



Not Just for Simulated Distillation: Broadly Applicable Fast GC

Ned Roques, Falcon Analytical

John Crandall, Falcon Analytical

Steve Bostic, Falcon Analytical





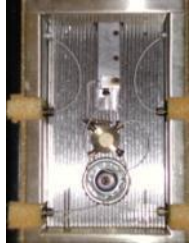
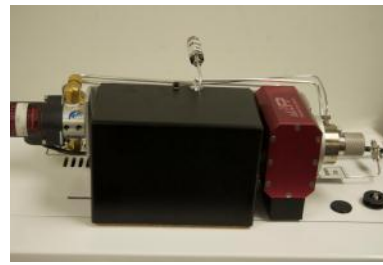
***What would the requirements be
for an Ultra-Compact, Fast GC with
Broad Commercial Utility and
Acceptance?***

Answer:

***Give it the best characteristics
of a conventional GC, only
FASTER.....and more.***



Specifics



- **Flexible Sample Introduction**

- *Accept gas or LIQUID phase samples*
- *Variable injection volumes through the use of a split/splittless type injector*
- *High injector temps for high MW components*
- *External accessory friendly (i.e. autosamplers, internal/external sample loop valves, purge & trap devices)*

- **Fast Temperature Programmable Columns**

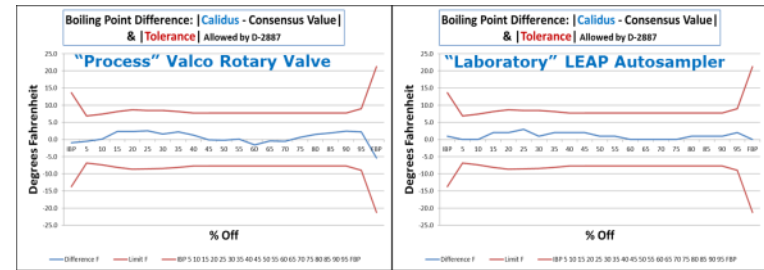
- *Employ low power, fast heating techniques for both rapid heating AND cooling*
- *High column temps for high MW components*
- *Only use column length necessary for the job*
- *Make a wide variety of familiar column types available*

- **Detector Variety**

- *Provide detector options to cover widest application range (FID, TCD, DBD, FPD,)*
- *High detector temps for high MW components*
- *Adequate data rates for capturing narrow peaks from fast TP columns*



Specifics



- **Expected Performance**

- **Repeatability and reproducibility MUST meet or exceed accepted conventional GC values**

- **Familiar Software**

- **User friendly**
- **Plays well with other programs (e.g. chromatographic alignment routines, simulated distillation software ,etc.)**
- **Feature rich enough to satisfy user requirements**

- **Minimize Maintenance Requirements**

- **Modularize columns for compactness and ease of replacement**
- **Modularize detectors for compactness and configurability**
- **Reduce number of switching valves to minimize leak potential and mechanical failure**
- **Employ system integrity checking routines to help identify upcoming maintenance events**

Our Approach

*easier, smaller,
faster, smarter, and
greener*



- ***Throw out conventional design paradigms.***
- ***Maximize use of microprocessors throughout the instrument for control and interpretation.***
- ***Address instrument size, ease of use, power consumption, and maintainability.***
- ***The approach spans innovations both in hardware and in software.***
- ***Create something commercially viable for all environments - Lab, at-line, transportable, on-line.***

Speed + Modularity + Form Factor

Conventional Designs

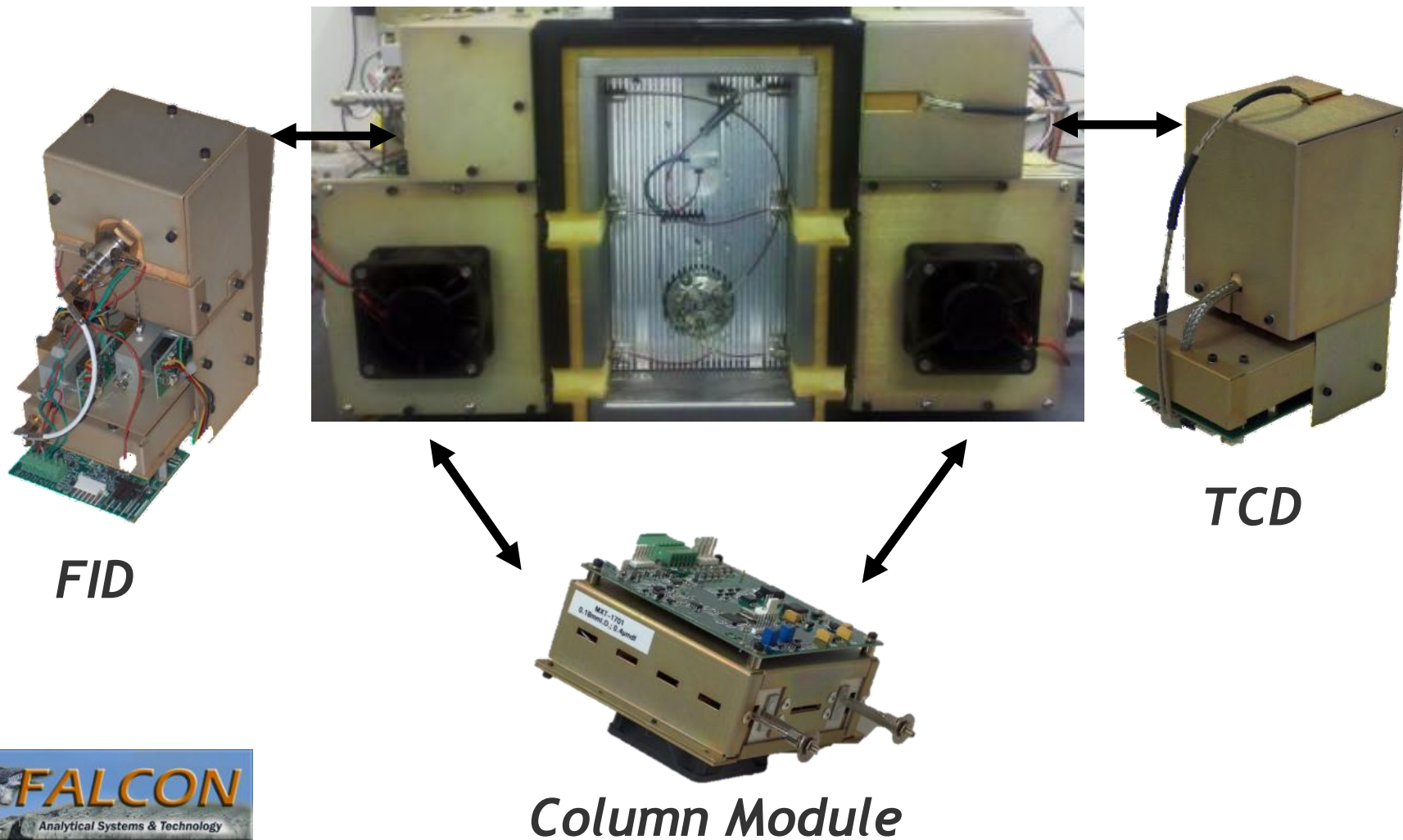
- **Thermal mass is your friend**
 - *Temperature stability*
 - *Slow to respond to change*
 - *Isothermal methods*
 - *Multiple column switching schemes*
 - *Heavy & large footprints*
 - *Kilowatt power requirement*
- **Large internal volumes**
 - *Lower resolution*
 - *Longer columns (long analysis times)*
 - *Or more columns needed for same separation*
 - *High consumable rates*

New Thinking

- **Minimize thermal mass**
 - *Rapid temperature program methods*
 - *Fast response time*
 - *Increased temperature repeatability and reproducibility*
 - *Minimal switching schemes*
 - *Low power requirement*
- **Minimal volume**
 - *Higher resolution*
 - *Shorter columns needed*
 - *Fast cycle times*
 - *Minimum consumables*



Calidus: *the Modular, Ultra-Compact GC*



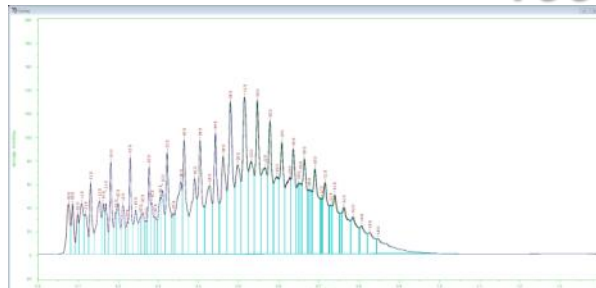
Separation & Detector HW Specs

101, 101-HT, 201, 301

- **Sample Inlet**
 - 100°C - 350°C
- **Column Modules**
 - 5°C above ambient to
 - Column material limit
 - Or 400°C
 - whichever is lower
- **Detector Modules**
 - 100°C - 350°C

CS

- **Sample Inlet**
 - 100°C - 250°C
- **Column Modules**
 - 5°C above ambient to
 - Column material limit
 - Or 400°C
 - whichever is lower
- **Detector Modules**
 - 100°C - 350°C



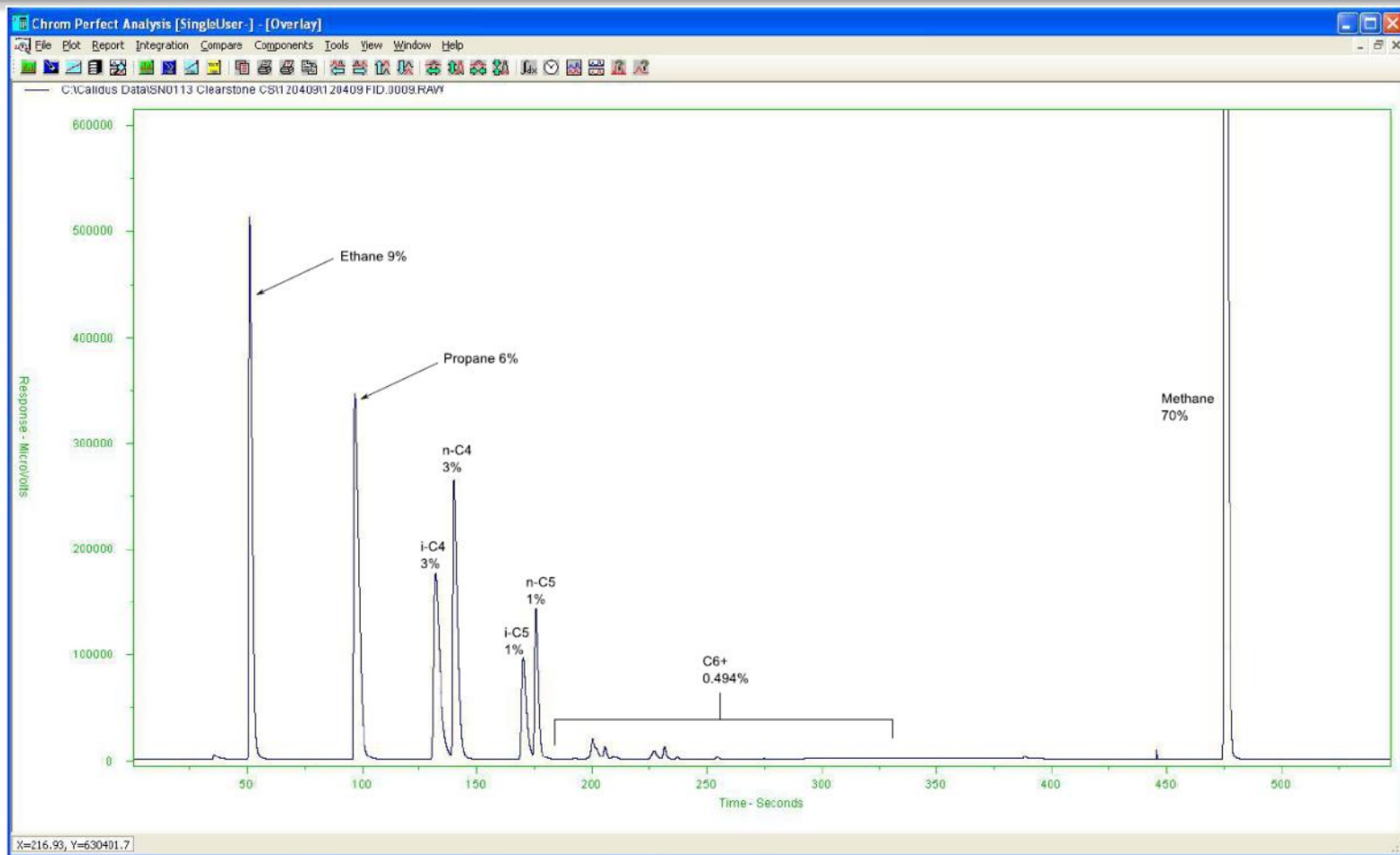
Result: fixed gases to n-C60



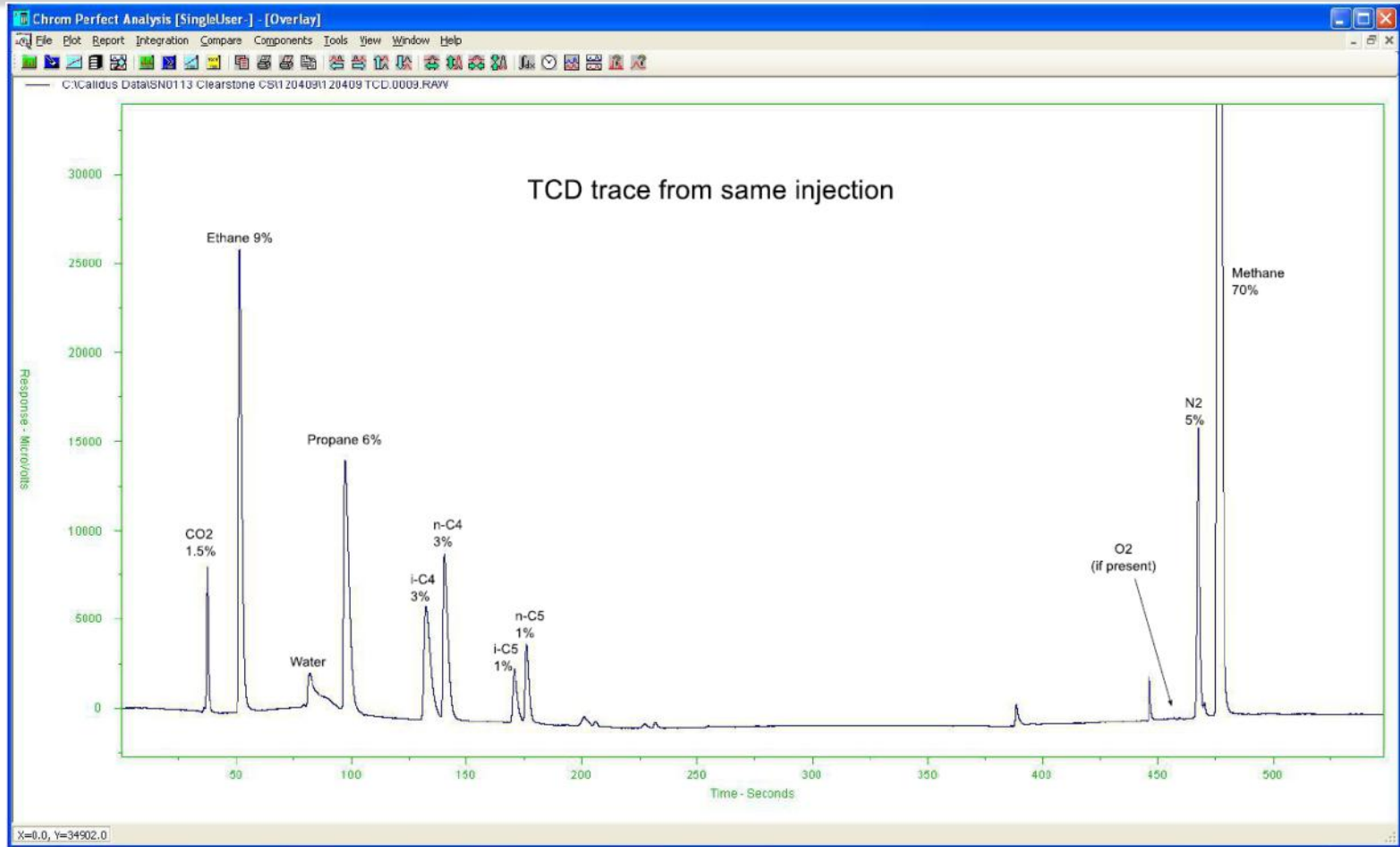
Extended Natural Gas with Heated Sample Valve



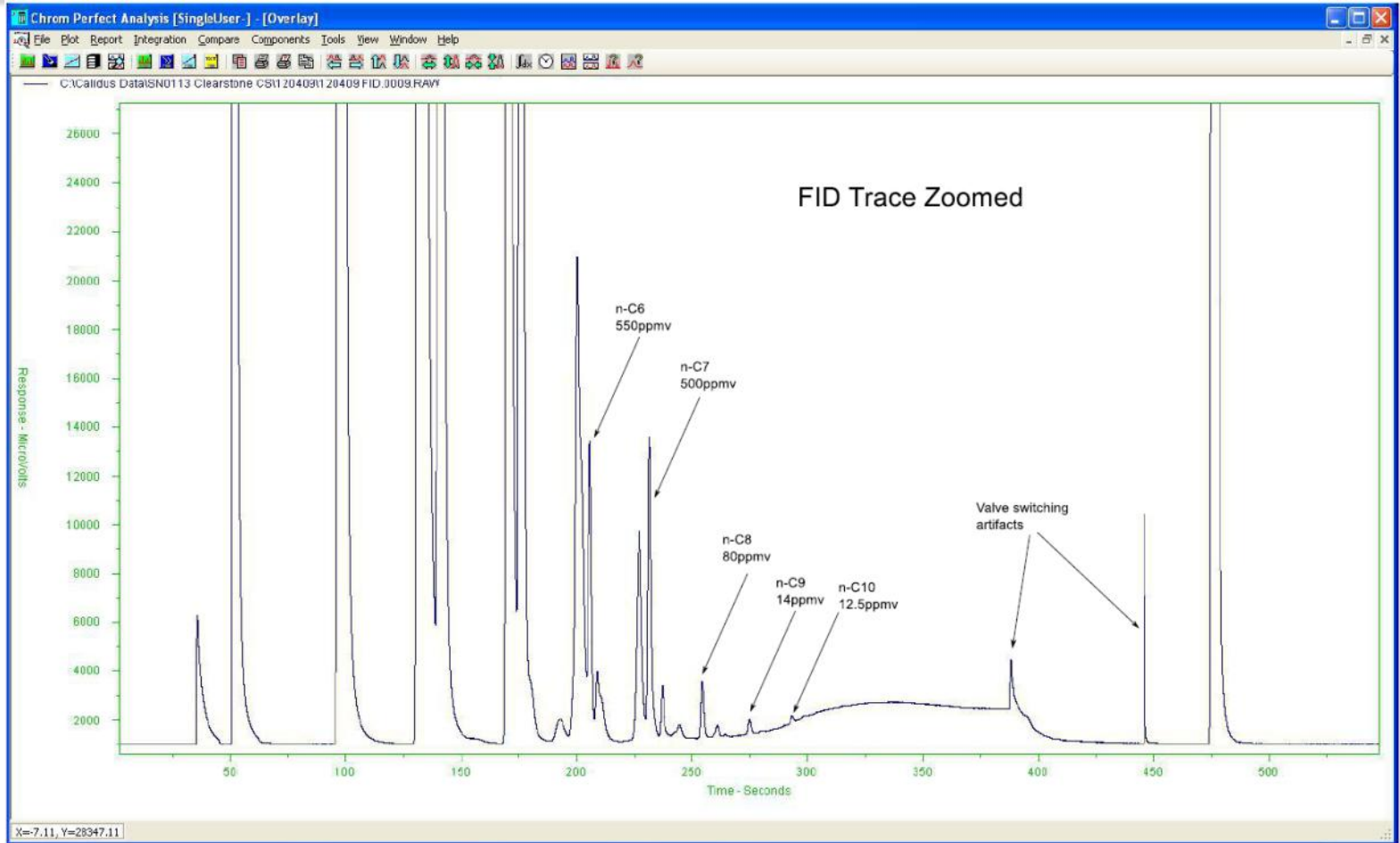
Trap on MXT MoleSieve while Bypass through MXT QBond to the FID



Trap on MXT MoleSieve while Bypass through MXT QBond to the TCD

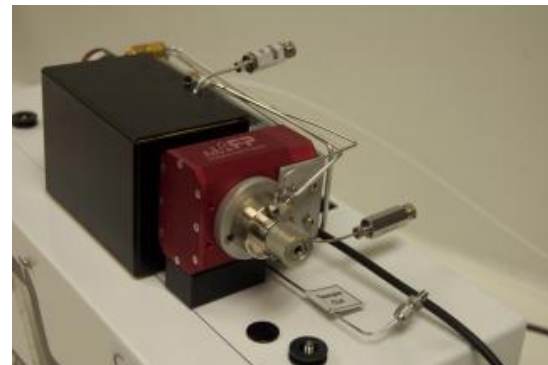


Trap on MXT MoleSieve while Bypass through MXT QBond to the FID - Zoomed



Expanded Application Capability to Include LPG

- **CALIDUS CS fitted with a combination inlet**
 - **Heated diaphragm/plunger gas sample valve**
 - **Unheated rotary liquid sample valve**
- **Connect pressurized samples appropriately**
 - **Vapor samples to the vapor inlet**
 - **Liquid samples to the liquid inlet**
- **Set the pneumatics switch to operate the appropriate valve**
- **It is that easy!**



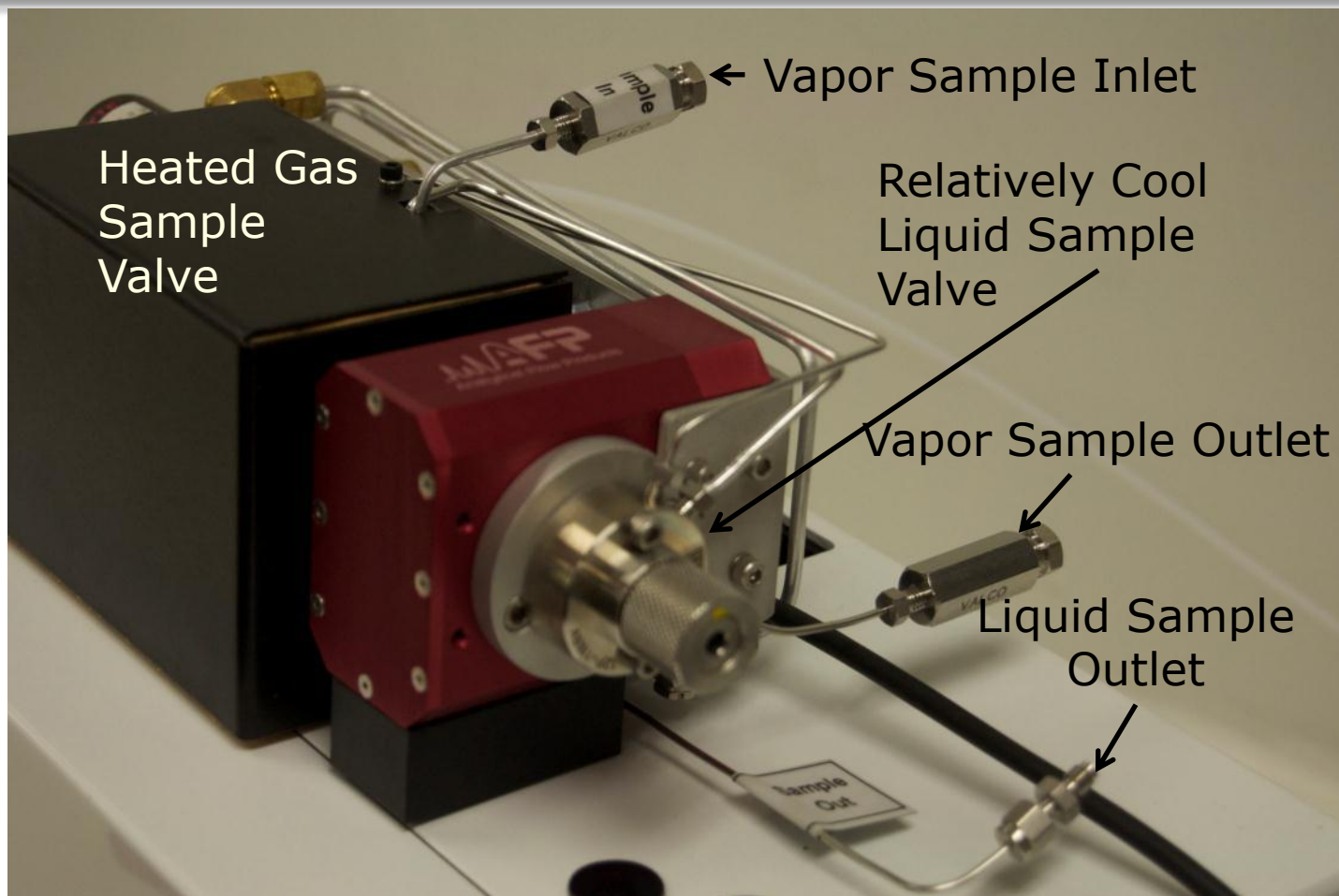
Extended Natural Gas System

(compressed natural gas and natural gas liquids, air components to C₁₂)

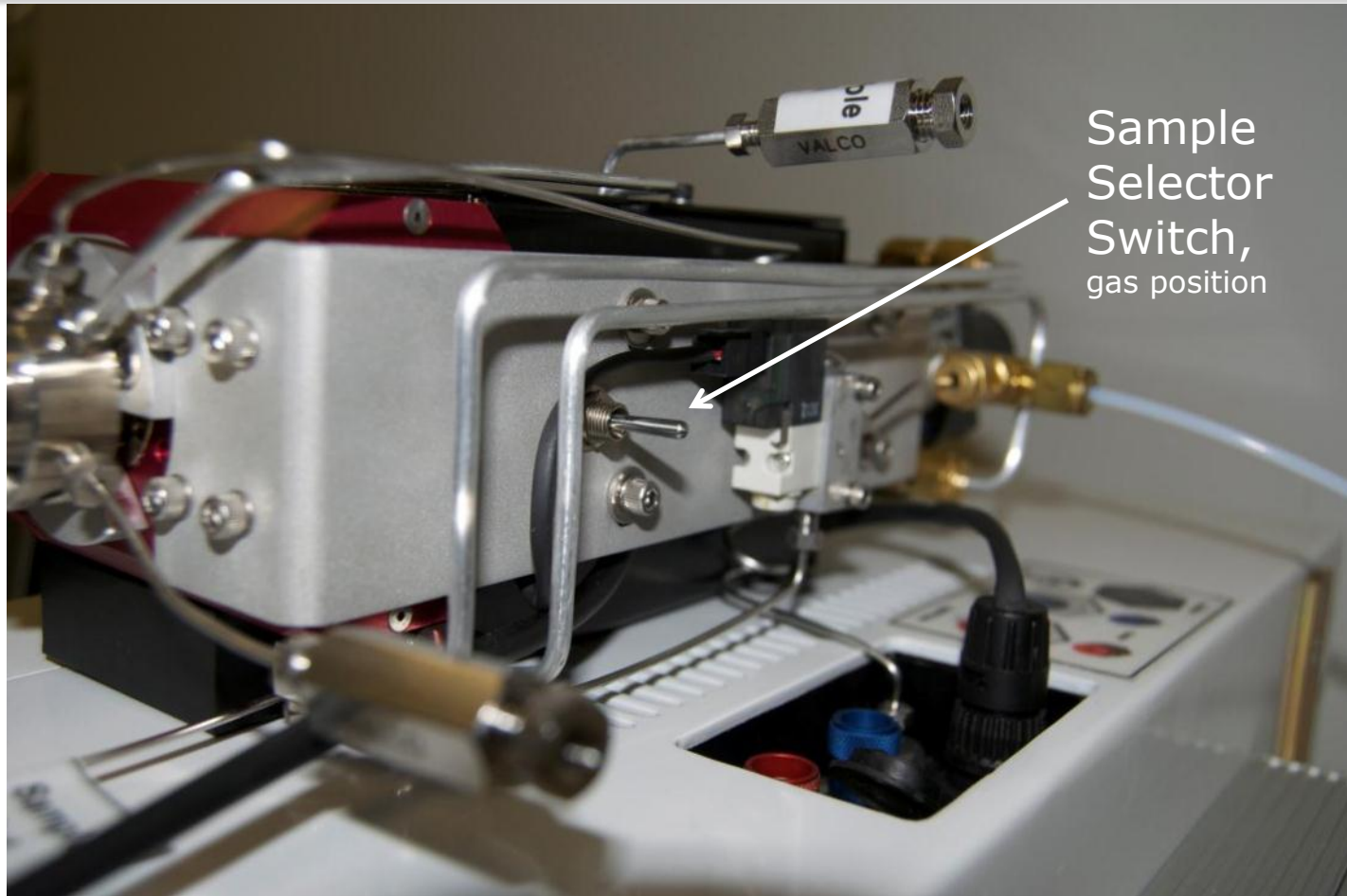


High Pressure Vapor and Compressed Liquid Sampling

(operation selected with a switch shown on next slide)

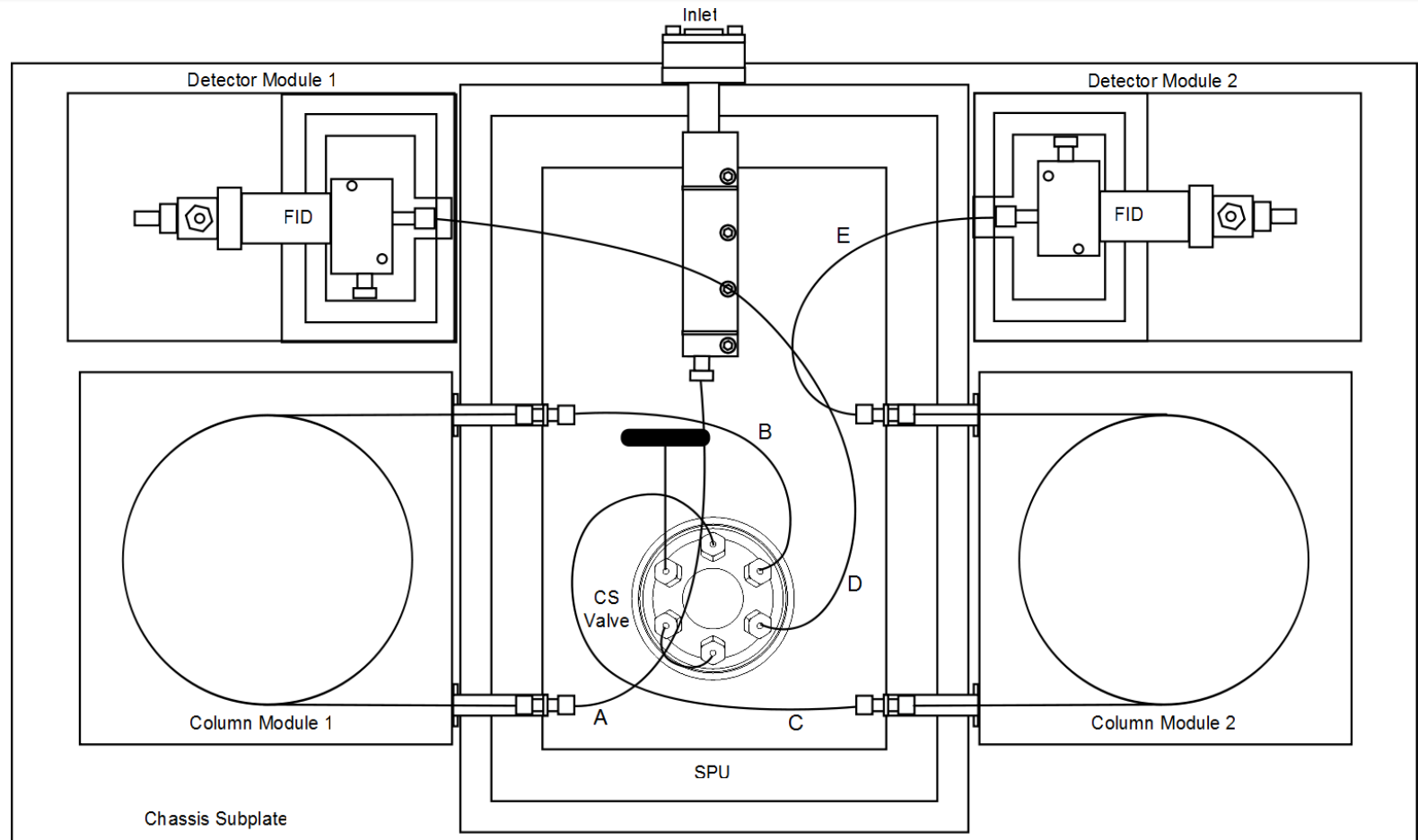


Gas or Liquid Selector Switch *(From the front of the GC the switch position points to the valve that will operate. Push left for gas, right for liquid. It is shown for gas sample valve operation here.)*

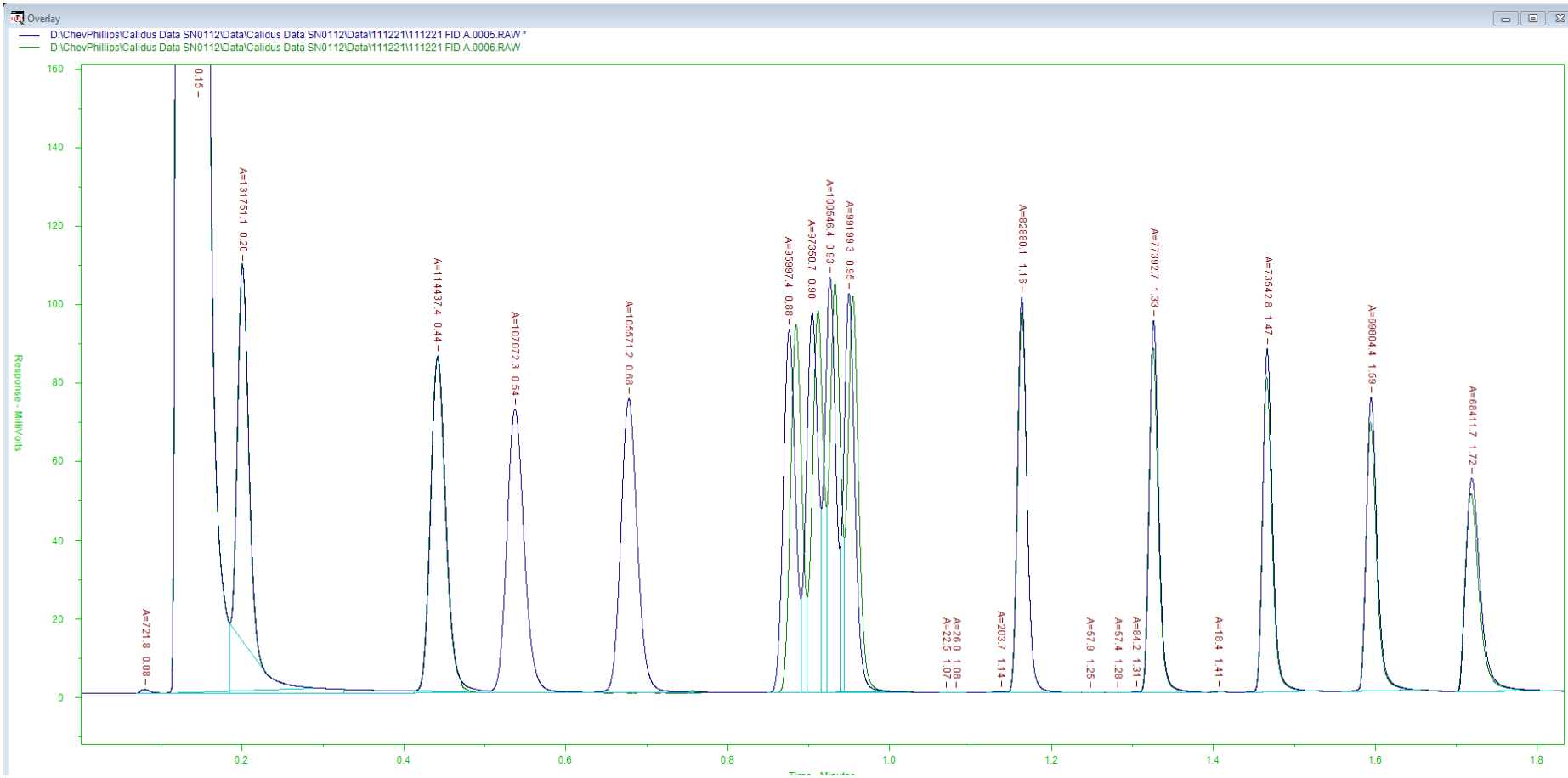


Sample Selector Switch, gas position

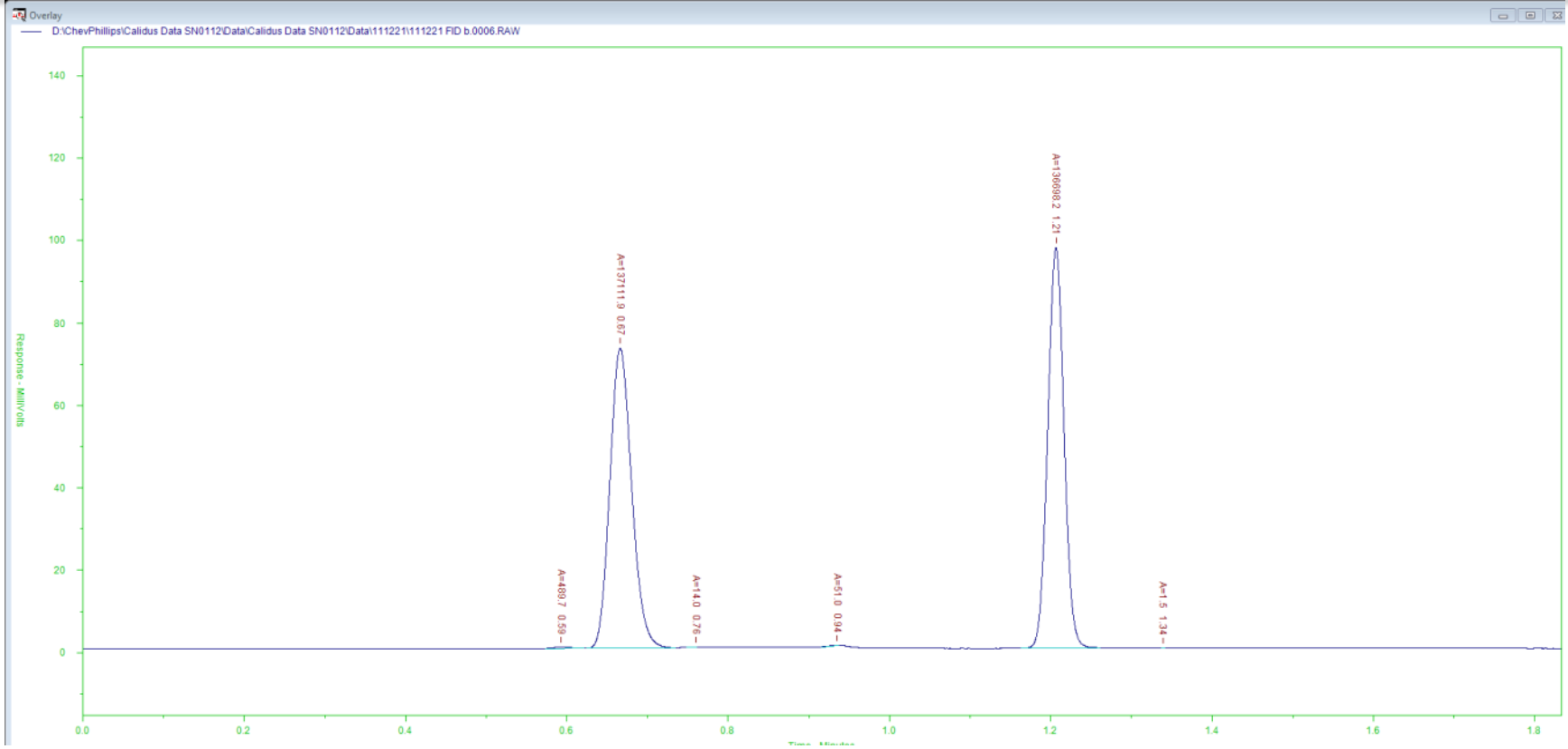
Middle Distillate & Petrochemicals Speciation: Calidus CS Configuration



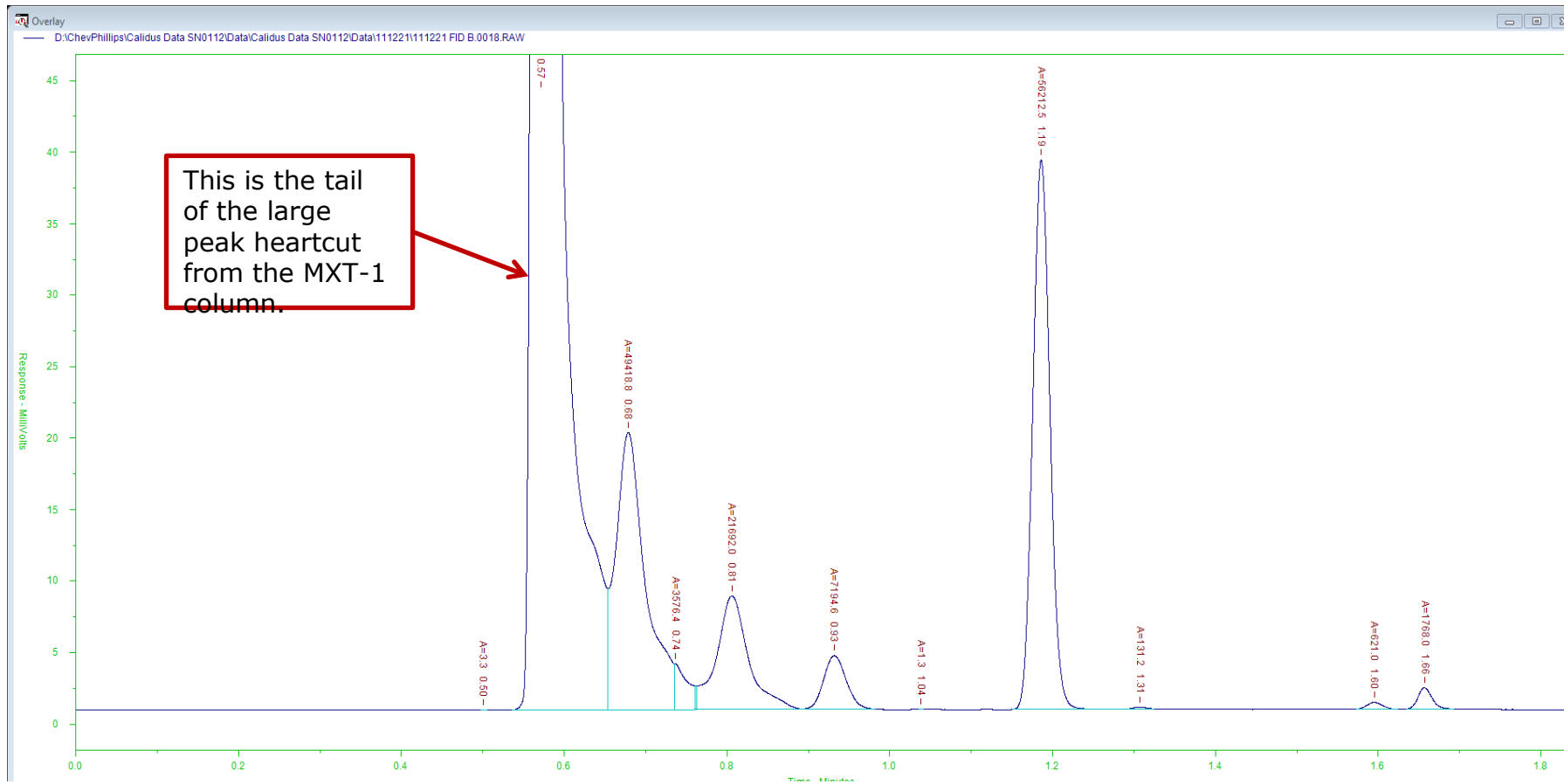
Example Chromatography



Example Chromatography



Real World Use



But What about Simulated Distillation?

- ***“Boiling Range Distribution of Petroleum Distillates With Final Boiling Points up to 535° C by Ultra Fast Gas Chromatography (UF GC)”*** draft authors Bostic, DiSanzo, Lubkowitz
- ***New method report will follow... however...***
- ***Here are current results demonstrating conformance with the existing D-2887 requirements.***

(Repeatability & Reproducibility requirements will be the same for the new method but require < 5 minute analysis time)



Purchased RT Calibration Standard

- **Standard GC**
- **Capillary column**
- **40 minute run time**



110 Benner Circle
 Bellefonte, PA 16823-8812
 Tel: (800)356-1688
 Fax: (814)353-1309

Certificate of Composition

FOR LABORATORY USE ONLY-READ MSDS PRIOR TO USE.

Catalog No. : 31674 Lot No.: A069249
 Description : ASTM D2887-01 Calibration Mix, 1% wt/wt
 Expiration Date¹: September 2016 Storage: Room Temperature

Elution Order	Compound	CAS #	Percent Purity ²	Concentration ³ (weight/weight%)	% Uncertainty ⁴ (95% C.L.; K=2)
1	n-Pentane (C5)	109-66-0	99%	1.000 wt./wt.%	+/-0.58 %
2	n-Hexane (C6)	110-54-3	99%	1.000 wt./wt.%	+/-0.58 %
3	n-Heptane (C7)	142-82-5	99%	1.000 wt./wt.%	+/-0.58 %
4	n-Octane (C8)	111-65-9	99%	1.000 wt./wt.%	+/-0.58 %
5	n-Nonane (C9)	111-84-2	99%	1.000 wt./wt.%	+/-0.58 %
6	n-Decane (C10)	124-18-5	99%	1.000 wt./wt.%	+/-0.58 %
7	n-Undecane (C11)	1120-21-4	99%	1.000 wt./wt.%	+/-0.58 %
8	n-Dodecane (C12)	112-40-3	99%	1.000 wt./wt.%	+/-0.58 %
9	n-Tetradecane (C14)	629-59-4	99%	1.000 wt./wt.%	+/-0.58 %
10	n-Pentadecane (C15)	629-62-9	99%	1.000 wt./wt.%	+/-0.58 %
11	n-Hexadecane (C16)	544-76-3	99%	1.000 wt./wt.%	+/-0.58 %
12	n-Heptadecane (C17)	629-78-7	99%	1.000 wt./wt.%	+/-0.58 %
13	n-Octadecane (C18)	593-45-3	99%	1.000 wt./wt.%	+/-0.58 %
14	n-Eicosane (C20)	112-95-8	99%	1.000 wt./wt.%	+/-0.58 %
15	n-Tetracosane (C24)	646-31-1	99%	1.000 wt./wt.%	+/-0.58 %
16	n-Octacosane (C28)	630-02-4	99%	1.000 wt./wt.%	+/-0.58 %
17	n-Dotriacontane (C32)	544-85-4	99%	1.000 wt./wt.%	+/-0.58 %
18	n-Hexatriacontane (C36)	630-06-8	99%	1.000 wt./wt.%	+/-0.58 %
19	n-Tetracontane (C40)	4181-95-7	99%	1.000 wt./wt.%	+/-0.58 %
20	n-Tetratetracontane (C44)	7098-22-8	99%	1.000 wt./wt.%	+/-0.58 %
	Solvent: Carbon Disulfide	75-15-0	99%		

Column:
 30m x .25mm x .25um
 Rtx-5 (cat.#10223)

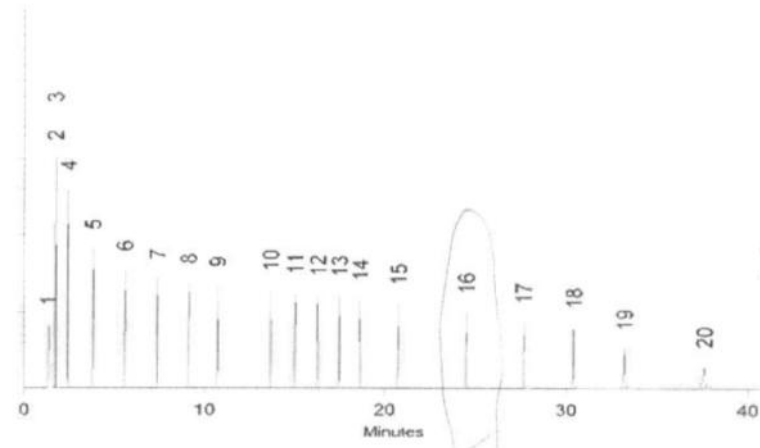
Carrier Gas:
 hydrogen-constant pressure 10 psi.

Temp. Program:
 40°C (hold 2 min.) to 330°C
 @ 10°C/min. (hold 10 min.)

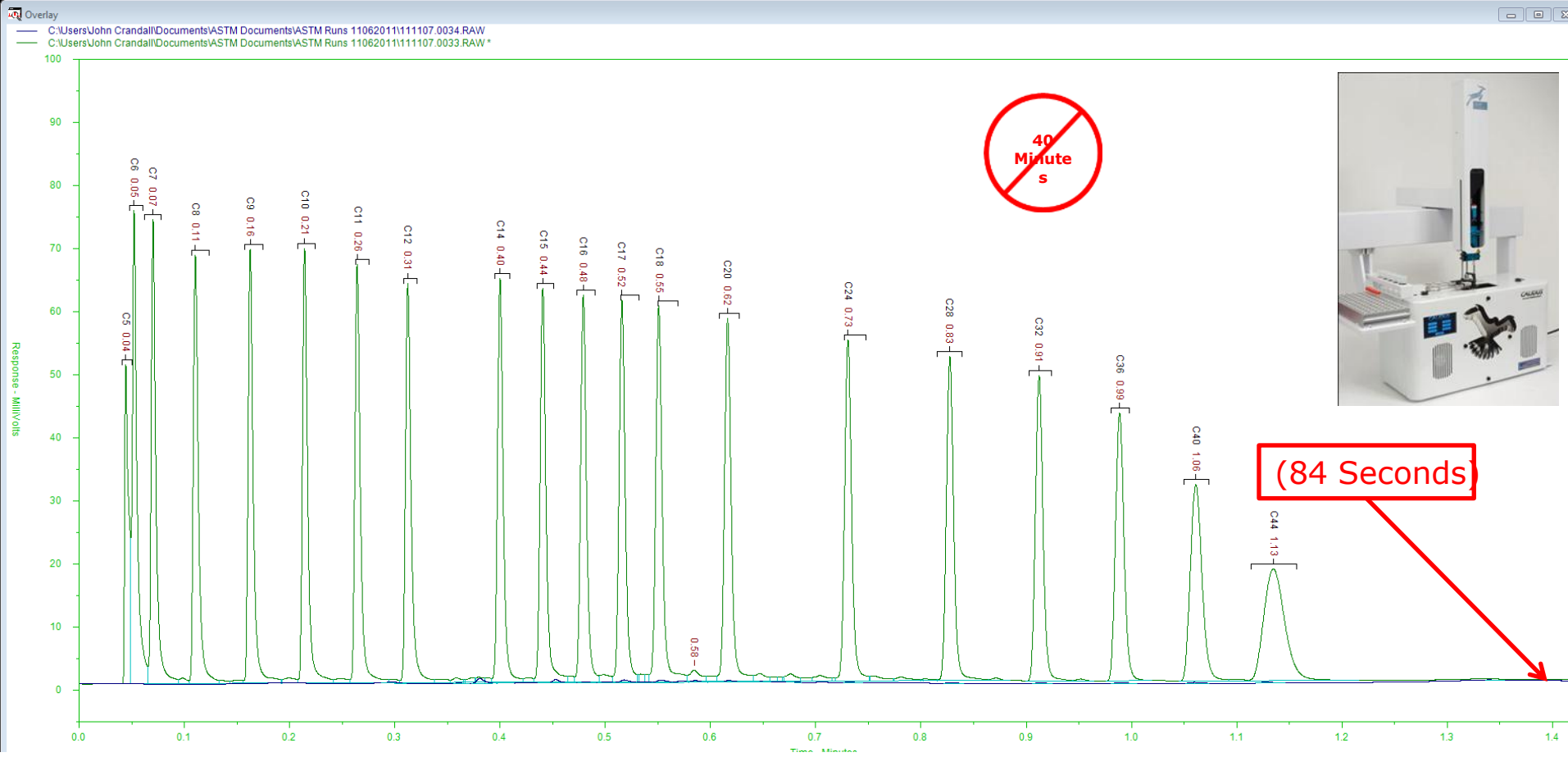
Inj. Temp:
 250°C

Det. Temp:
 330°C

Det. Type:
 FID



Calidus 101-HT Purchased Restek D-2887 Standard Overlaid Blank



Purchased Standard Gas Oil

- **Certificate of analysis**
 - **Consensus values**
 - **30 participating laboratories**

ASTM D-2887 REFERENCE GAS OIL NO. 1

LOT NO. 2 Consensus Analysis*

	Batch 2	95% conf.	Batch 2	95% conf.
	°F	°F	°C	°C
IBP	239	+/- 1	115	+/- 0.6
5%	304	+/- 0.7	151	+/- 0.4
10	349	+/- 1.2	176	+/- 0.7
15	393	+/- 1.5	201	+/- 0.8
20	435	+/- 1.7	224	+/- 0.9
25	469	+/- 1.7	243	+/- 0.9
30	499	+/- 1.6	259	+/- 0.9
35	526	+/- 1.6	275	+/- 0.9
40	552	+/- 1.2	289	+/- 0.7
45	576	+/- 0.9	302	+/- 0.6
50	594	+/- 1.1	312	+/- 0.5
55	610	+/- 0.9	321	+/- 0.4
60	629	+/- 0.8	332	+/- 0.4
65	649	+/- 0.8	343	+/- 0.4
70	669	+/- 0.7	354	+/- 0.4
75	690	+/- 0.8	365	+/- 0.4
80	712	+/- 0.7	378	+/- 0.4
85	736	+/- 0.7	391	+/- 0.4
90	764	+/- 0.8	407	+/- 0.4
95	803	+/- 1.1	428	+/- 0.6
FBP	887	+/- 2.6	475	+/- 1.4

* Analysis by members of ASTM D-2 R&D D-IV L Study Group on Boiling Range Distribution by Gas Chromatography. The number of participating labs for batch 2 was 30. Based on preliminary data, pending final approval of Section D.02 04, Section H.

NOTE: This sample is nitrogen blanketed. If transferred to other containers for storage, nitrogen blanketing is recommended. Store in a cool, dark place. Be sure the sample is at room temperature and well mixed before use. The wax point on this product is 55 °F.

M. E. Lopez

M. E. Lopez
Process Control Lab Team Leader

Purchased Standard Gas Oil

- **Standard GC**
 - **Packed column**
 - **20 minute run time**
 - **Certificate of analysis follows**

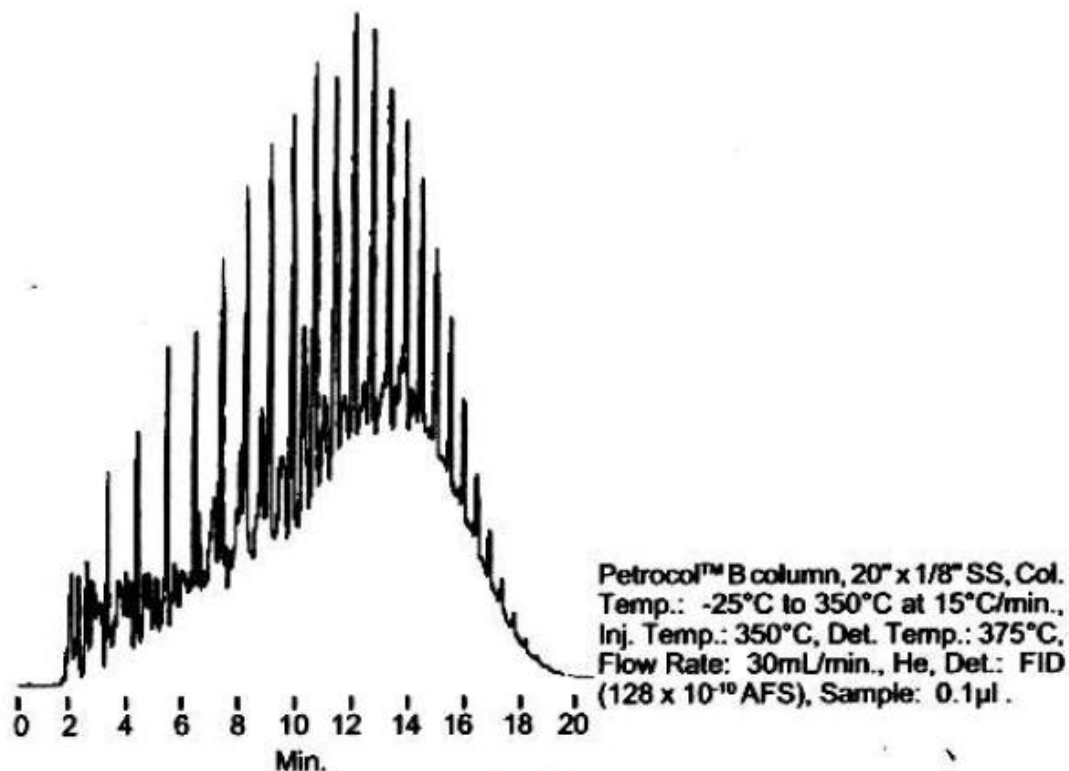
SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

ASTM D2887 Reference Gas Oil

Catalog No. 506419 1 x 1mL

Catalog No. 48873 6 x 1mL

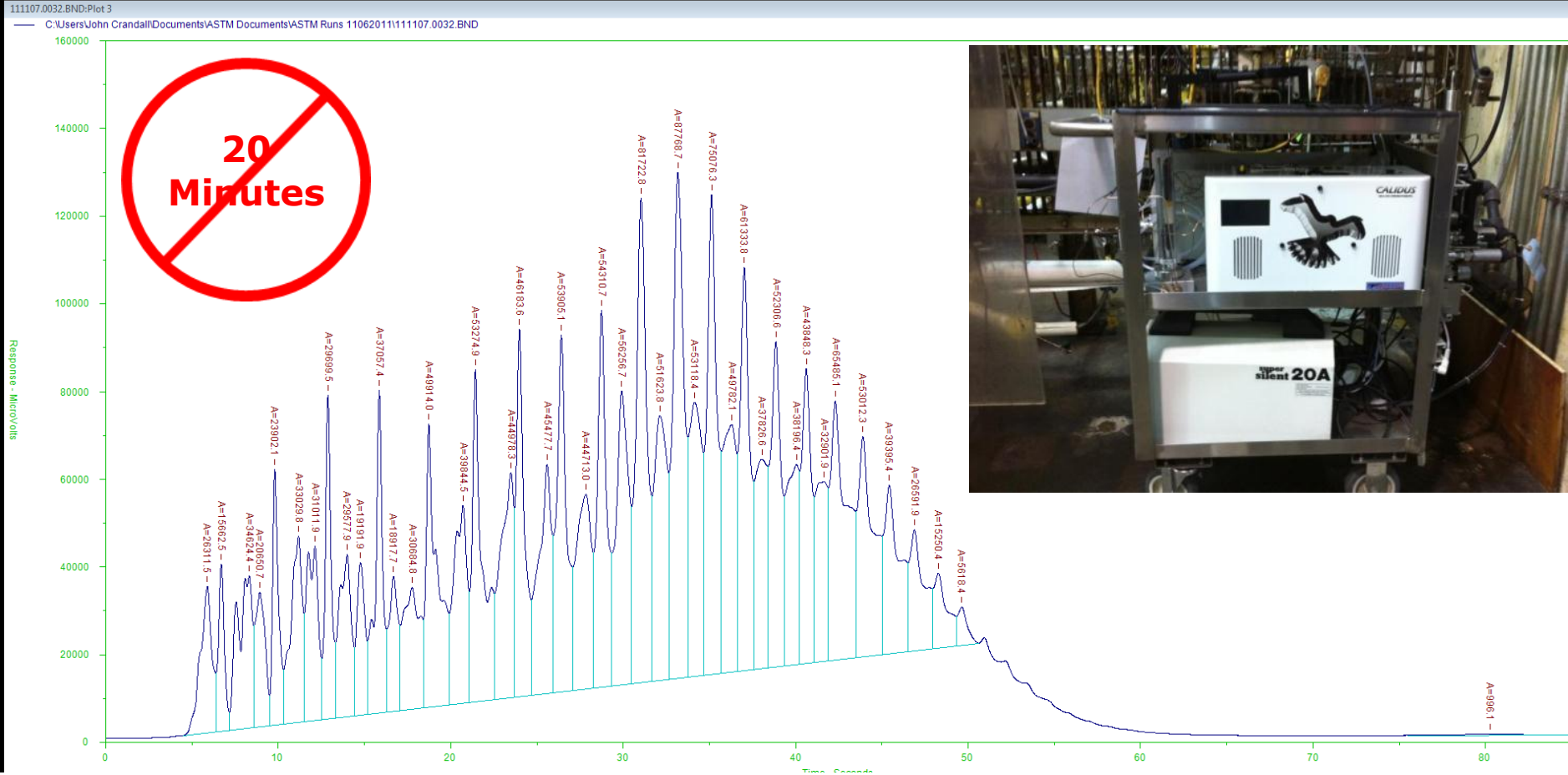
This sample is a petroleum fraction with an approximate boiling point range of 250°F-850°F. ASTM consensus values are listed on the certificate of analysis.



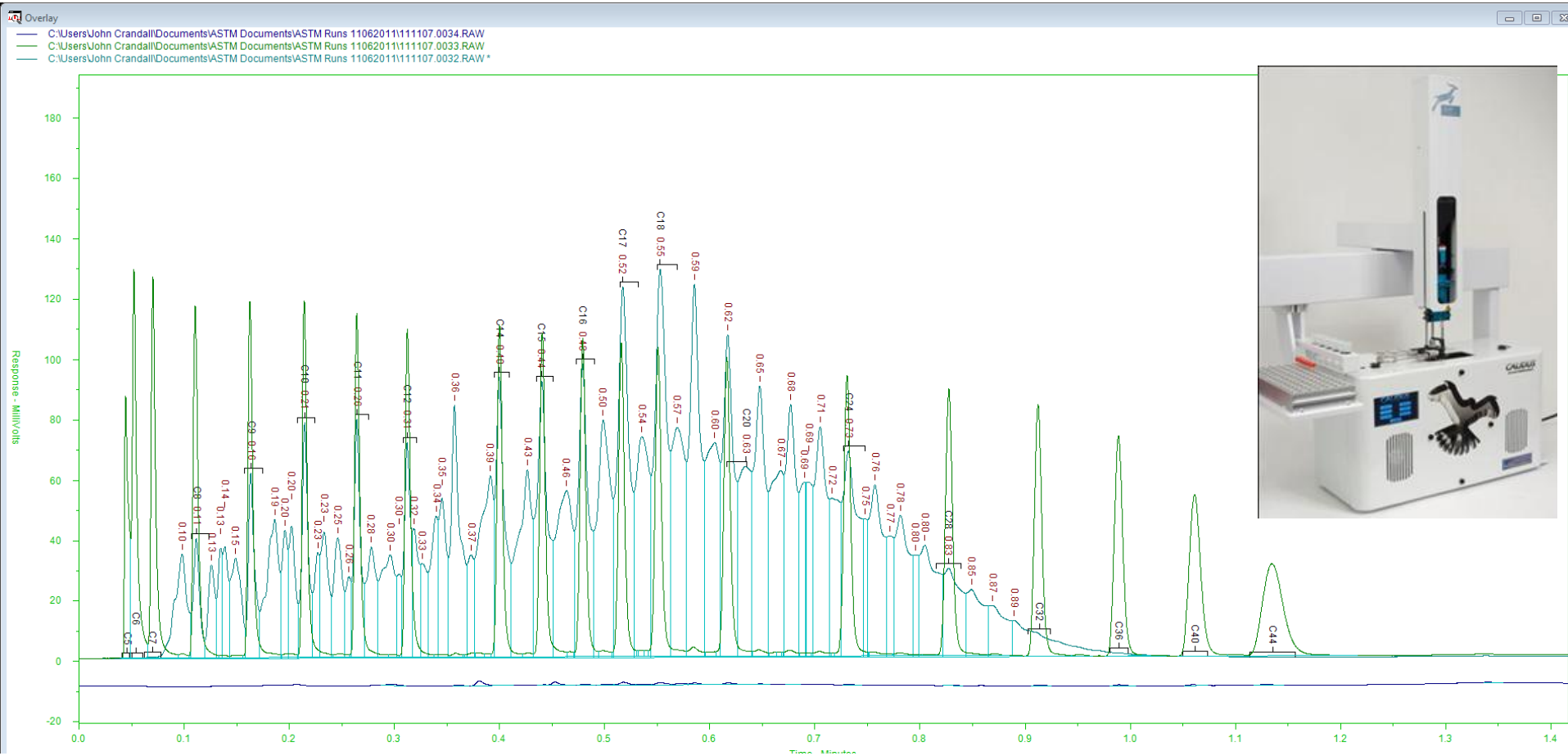
712-0413



Calidus 101-HT Purchased Supelco D-2887 Standard Gas Oil, Run Time 84 Seconds



Blank, RT Standard & Gas Oil Overlaid, Run Time 84 Seconds



D-2887 Report

- **Points of Interest**
 - **Chromatogram shown with BP curve and blank chromatogram overlaid**
 - **Selected BP data shown in the table.**
 - **Comparison follows**

D2887

Page: 1

Injected On: 20111107164005-0500 by

Procedure File: FalconD2887.prc

Data File: C:\Users\John Crandall\Documents\ASTM Documents\ASTM Runs 11062011111107.0032.CDF

Blank File: C:\Users\John Crandall\Documents\ASTM Documents\ASTM Runs 11062011111107.0034.CDF

Calib File: C:\Users\wayne\Documents\Falcon D2887 Demos\Marathon111107.0033.CDF

Solvent Exclusions: Mins

BaseLine Zero: 1001.00000

Quench Region: No Quenching Correction

Uncorr Total Sample Area: 2.3028E8

Corr Total Sample Area: 2.2925E8

Start Of Material (mins): 0.043

End Of Material (mins): 0.998

Sample Weight (g): 0.0000

SOM Thrsh: (0.00001000%)

EOM Thrsh: (0.00032000%)

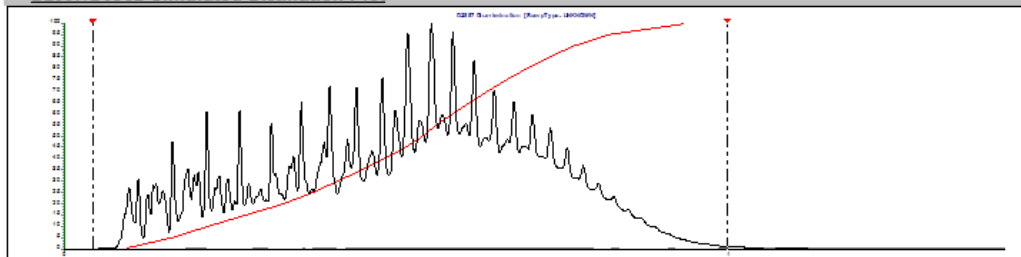
Solvent Weight (g): 0.0000

Material Search Restricted To: 1.100

Material End Forced To: NO FORCE

Warnings: EOM Accuracy may be affected by BLEED at END OF RUN

D2887/D6352 Simulated Distillation Plot



D2887/D6352/D7213 Boiling Point Mass Distribution

IBP ... 239.34	80.00% ... 710.94
5.00% ... 302.95	85.00% ... 735.05
10.00% ... 347.64	90.00% ... 763.54
15.00% ... 393.12	95.00% ... 803.32
20.00% ... 434.54	FBP ... 885.16
25.00% ... 468.80	
30.00% ... 497.77	
35.00% ... 525.00	
40.00% ... 551.77	
45.00% ... 575.14	
50.00% ... 592.50	
55.00% ... 608.68	
60.00% ... 627.63	
65.00% ... 647.32	
70.00% ... 667.09	
75.00% ... 688.68	

Calidus 101-HT Results Compared to Consensus Values *Reported by Certificate of Analysis*

Degrees	Measured	Accepted	Difference F	Limit F
IBP	240	239	1.0	13.7
5	304	304	0.0	6.8
10	349	349	0.0	7.4
15	395	393	2.0	8.1
20	437	435	2.0	8.6
25	472	469	3.0	8.5
30	500	499	1.0	8.5
35	528	526	2.0	8.1
40	554	552	2.0	7.7
45	578	576	2.0	7.7
50	595	594	1.0	7.7
55	611	610	1.0	7.7
60	629	629	0.0	7.7
65	649	649	0.0	7.7
70	669	669	0.0	7.7
75	690	690	0.0	7.7
80	713	712	1.0	7.7
85	737	736	1.0	7.7
90	765	764	1.0	7.7
95	805	803	2.0	9.0
FBP	887	887	0.0	21.2

- **Values Shown**

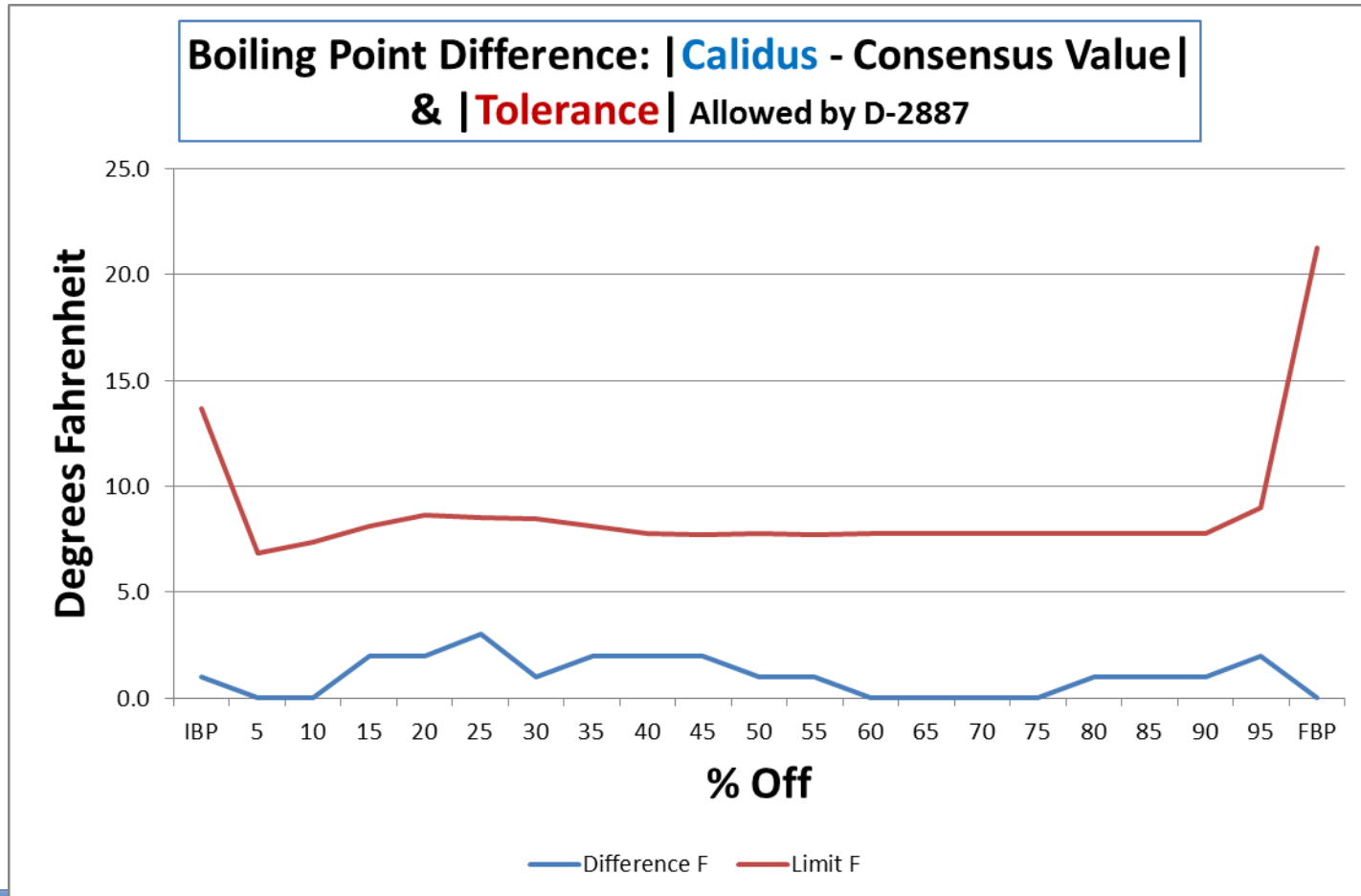
- *Correspond to the cut points reported in the certificate*
- *Indicate excellent comparison*
- *Calculated using raw chromatograms*
- *LineUp will improve all values*

- **LineUp use**

- *Absolutely necessary over time for data QC automation, no human can keep up with ~500 runs/day (~ 3 minute cycles)*
- *Extend maintenance interval time*
- *Elevate confidence in the results*

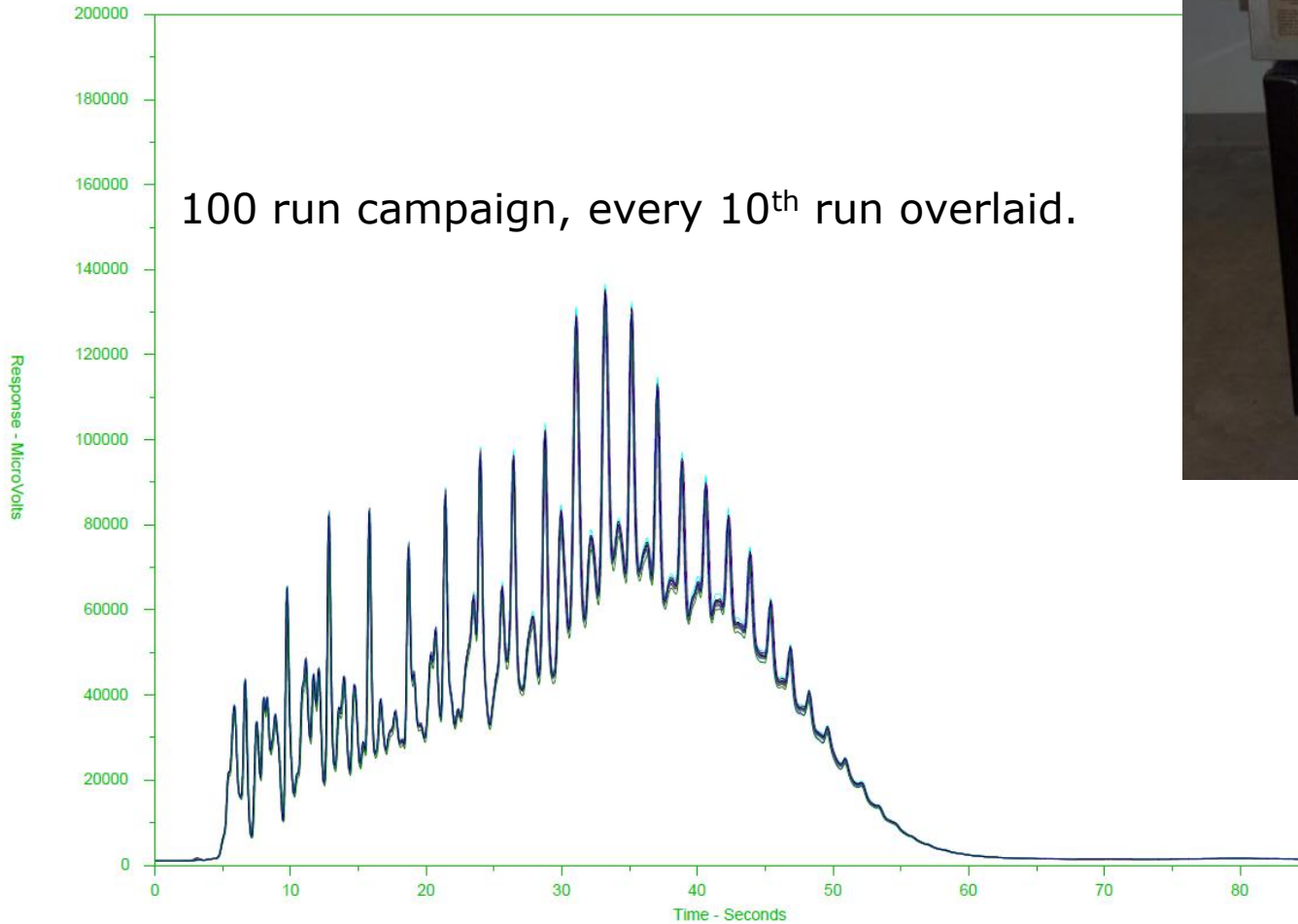


Absolute Values of Difference from the Consensus Values (red is the D-2887 tolerance)



What about Repeatability?

Chrom Perfect Chromatogram Report



Refinery Plant Lab Results: Reference Gas Oil, 15 Replicates

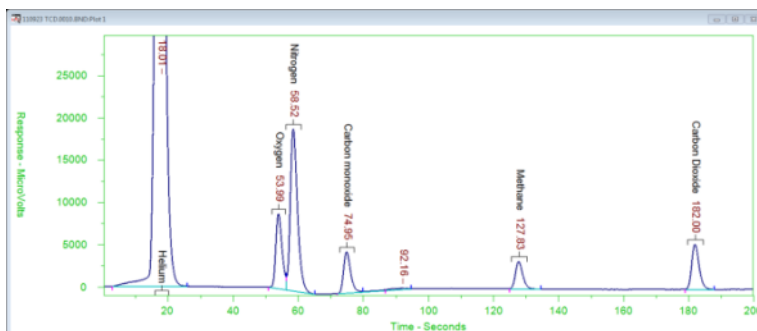


Rep #	0.50%	5.00%	10.00%	15.00%	20.00%	25.00%	30.00%	35.00%	40.00%	45.00%	50.00%	55.00%	60.00%	65.00%	70.00%	75.00%	80.00%	85.00%	90.00%	95.00%	99.50%
1	241.3	304.6	349.1	394.8	436.5	471.3	500.0	527.3	553.5	577.5	594.6	610.7	629.3	648.7	668.6	690.1	712.8	737.2	765.3	804.4	885.6
2	240.5	304.4	349.1	394.9	436.8	471.3	500.3	527.7	553.6	577.7	595.0	611.1	629.7	649.3	669.1	690.6	713.3	737.7	766.1	805.3	886.9
3	241.0	304.4	349.2	394.7	436.8	471.3	500.5	527.8	553.5	577.5	594.6	610.7	629.1	648.8	668.5	690.3	712.8	737.0	765.3	804.6	885.7
4	240.5	304.5	349.1	394.9	437.0	471.4	500.4	527.7	553.7	577.6	594.7	610.9	629.3	648.9	668.6	690.5	712.9	737.2	765.7	804.9	888.8
5	240.9	304.4	349.3	395.0	437.1	471.6	500.4	527.7	553.9	577.6	594.8	610.7	629.3	648.7	668.6	690.2	712.6	737.0	765.5	804.9	886.2
6	240.6	304.3	349.0	394.6	436.7	471.2	500.2	527.3	553.4	577.3	594.4	610.5	629.0	648.7	668.4	690.0	712.6	736.8	765.2	804.7	887.6
7	240.7	304.4	349.2	394.8	436.7	471.2	500.0	527.3	553.3	577.4	594.5	610.4	629.0	648.5	668.3	689.8	712.4	736.7	765.0	804.0	886.8
8	239.5	304.1	349.1	395.1	437.3	471.6	500.4	527.5	553.4	577.3	594.6	610.4	628.9	648.5	668.3	689.9	712.3	736.6	765.1	804.4	885.5
9	240.5	304.5	349.3	394.9	436.9	471.5	500.5	527.6	553.6	577.3	594.6	610.5	629.1	648.7	668.7	690.4	713.0	737.2	765.4	804.4	885.8
10	240.8	304.6	349.4	395.1	437.3	471.8	500.8	528.0	553.8	577.6	595.0	611.1	629.5	649.2	668.9	690.5	713.1	737.2	765.3	804.7	887.7
11	240.8	304.4	349.4	394.8	437.1	471.7	500.7	527.8	554.0	577.7	595.0	611.1	629.7	649.3	668.9	690.4	712.8	737.0	765.1	804.4	885.4
12	240.9	304.5	349.1	394.9	437.0	471.5	500.4	527.6	553.4	577.4	594.6	610.4	629.1	648.5	668.3	689.8	712.4	736.6	764.7	803.8	885.0
13	241.0	304.6	349.4	395.3	437.3	472.0	500.9	528.1	554.0	577.6	594.8	610.5	629.0	648.5	668.3	689.8	712.4	736.8	764.9	804.0	885.4
14	241.0	304.5	349.1	394.9	436.8	471.4	500.5	527.8	553.8	577.7	595.0	611.0	629.6	649.0	668.8	690.5	713.0	737.4	766.0	805.2	886.7
15	240.7	304.5	349.4	395.2	437.6	472.1	501.1	528.1	553.8	577.5	594.7	610.7	629.0	648.9	668.6	690.4	712.9	737.4	765.7	805.4	888.4
AVE	240.7	304.5	349.2	394.9	437.0	471.5	500.5	527.7	553.6	577.5	594.7	610.7	629.2	648.8	668.6	690.2	712.7	737.1	765.3	804.6	886.5
SDEV	0.39	0.12	0.13	0.19	0.28	0.27	0.29	0.24	0.22	0.14	0.20	0.25	0.25	0.27	0.24	0.27	0.30	0.31	0.39	0.47	1.13
RSD	0.16%	0.04%	0.04%	0.05%	0.07%	0.06%	0.06%	0.05%	0.04%	0.02%	0.03%	0.04%	0.04%	0.04%	0.04%	0.04%	0.04%	0.04%	0.05%	0.06%	0.13%
Consensus	239	304	349	393	435	469	499	526	552	576	594	610	629	649	669	690	712	736	764	803	887
Difference	1.71	0.45	0.21	1.94	1.99	2.53	1.47	1.69	1.64	1.52	0.73	0.72	0.24	-0.19	-0.41	0.22	0.75	1.06	1.35	1.59	-0.50

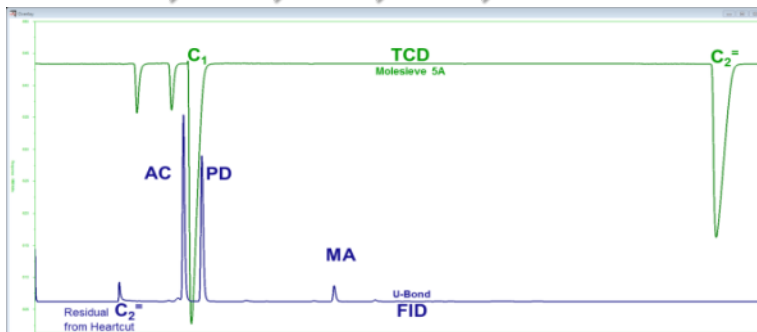


- **Initial BP = 241°F**
- **Final BP = 886°F**
- **Ave. Sdev = 0.3°F**
- **Ave. RSD = 0.05%**
- **Ave. Difference = 1.0°F**

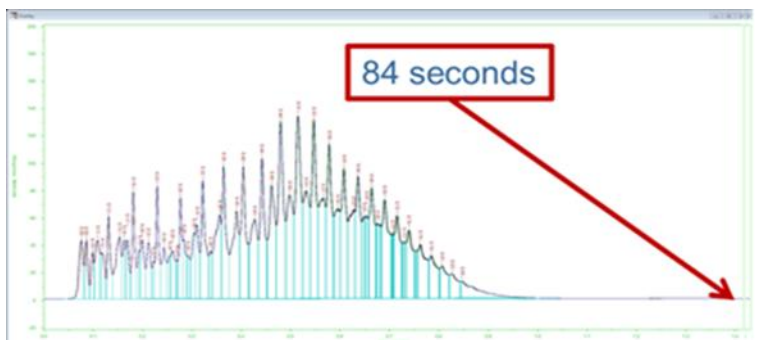
Application Range Examples



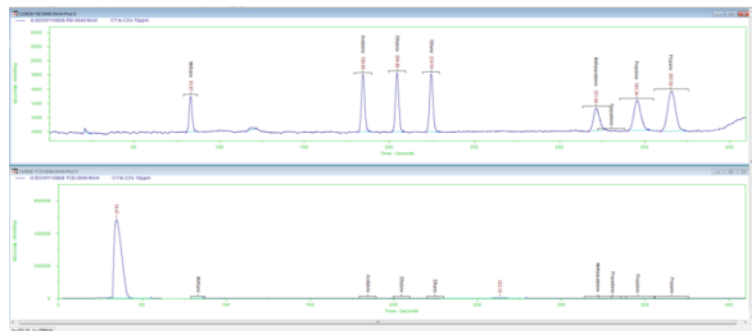
● **He, O₂, N₂, CO, C₁ CO₂**



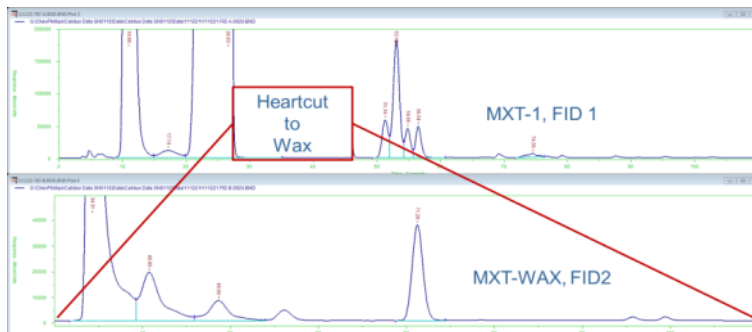
● **Air, CO, C₁, C₂=, AC, PD, MA**



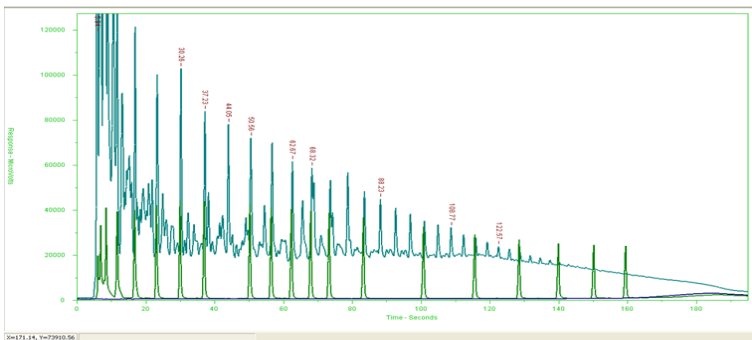
● **ASTM D-2887 & UltraFast D-2887**



● **C₁, AC, C₂=, C₂, MA, C₃=, C₃**



● **C₆ to C₉ Heartcut**



● **Crude Characterizations**

*Falcon Analytical
makers of the . . .*

CALIDUS
micro GAS CHROMATOGRAPH

in the lab...

in the process...

in the field.



***Thank you for your
attention.***

10/16/2012