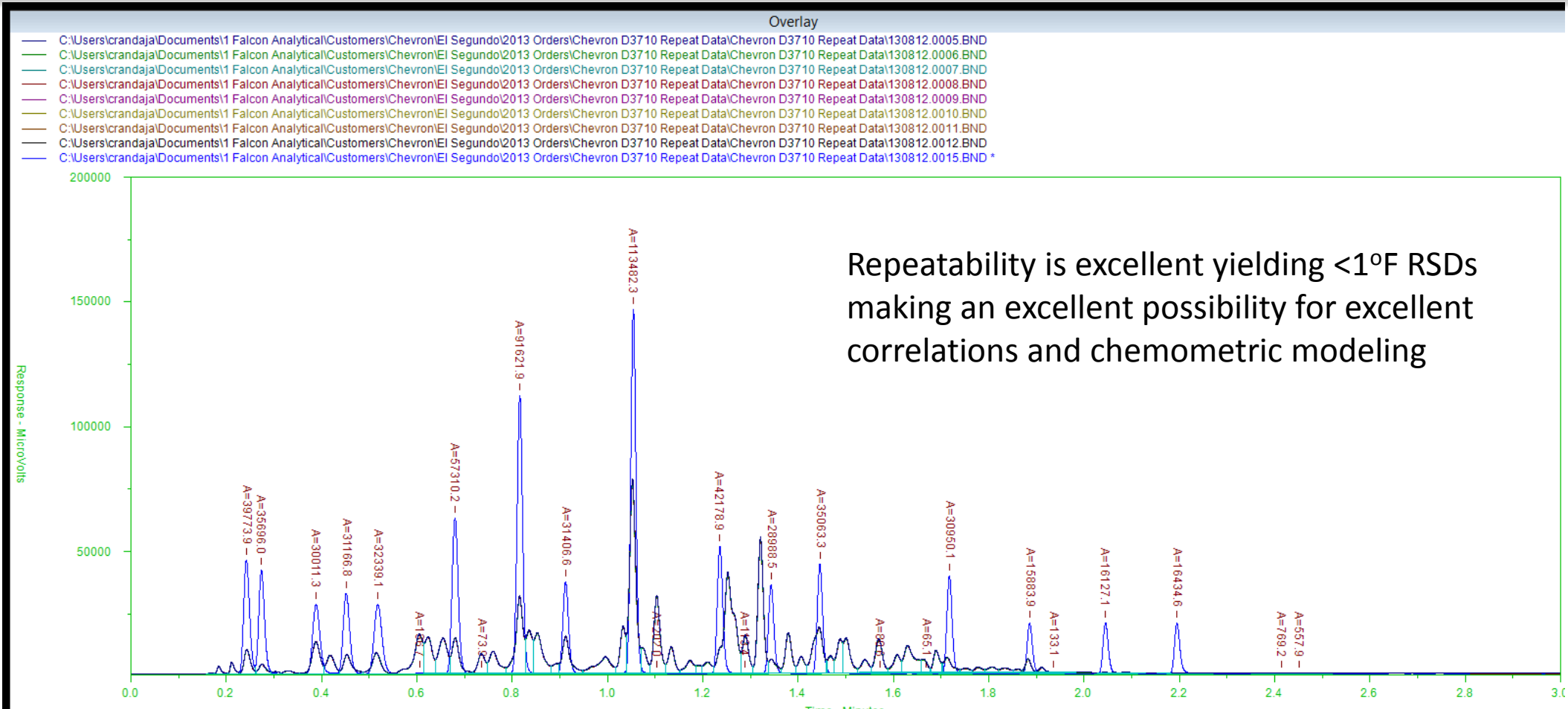
- **Modern analytical chemistry mandates Simulated Distillation**
  - **However, specifications and regulations require D86**
  - **Correlations from simulated to actual distillation have been used with some success**
  - **Fast GC for D3710 is more timely, more precise and should lead to more accuracy... but correlating to D86 depends upon**
    - **D86 apparatus and operator capabilities**
    - **And the techniques are fundamentally different**
    - **Thus correlations can be fragile but NOT with excellent repeatability of both the reference method and the data to be correlated like D3710**



# As Demonstrated, Fast Simulated Distillation Repeatability & Reproducibility Is Superior



# RT Standard & 8 Gasoline Replicates



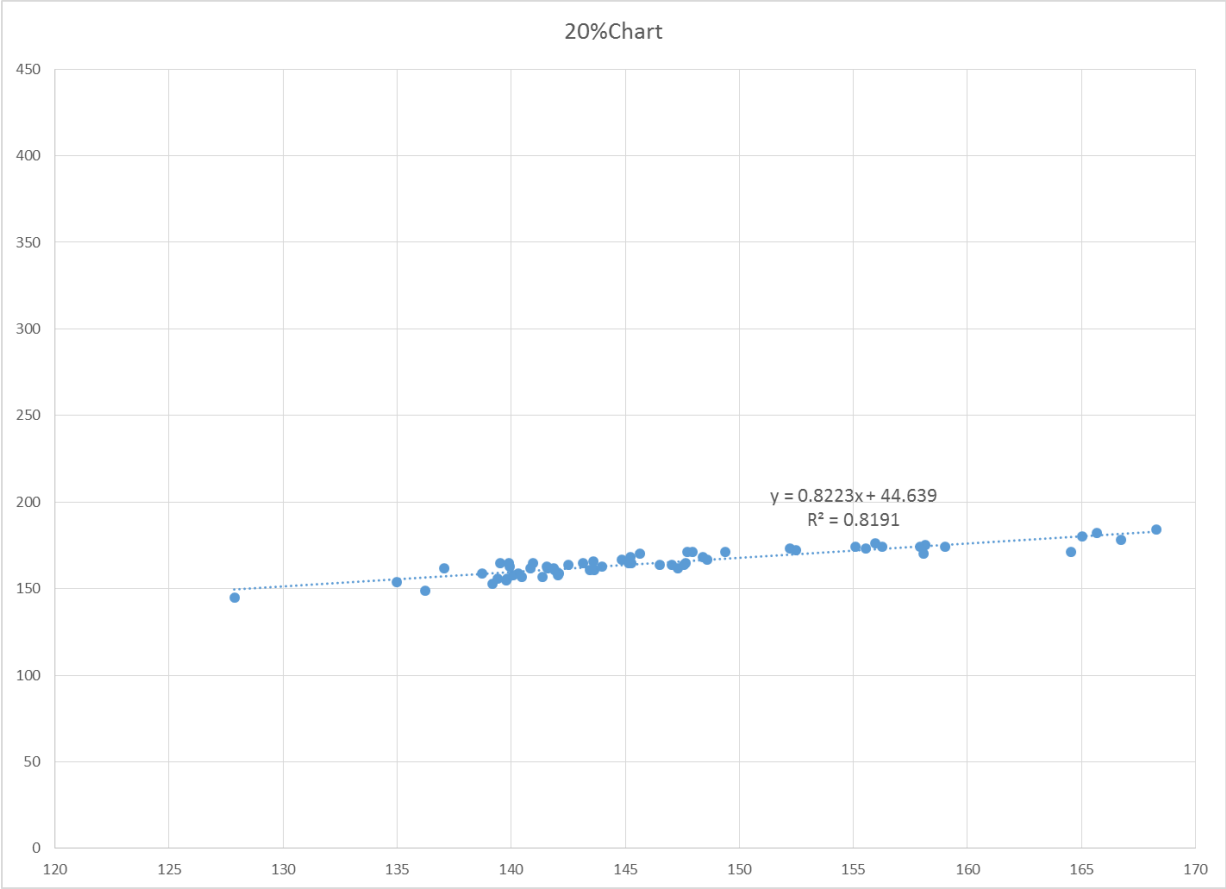
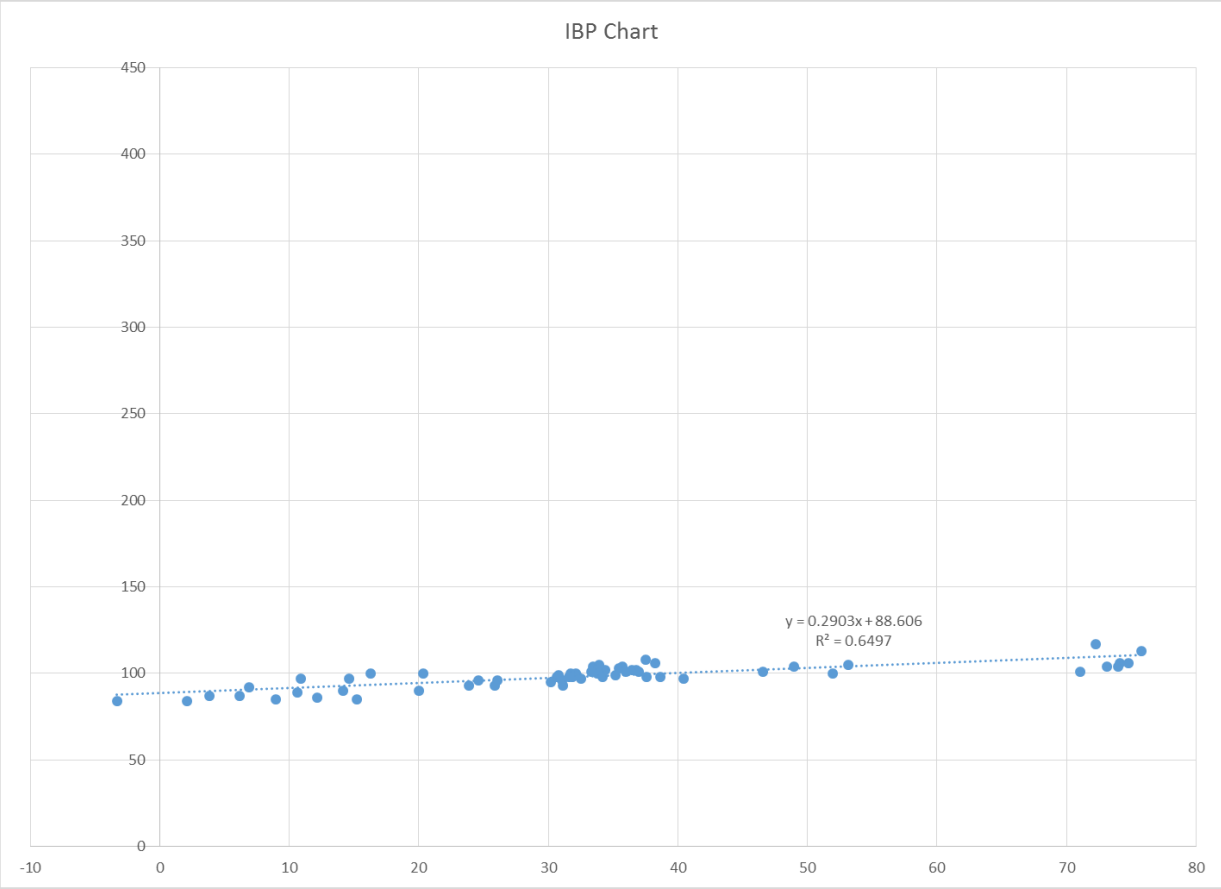
# Many Results from Many Blends, 4°F STDEV Average

	SUBXAN-A4	SBCAE-CA2	SUBVCN-A1	SBCAE-CA2	SUBXAN-A4	SPCAE-CA2	SBCAE-CA2	SUBVCN-A1	SBCAE-CA2	SPCAE-CA2	SUPXRN-AX2	SPCAE-CA2	SPCAE-CA2	SUBVCN-A1	SBCAE-CA1
Unmatched 0	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	START-UP	START-UP	START-UP	START-UP	START-UP	START-UP	START-UP	START-UP	START-UP	START-UP	START-UP	MIX	START-UP	START-UP	START-UP
	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Date	04/03/2015	04/03/2015	04/04/2015	04/07/2015	04/08/2015	04/09/2015	04/10/2015	04/12/2015	04/15/2015	04/18/2015	04/17/2015	04/04/2015	04/24/2015	06/27/2015	06/04/2015
Time	01:45:00	13:55:16	21:20:49	17:56:25	08:05:11	22:30:25	15:40:01	13:38:44	13:30:00	08:25:39	01:50:42	10:20:42	23:00:57	15:15:05	20:20:03
	Result	Result	Result	Result	Result	Result	Result	Result	Result	Result	Result	Result	Result	Result	Result
IBP	93	105	90	104	93	98	104	85	101	96	113	99	98	89	100
10	136	154	137	148	137	151	148	128	147	150	168	147	154	135	152
20	153	171	161	163	156	171	164	155	162	172	184	167	174	156	170
50	215	222	229	216	216	222	214	241	212	226	219	223	225	234	224
90	313	309	315	310	313	312	304	321	304	314	301	315	317	339	312
FBP	374	385	371	386	385	398	382	365	383	401	398	401	406	390	391
➤ ➤ ➤															
Falcon D86												98.0	97.9	91.7	98.5
IBP	95.5	98.4	92.7	99.0	96.1	97.5	98.3	91.2	99.0	97.6	110.6	139.6	151.7	141.5	149.3
10	140.6	151.6	144.8	144.6	139.6	150.9	149.9	136.9	147.1	150.0	157.8	163.7	175.4	159.3	164.4
20	159.1	166.3	161.3	161.0	159.6	167.5	161.8	159.6	161.1	170.0	183.0	219.3	223.6	226.0	221.1
50	212.8	222.7	230.6	216.9	215.7	219.2	215.9	242.8	215.5	222.7	221.7	311.7	313.5	331.0	310.6
90	313.0	307.0	316.3	310.2	311.5	311.3	304.1	318.3	304.8	312.5	304.8	390.4	393.3	403.5	388.6
FBP	380.0	375.7	380.9	378.0	377.5	391.8	373.5	377.1	376.2	391.8	391.4				
Delta's												1.0	0.1	-2.7	1.5
IBP	-2.5	6.6	-2.7	5.0	-3.1	0.5	5.7	-6.2	2.0	-1.6	2.4	7.4	2.3	-6.5	2.7
10	-4.6	2.4	-7.8	3.4	-2.6	0.1	-1.9	-8.9	-0.1	0.0	10.2	3.3	-1.4	-3.3	5.6
20	-6.1	4.7	-0.3	2.0	-3.6	3.5	2.2	-4.6	0.9	2.0	1.0	3.7	1.4	8.0	2.9
50	2.2	-0.7	-1.6	-0.9	0.3	2.8	-1.9	-1.8	-3.5	3.3	-2.7	3.3	3.5	8.0	1.4
90	0.0	2.0	-1.3	-0.2	1.5	0.7	-0.1	2.7	-0.8	1.5	-3.8	10.6	12.7	-13.5	2.4
FBP	-6.0	9.3	-9.9	8.0	7.5	6.2	8.5	-12.1	6.8	9.2	6.6				

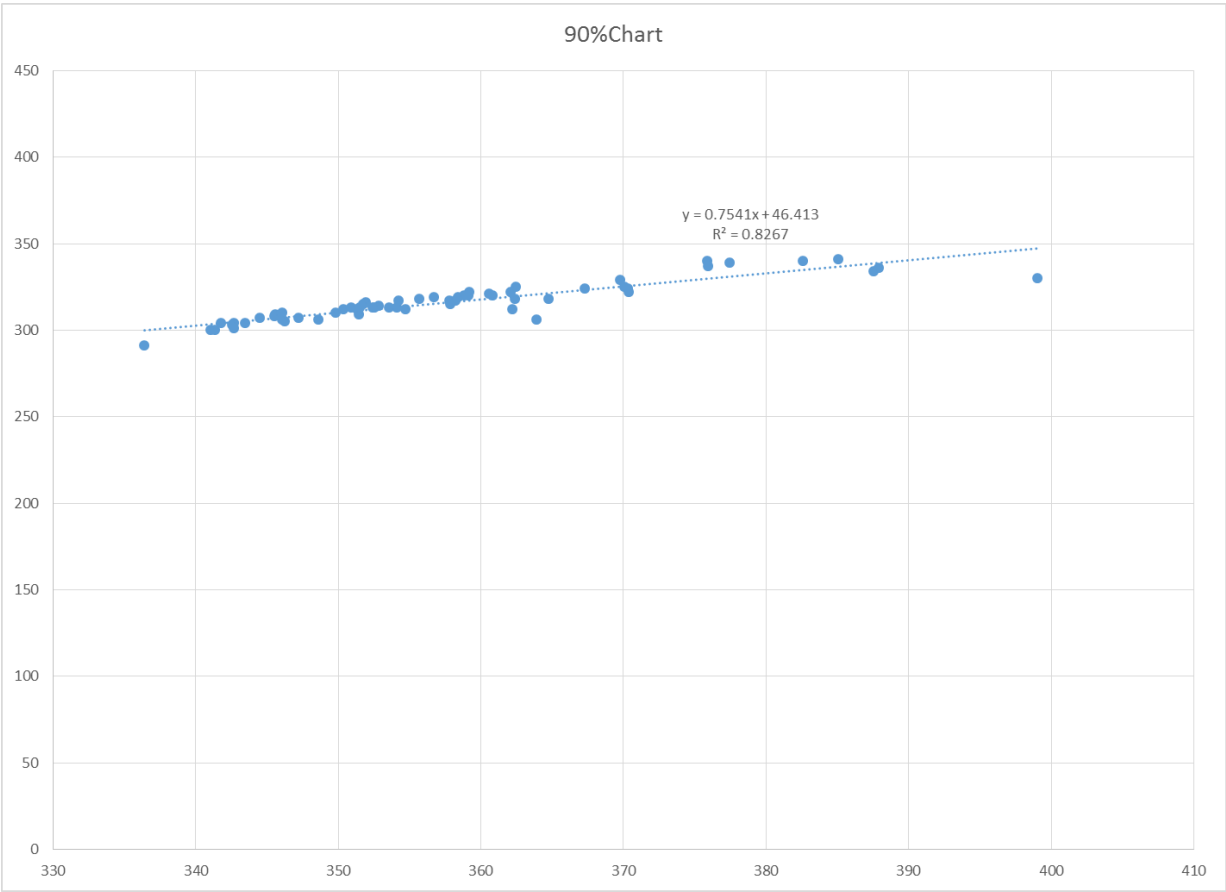
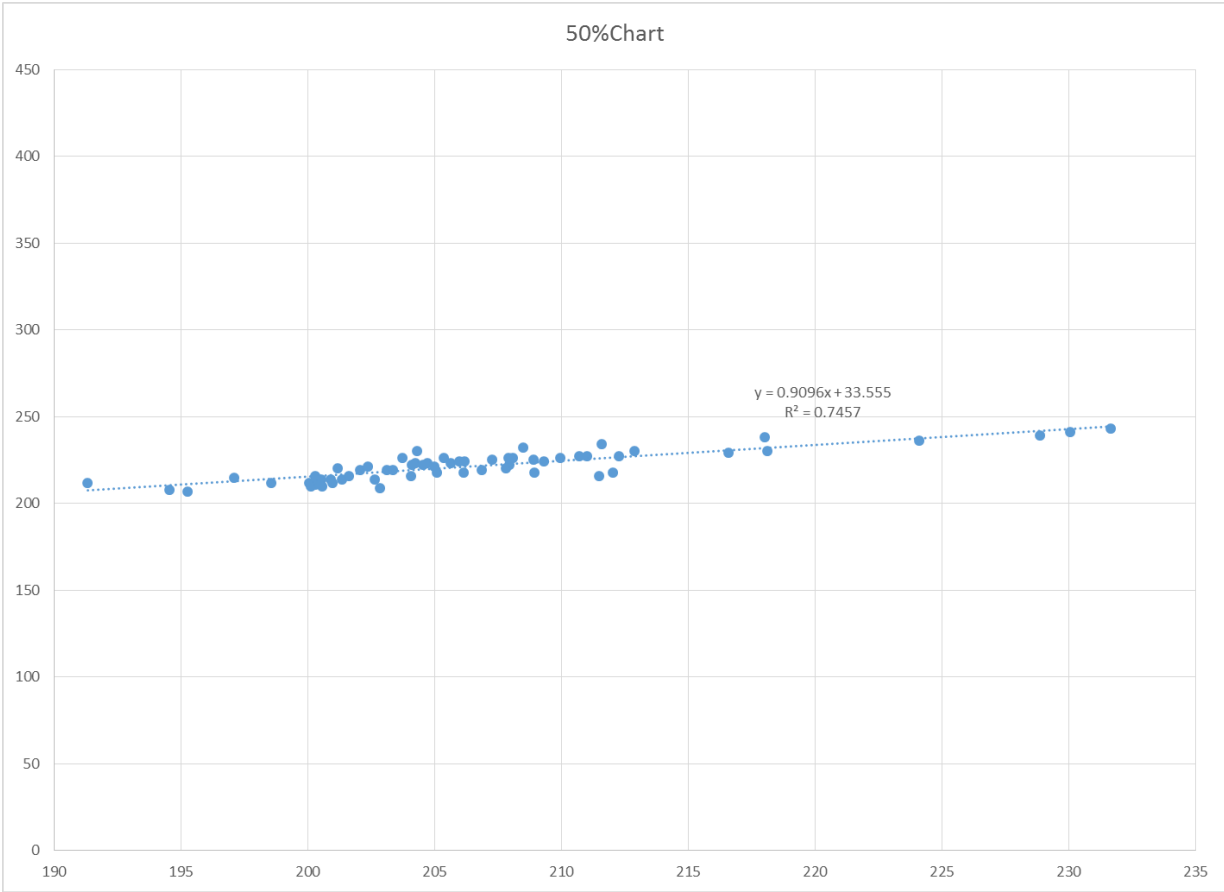
**STDEV**  
 4.0  
 5.6  
 3.3  
 4.2  
 4.6  
 11.4  
**4.3**



# Correlations for IBP and 20%

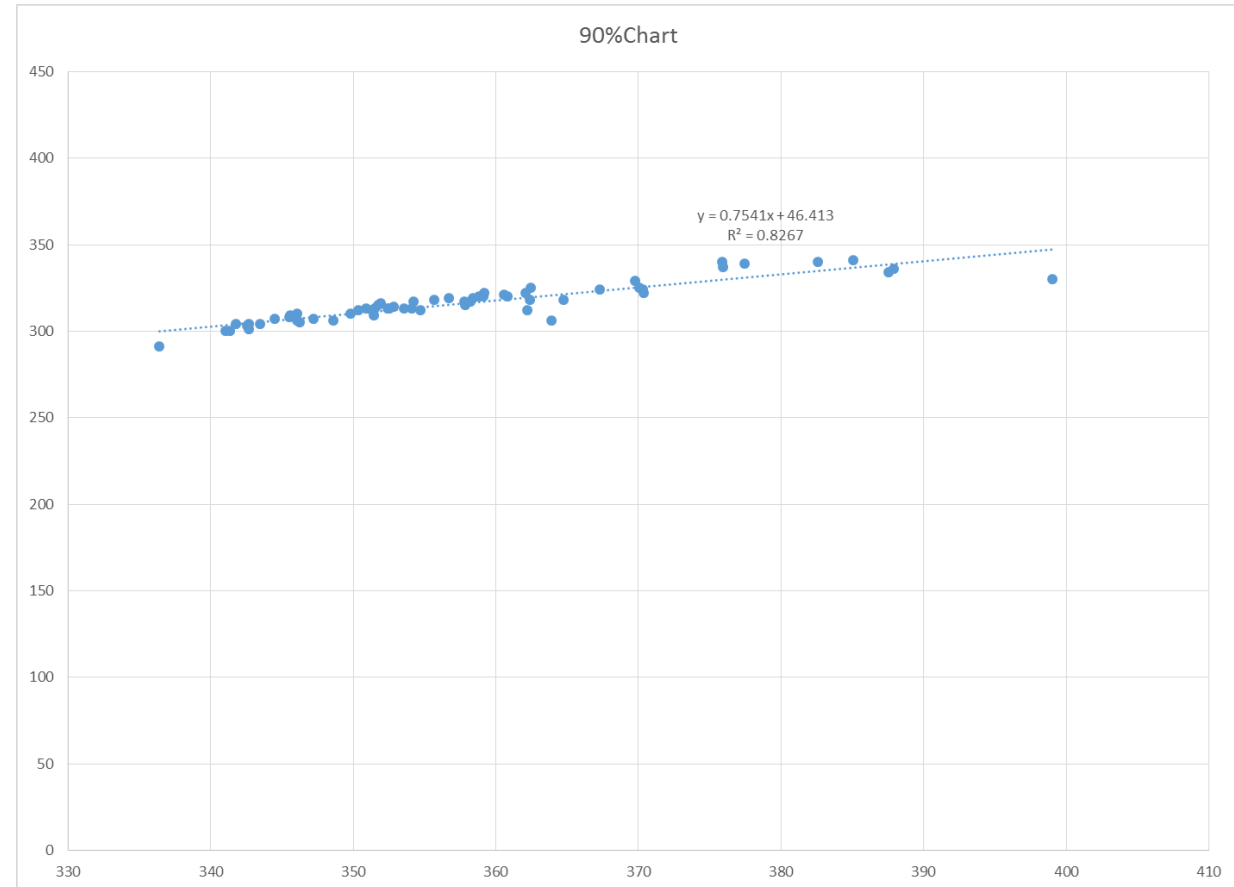


# Correlations for 50% and 90%



# Correlation for FBP

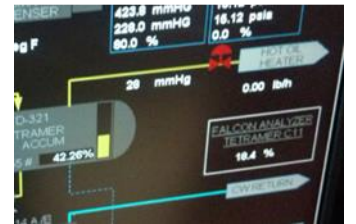
- **D3710 repeatability is superior to D86 as defined by the relevant ASTM methods**
- **The reference D86 values are matched by the D3710 correlations within the tolerance of the D86 method**
- **The correlation is robust for the fuel blends encountered**



# 3. Olefin Polymerization Control



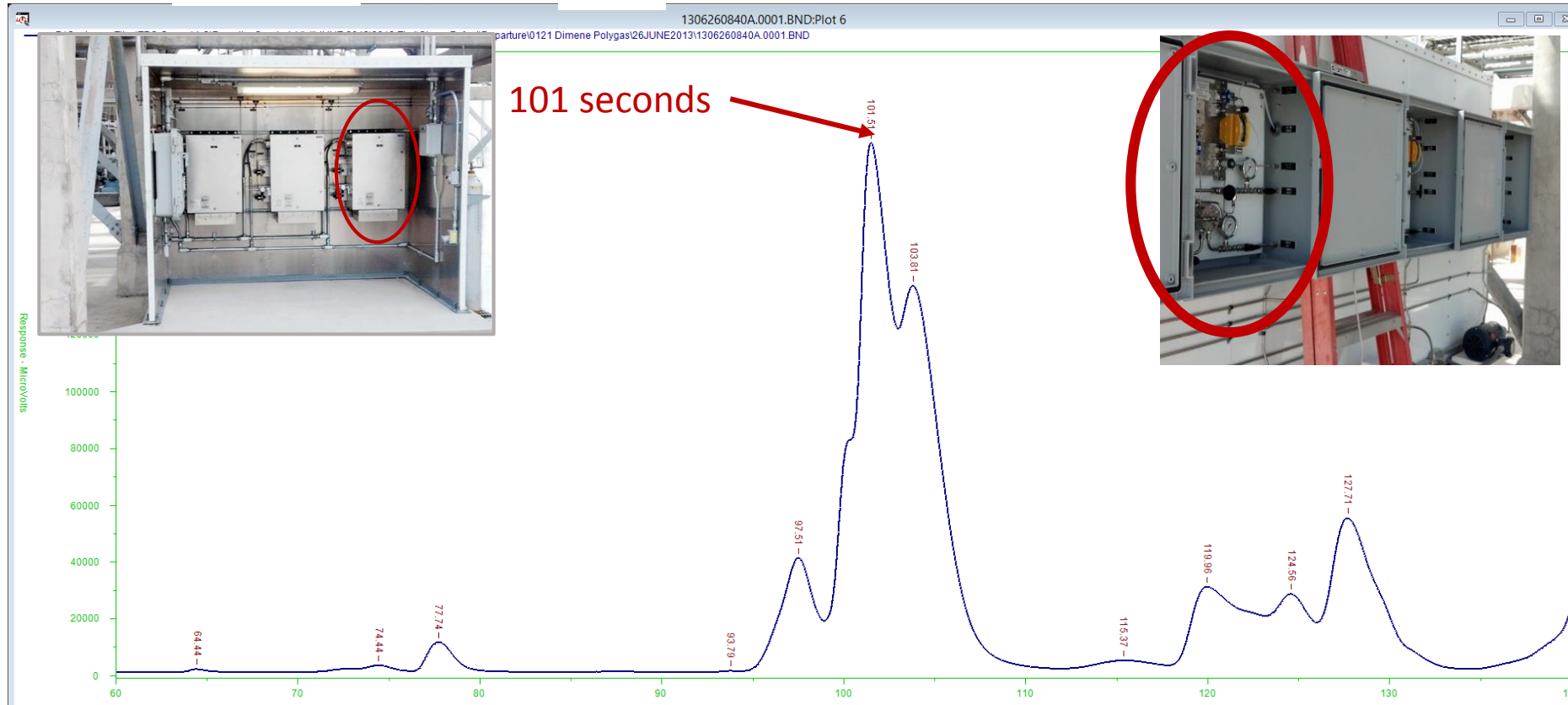
- **Calidus installed since late March 2014, no downtime to date**
- **Measurement is to optimize plant production i.e., meet product grade specifications without excess processing**
- **Negative financial impacts of excess processing are extra raw material consumption, higher steam consumption and delivery of above spec quality product (appropriate impurity content, less give away)**





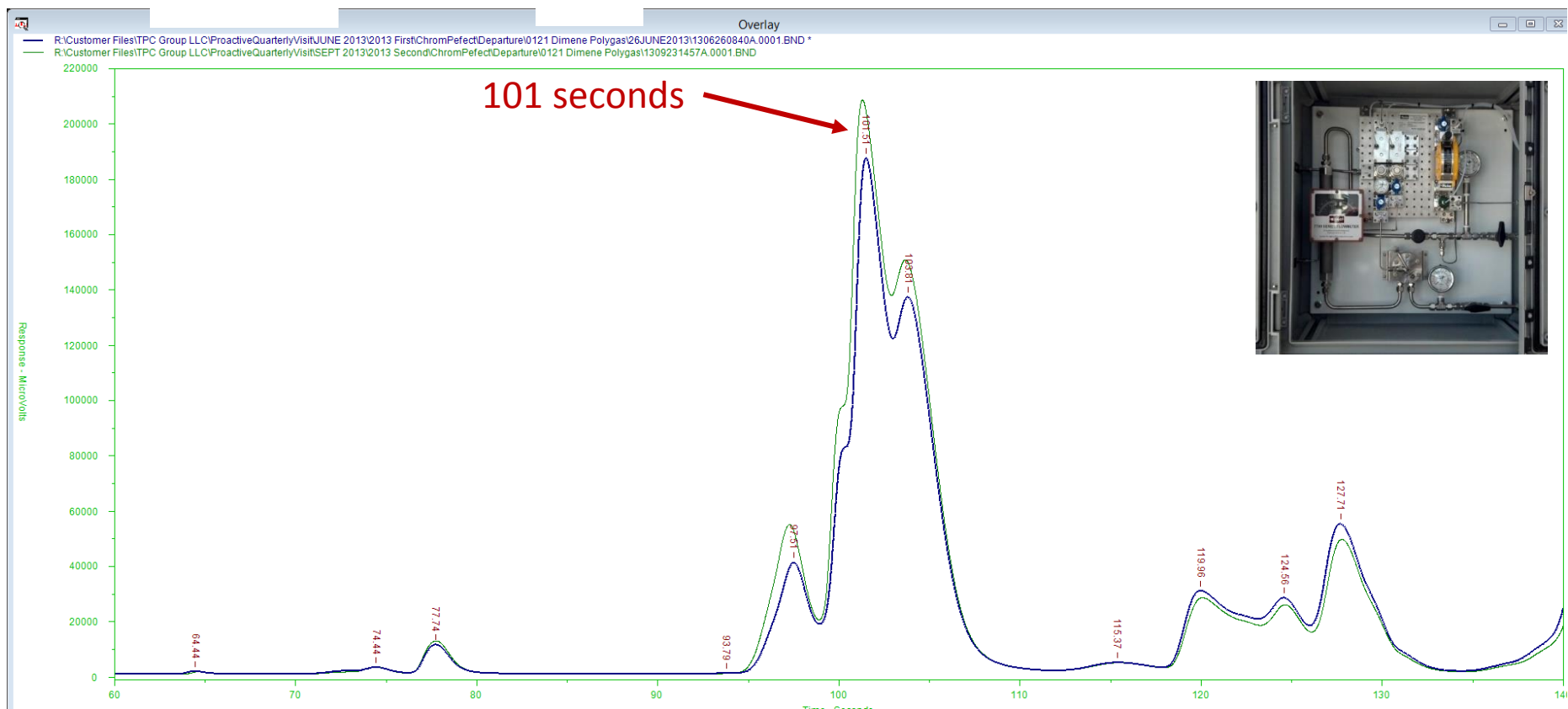
# What about Stability?

Q 1 Visit: part of last run showing 60 to 140 seconds – Retention time alignment by Infometrix LineUp implemented – dimer, trimer & tetramers of olefin



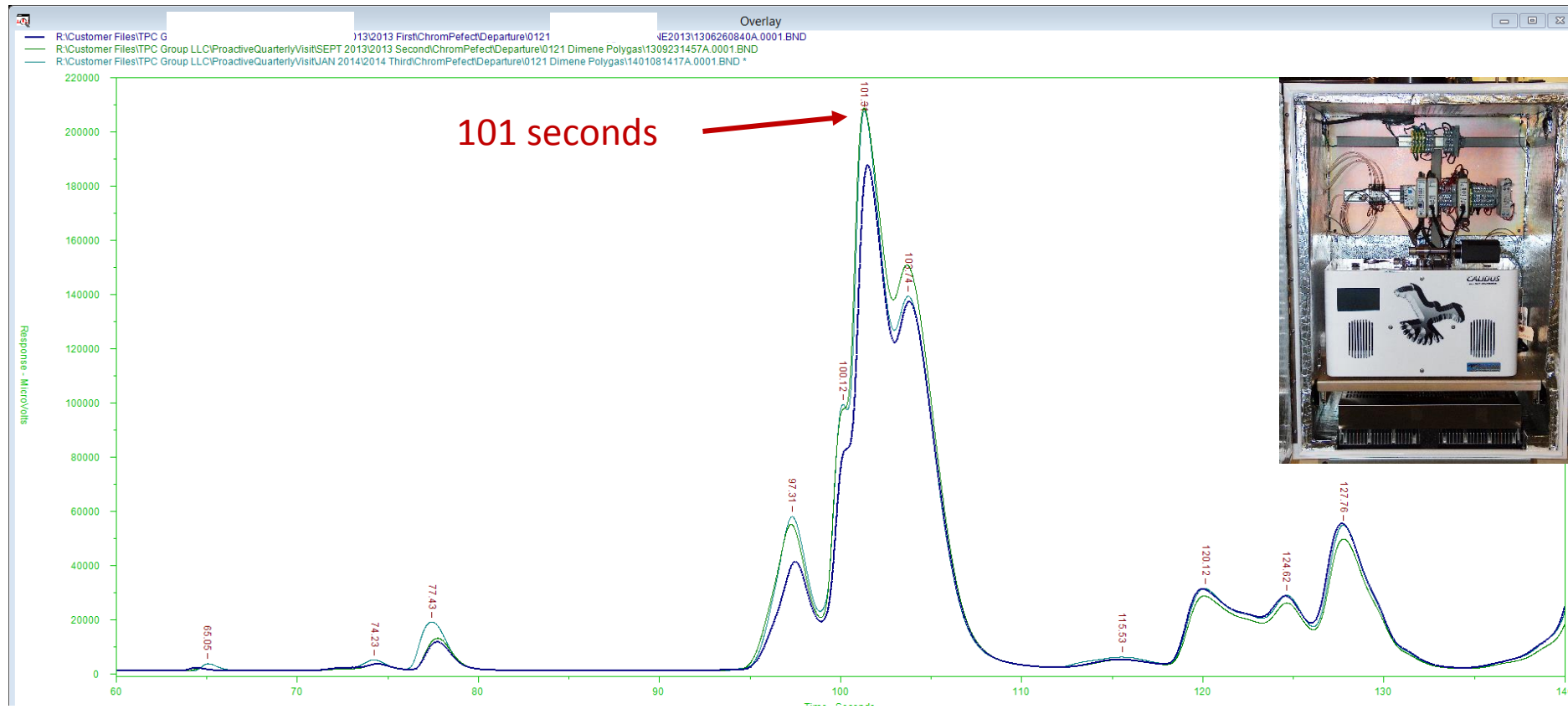
# What about Stability?

Q 1 & 2 Visits Overlaid: part of last run showing 60 to 140 seconds



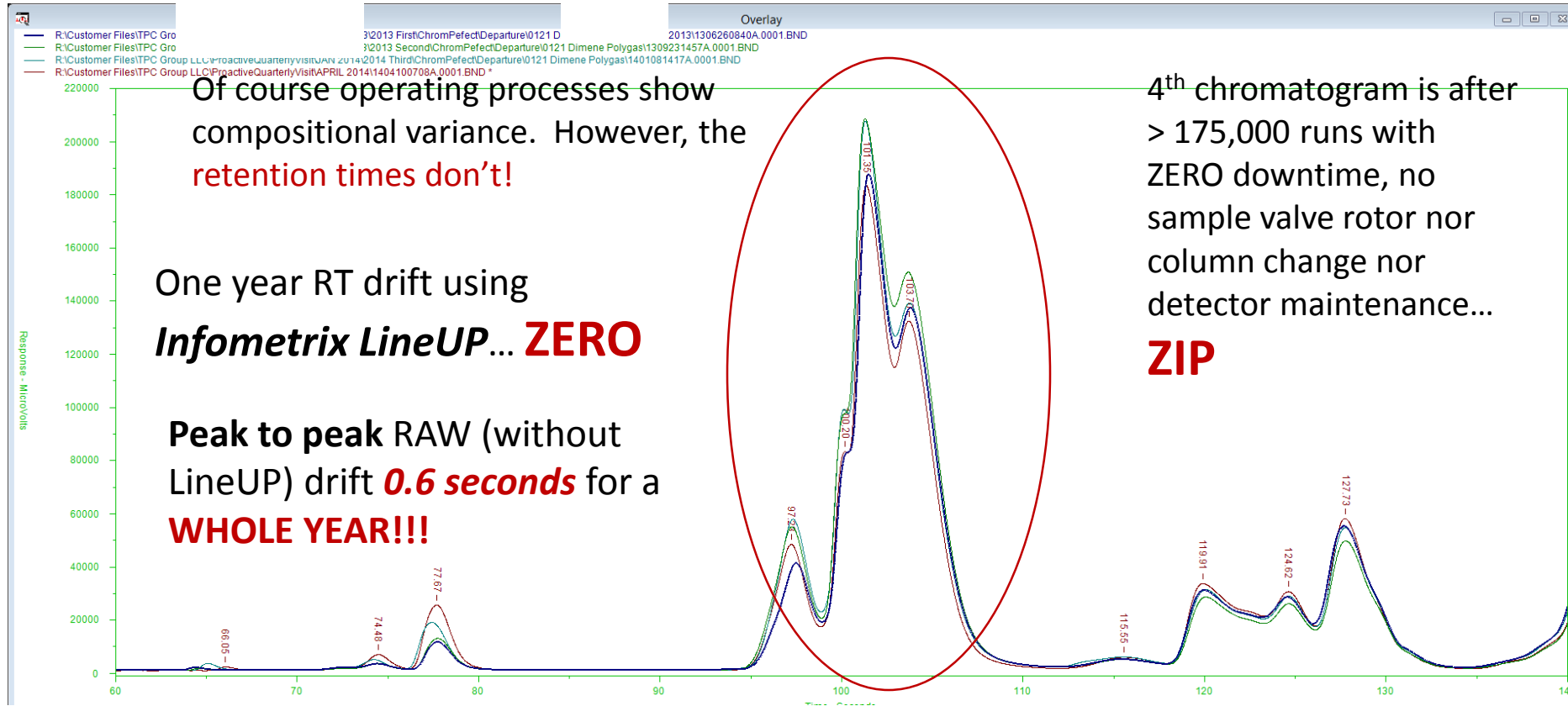
# What about Stability?

Q 1, 2 & 3 Visits Overlaid: part of last run showing 60 to 140 seconds

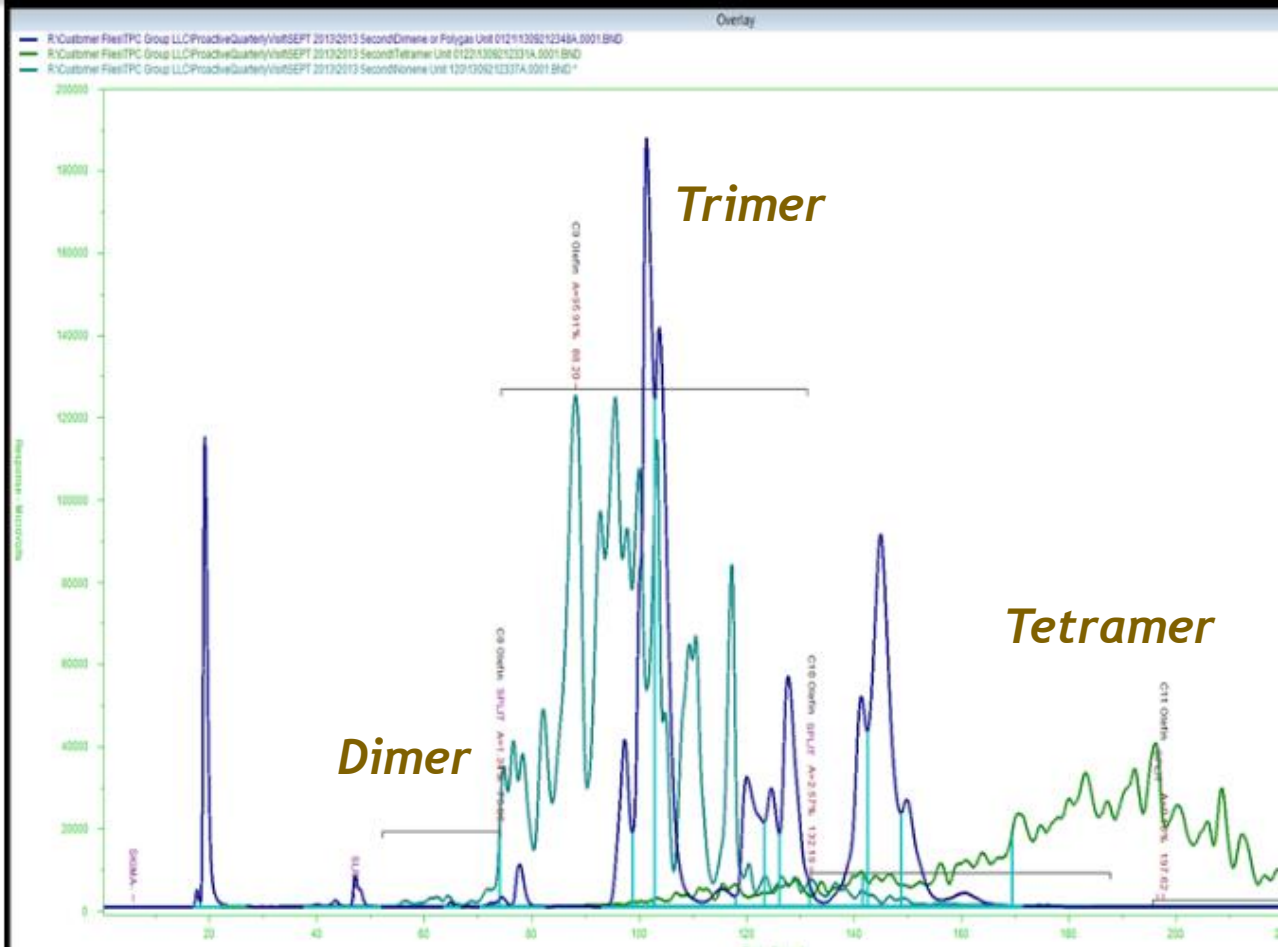


# What about Stability?

Q 1, 2, 3 & 4 Visits Overlaid: part of last run showing 60 to 140 seconds



# Polymerization Distribution Readily Differentiated

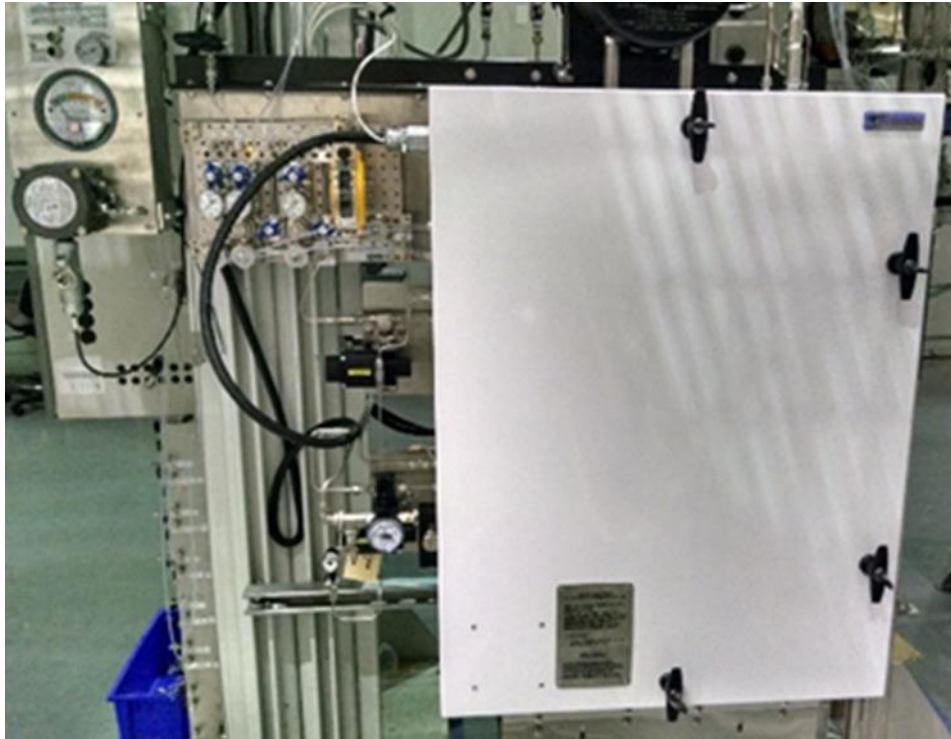


## 4. Monomer Product Purity (polymer grade petrochemical)

- **High concentration product needs separation from critical impurities**
- **Speed of analysis is critical to make the measurement relevant for process control**
- **Removal of polymerization terminators (impurities) is critical**
- **Costs of over processing (giving higher than needed purity) can reduce or eliminate profit margins through**
  - **Cost of Steam**
  - **Excess Raw Materials Consumption**
  - **Reduced Production Throughput**

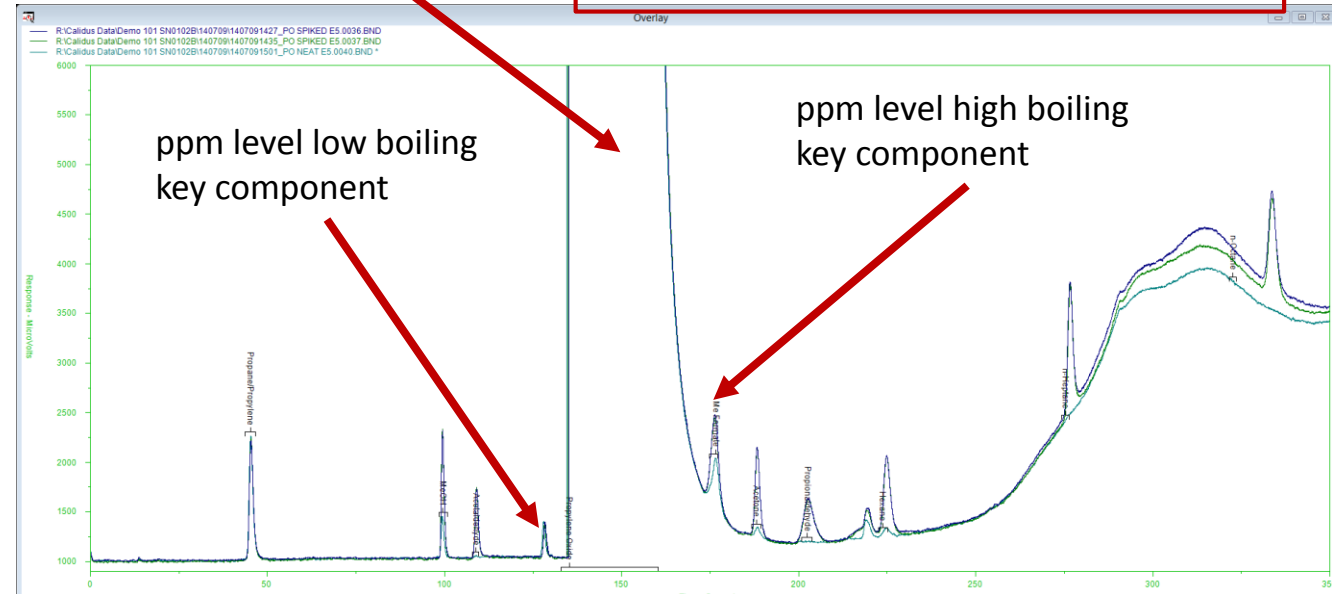


# Measurement Need: Removal of Byproduct Impurities



99.9+% Product

Minimizing key components in distillations infers that all components are below the requirement.



Duplicate calibration samples overlaid production sample.

# Acknowledgements

**The presenter would like to thank all those who helped make this presentation possible:**

**Staff at Falcon Analytical, especially John Crandall and Ned Roques.**

**The happy customers using the Calidus GC for sharing their data while making a difference at their companies.**

**Chevron Energy Technology Co. for allowing use of previously shown figures.**

