Calidus ultraFAST GC from Falcon Analytical

Rethinking Gas Chromatography

"Customers need and want the answers…

Not just the hassles often associated with analytical chemistry!"

Falcon Analytical Team

- John Crandall, President & Partner
  - 38 year veteran, analytical chemical instrumentation
  - Siemens/Applied Automation, PerkinElmer, ABB
  - From research chemist to president
  - **Co-inventor**
- Ned Roques, Chief Chromatography Engineer & Partner
  - **Co-inventor**
  - 18 year veteran micro gas chromatography systems engineering
  - Electrical engineering, chromatography systems & applications development
  - B.S. Electrical Engineer
- Larry Nickell, CTO & Partner, and also President AEI
  - 39 year veteran, M.S. Electrical Engineer, control systems – AEI
  - Textile measurement & control systems from research to general manager
  - Electro, mechanical, optical & software engineering
- Joe Warren, CFO, partner & Vice President AEI
  - 38 year veteran, B.S. Agriculture, resource management & finance
  - Energy extraction (coal), land management, textile measurement & control systems
  - Controller AEI for more than 16 years
- Steve Bostic, Marketing Consultant
  - 37 year veteran, B.S. Business/Marketing, microwave communications, electronics and process analytics
  - “Mr. ABB Process Analytics” – Sales, Marketing, SERVICES, Applications, GM

Summary

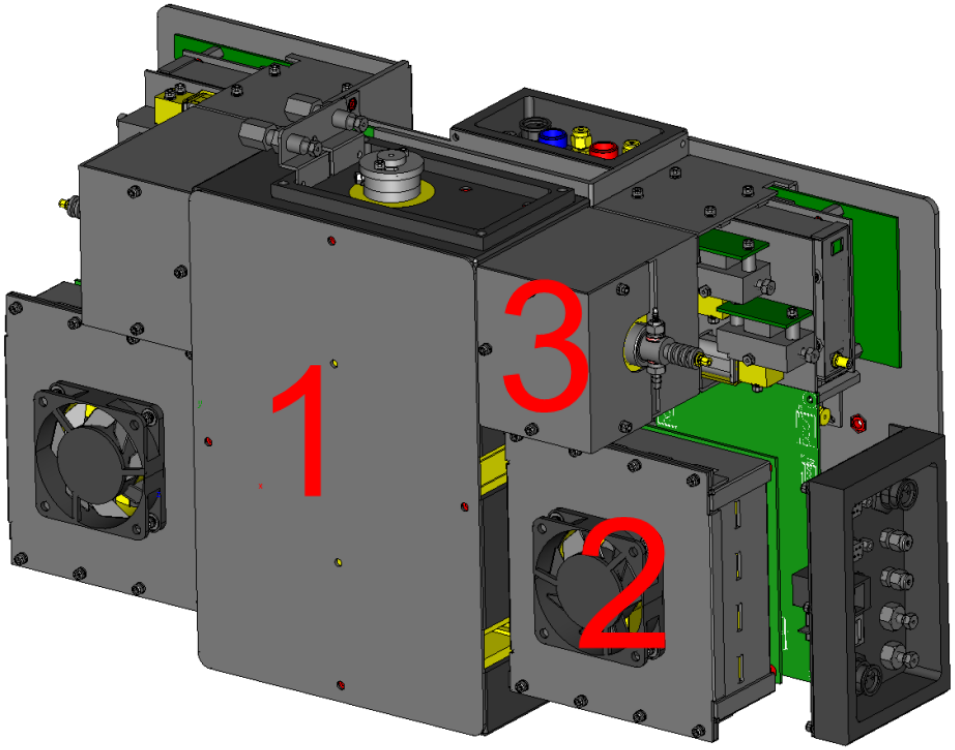
easier, smaller, faster, smarter, and greener

- Throw out 100-year-old design constraints
- Maximize use of computer control and interpretation.

- Ground-up **re**thinking of how a chromatograph should function has resulted in a breakthrough, both for the hardware and for the software.
  - We addressed instrument size, ease of use, power consumption, and maintainability.
  - The **re**designed approach field tested at Chevron.
  - The approach spans innovations both in hardware and in software.
  - And is now ready for commercial implementation in all environments – Lab, at-line, transportable, on-line.

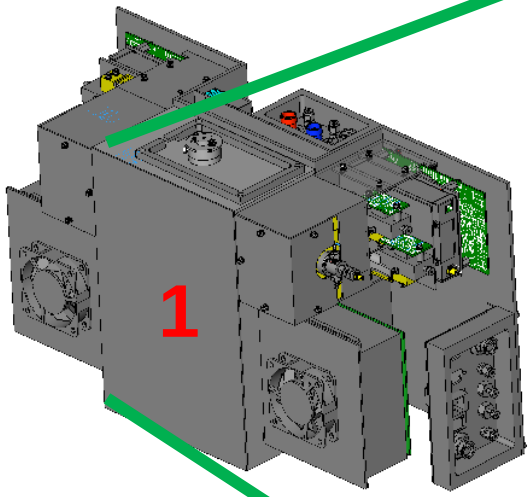
Modules, Its All about Modules
("Bill of Materials")

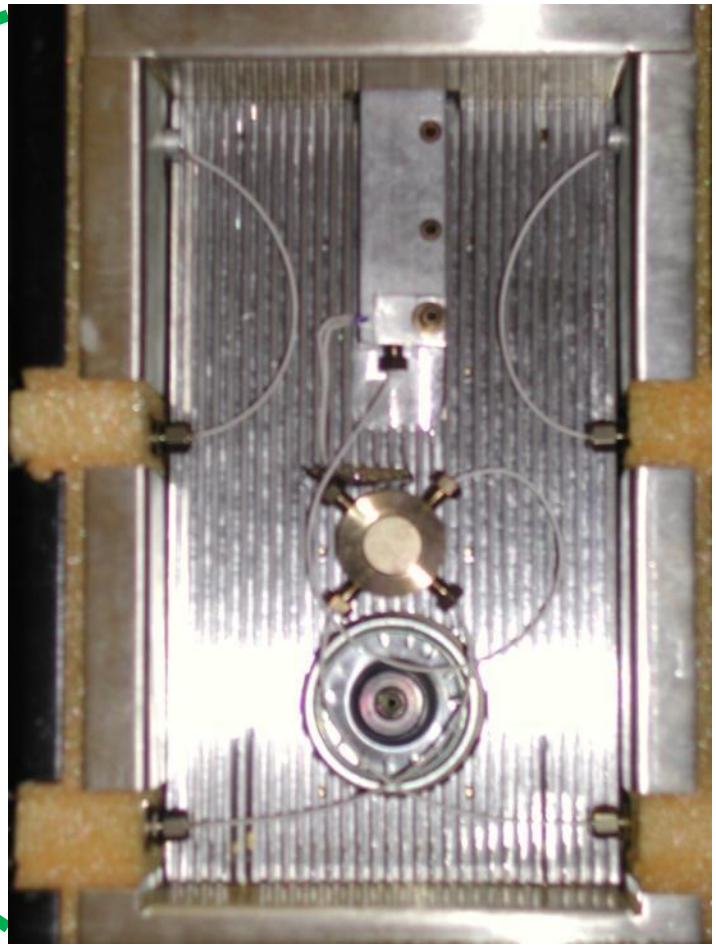
- The Chassis
  - Begins with the inlet – sampling
  - Then separations
  - Then detection
- Yes, it is a GC
  - Split/splitless inj.
  - Capillary columns
- Detectors, both TCD & FID



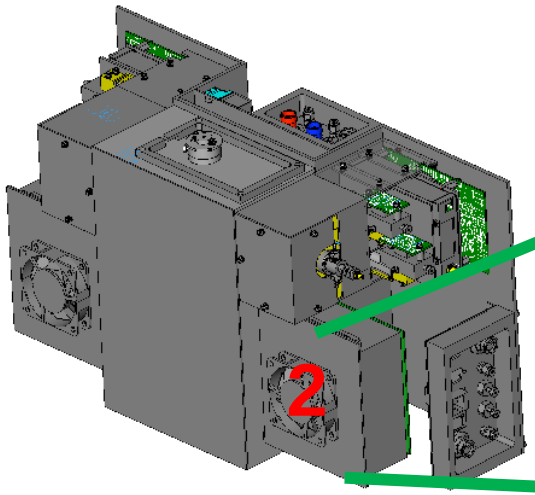
. . . more coming FPD, Barrier Discharge (PID, ECD mode)
mini Ion-Trap Mass Spec : Calidus GC/MS . . . 2013

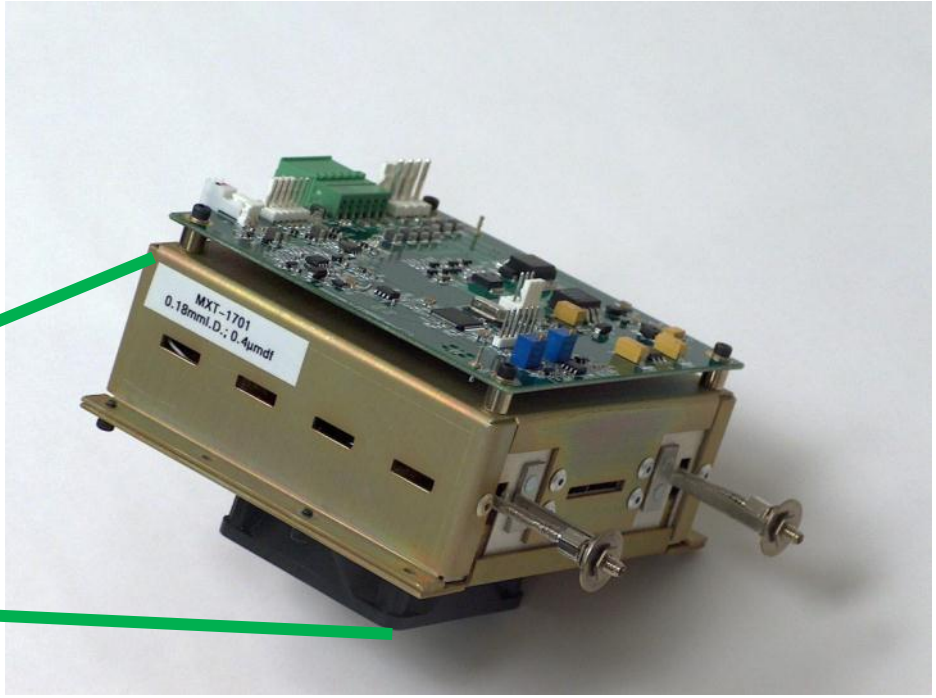
Sample Processing Module (inlet): the core of the microGC platform (required for all versions).

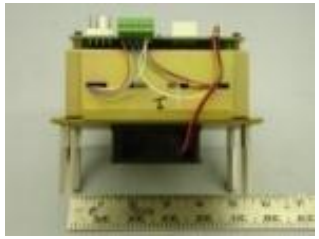




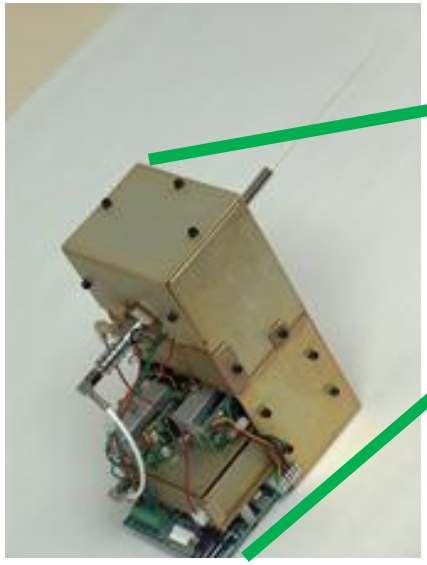
Chromatography Module: the secret sauce.
One or optionally two used in every system.



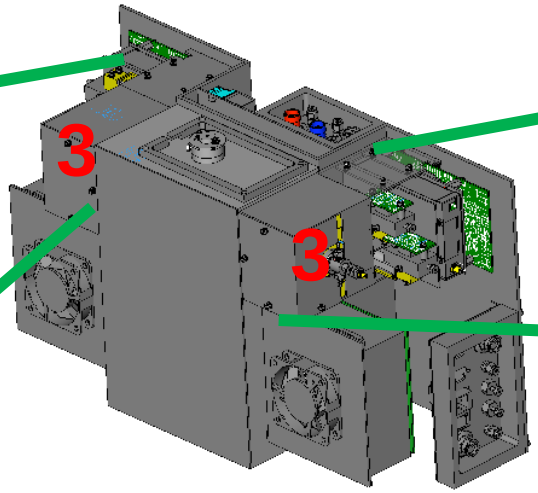


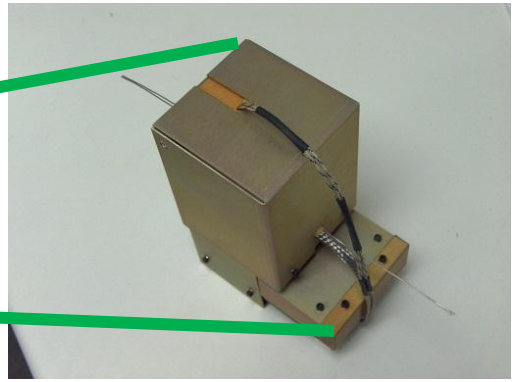


Detector Module: the sensing options. One or optionally two used in every system, TCD & FID.



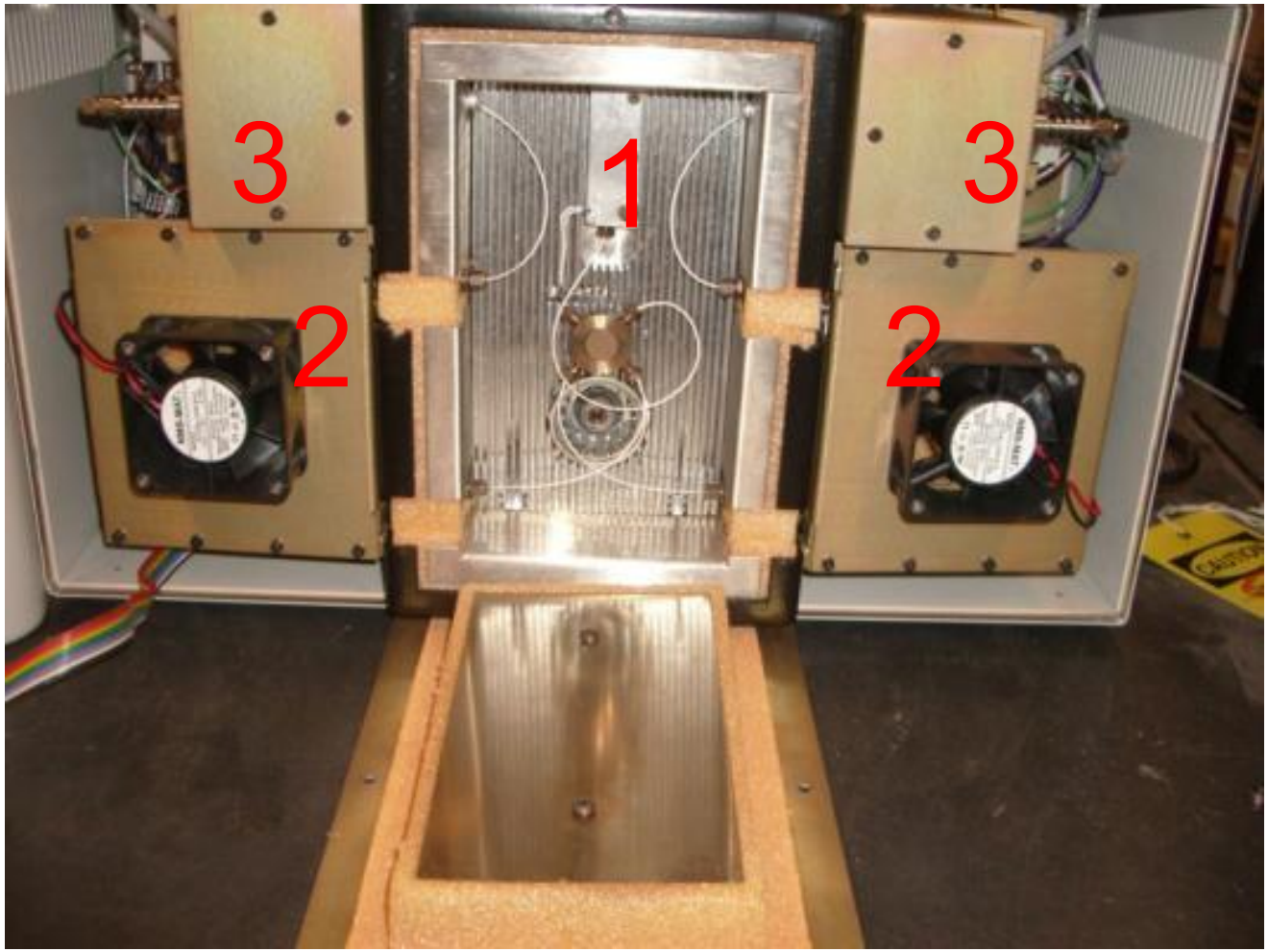
FID



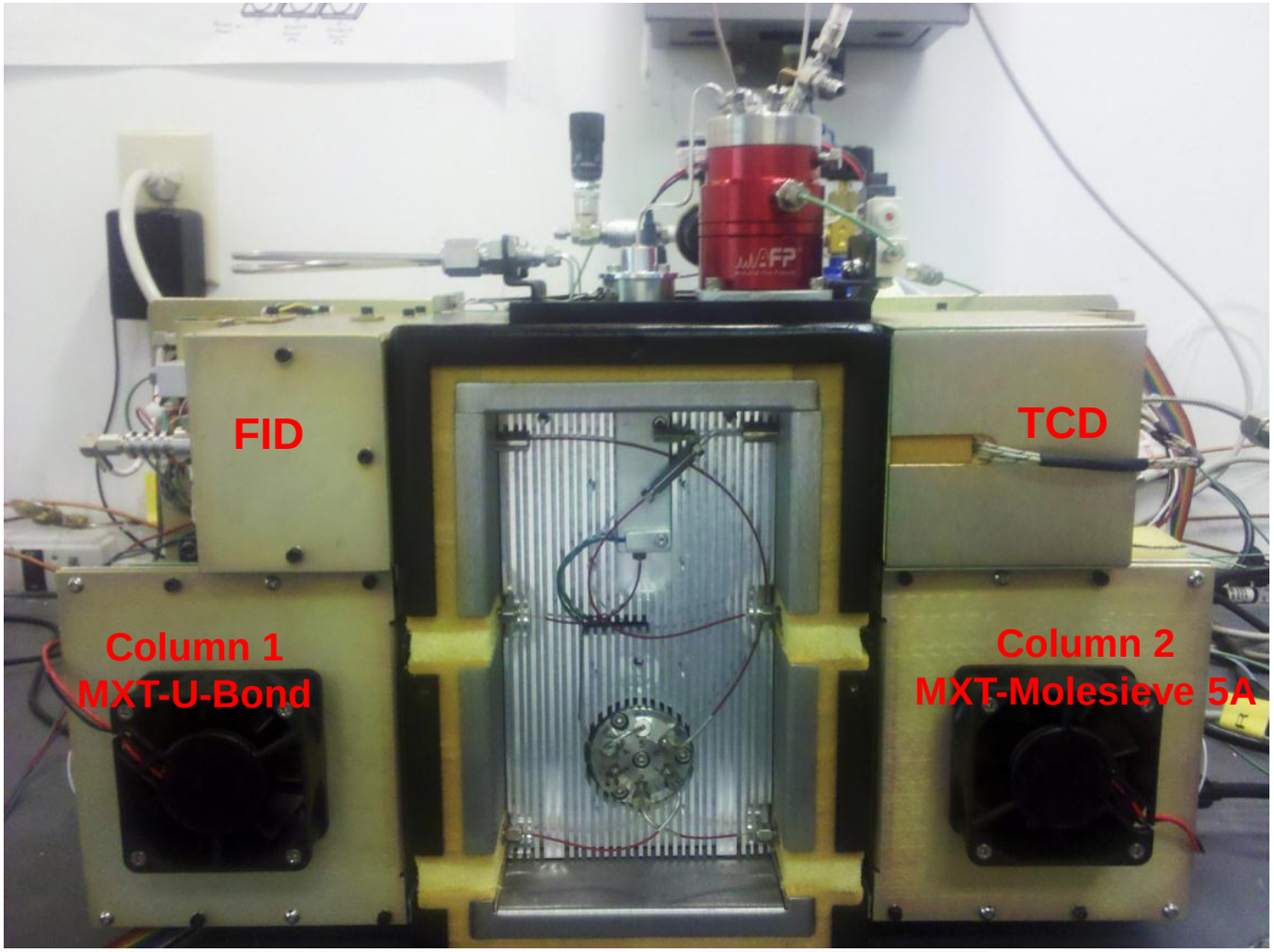


TCD

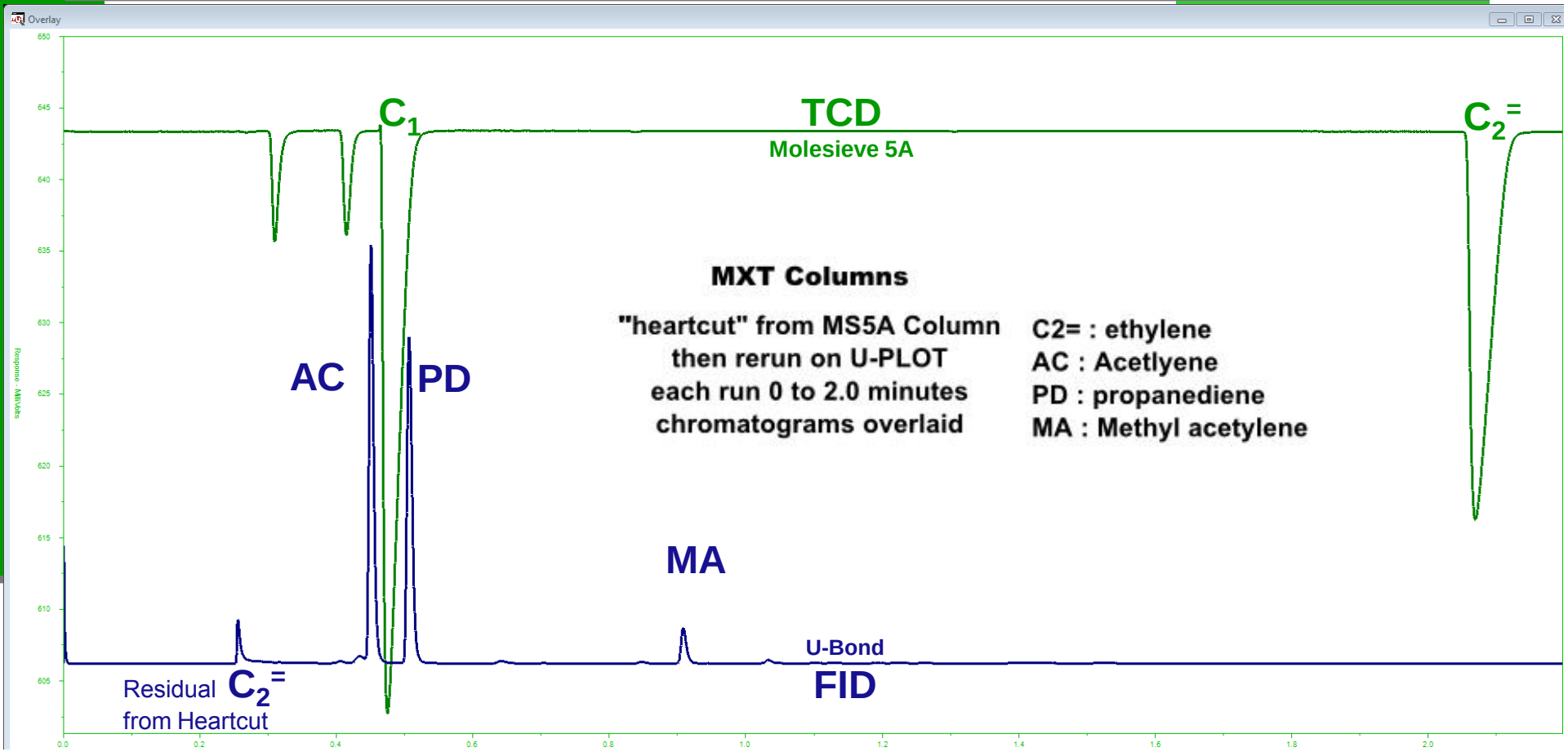
Sample processing module with dual column module, dual detector configuration.



Sample processing module with heartcut valve, dual column module and TCD & FID.



One Resultant Chromatogram



Module Assemblies Make a GC

Transportable or At-Line Configuration

Automation Makes An Analytical System

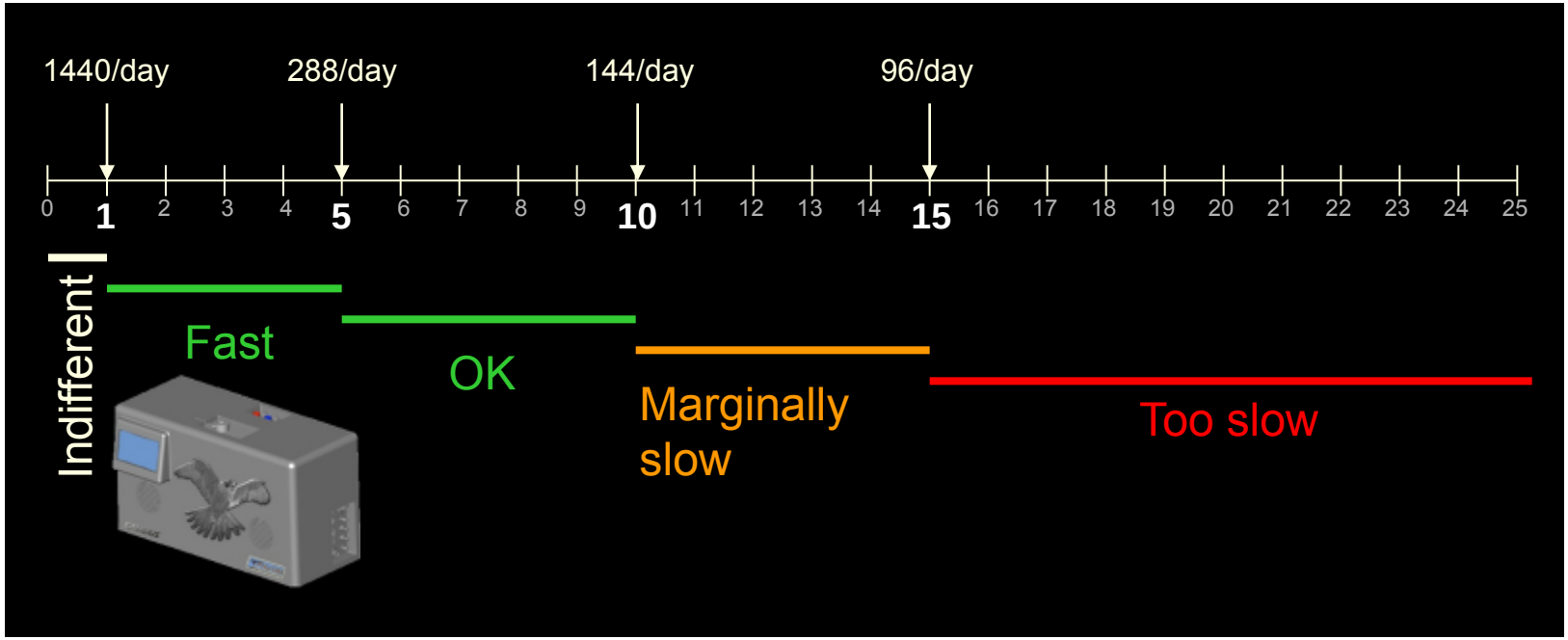
But What about Process Design?

The challenge is to design a GC that can span most of the applications in laboratory, at-line and on-line settings.

1. Speed of analysis (use to control the process)
2. Appropriate detection scheme (flexible detectors)
3. Application coverage (common instrument platform)
4. Form factor (size, weight, footprint)
5. Cost (price, shelter, maintenance, periphery)

Speed of Analysis

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



If we are really going to use GC for **control**, speed means under 10 minutes for most applications.

Poll of Process Users

Speed + Applications + Form Factor

Old School

- High thermal mass
  - Temperature stability
  - Slow to respond to change
  - Isothermal methods
  - Column switching schemes
  - Heavy & large footprints
  - Kilowatt power requirement
- Large unswept (dead) volumes
  - Inferior resolution
  - Peak tailing
  - Longer columns
  - Long analysis times
  - High consumable rates

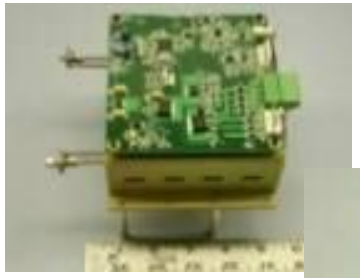
New Thinking

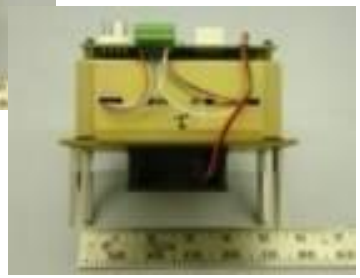
- Low thermal mass
  - Temperature repeatability and reproducibility
  - Quick response
  - Programmed temperature methods
  - Minimal switching schemes
  - Low power requirement
- "Zero" dead volume
  - High resolution
  - Short columns
  - Fast cycle times
  - Minimum consumables

New Thinking: CALIDUS

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

- Sample processing module power
  250°C = 40 W
- Column module power (1 or 2 columns)
  35°-350°C @ 5°C/second = 70 W each
- Detector module power (1 or 2 detectors, each)
  - 150°C = 7 W
  - 250°C = 15 W
  - 350°C = 19.5 W
- System power
  - Application dependent
  - 300 W maximum
  - Average = ***225 W***





Cost Considerations

Equipment Costs

- Instrument, shelter, installation, supplies
- Commonality with laboratory devices (data agreement)

Maintenance Costs

- Robust construction
- Automated data and instrument validation

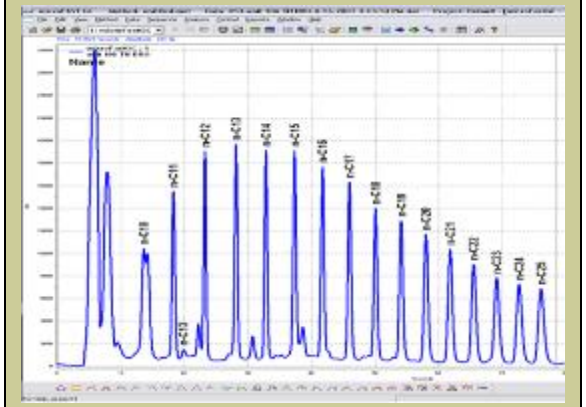
Peripheral Costs

- Supplies
- Energy

It is essential to look at the energy requirements: likely the largest hidden cost of analysis.

A GC must still make measurements

- Sampling
  - *Accepts either gas or liquid phase samples*
  - *Manageable volumes: 60 nanoliters to ~100 microliters injected*
  - *Boiling ranges from permanent gases up to C_{60}*
  - *Pre-concentration possible (trap or purge & trap techniques)*
- Separations
  - *Adequate resolution for the application*
  - *Accepts available column material*
  - *Makes use of column specificity characteristics*
  - *Adequate column capacity (sample loading)*
- Detection
  - *Universal detection required such as TCD*
  - *Hydrocarbon specific such as FID*
  - *Sulfur specific such as FPD*
  - *Halogen specific such as ECD*



Diesel-range, 80 seconds

A GC must still make measurements

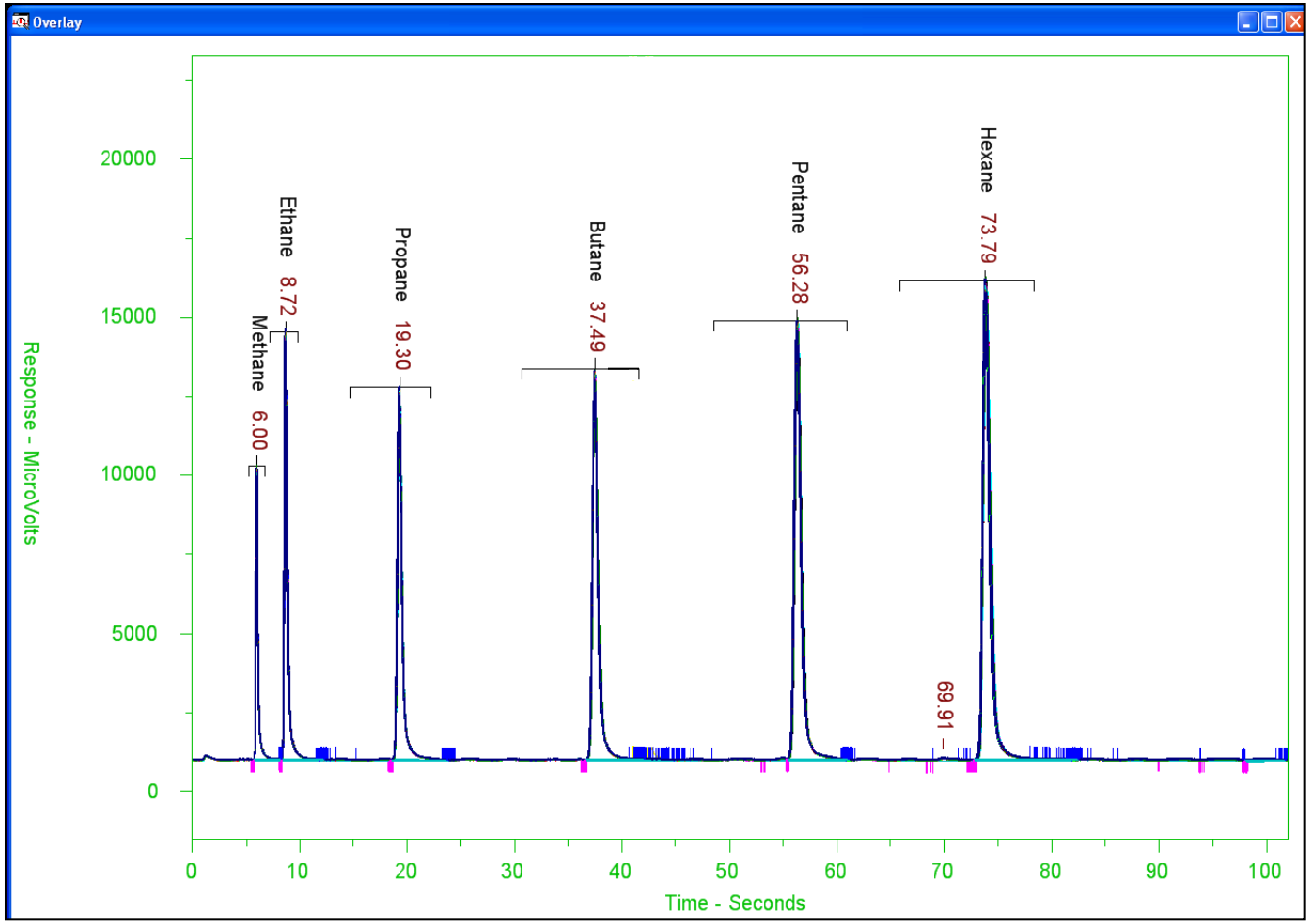
- Data processing
  - *Proper peak retention time and area determination*
  - *Chromatographic peak alignment*
  - *Proper integration of alignment results, response factor and integration*
  - *Various calibration techniques available*
- Statistics
  - *System must perform with acceptable precision and accuracy to yield*
  - *Repeatable and reproducible measurements*
- And the GC should deliver
  - *System suitability assessments*
    - *Is the sample OK?*
    - *Is the GC OK?*
    - *Does the sample "pass or fail" the established criteria?*
  - *And an acceptable reporting format*

Sample	Quality	TNMHC	Ethane	Ethylene
10-27-2005 12-26-53 pm_microfast 01_032.dat	Event	1198	0	3
10-27-2005 2-14-07 pm_microfast 01_004.dat	Event	473	0	0
10-27-2005 2-54-00 pm_microfast 01_008.dat	Calibration	12744	491	487
10-27-2005 2-34-04 pm_microfast 01_006.dat	Event	1547	58	67
10-27-2005 2-24-05 pm_microfast 01_005.dat	Event	477	21	22
10-27-2005 2-44-02 pm_microfast 01_007.dat	Event	4046	141	160
10-27-2005 3-13-55 pm_microfast 01_010.dat	N/A	207	0	0
10-27-2005 1-31-07 pm_microfast 01_003.dat	Flame out	47	4	0
10-27-2005 1-21-06 pm_microfast 01_002.dat	Flame out	49	0	0
10-27-2005 3-03-57 pm_microfast 01_009.dat	Calibration	25447	1005	1003
10-27-2005 7-26-55 am_microfast 01_003.dat	Background	110	36	0
10-27-2005 7-16-55 am_microfast 01_002.dat	Background	84	50	0
10-27-2005 7-06-54 am_microfast 01_001.dat	Background	89	31	3
10-27-2005 6-56-54 am_microfast 01_071.dat	Background	115	22	7
10-27-2005 6-46-55 am_microfast 01_070.dat	Background	72	23	0

HRVOC Fence Line Analysis

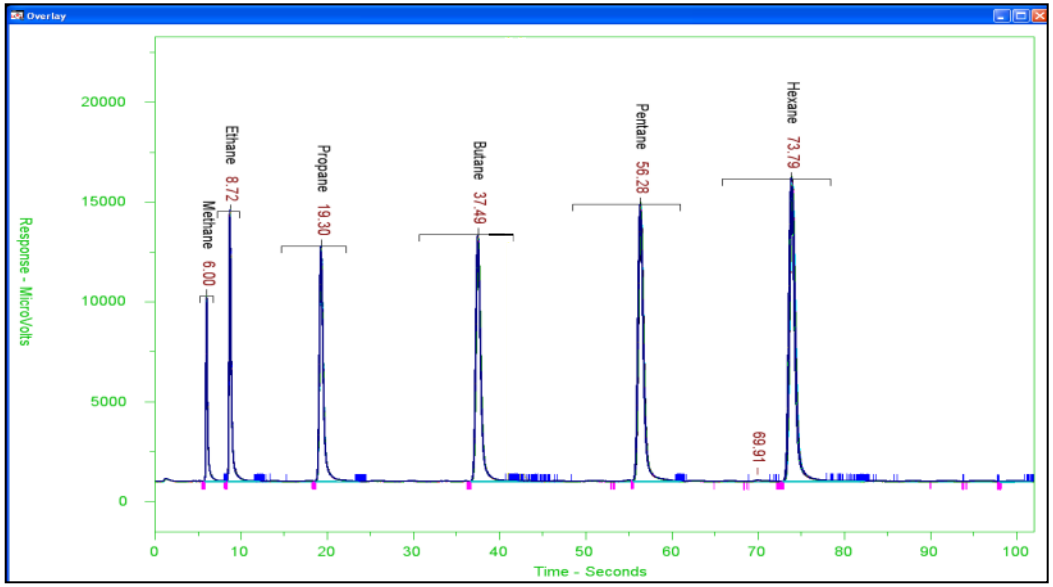
Methane through Hexane

100 Consecutive Runs Overlaid



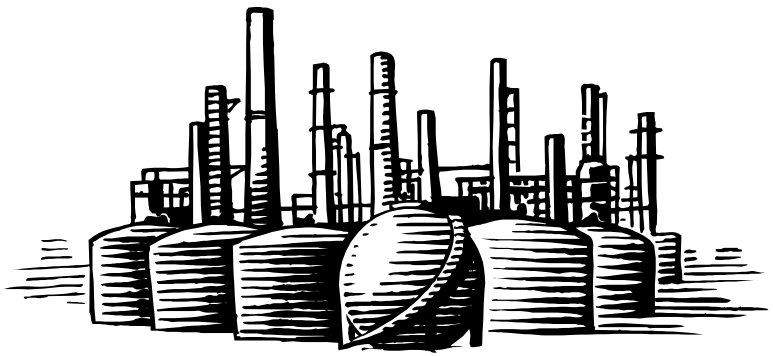
Methane through Hexane Summary

100 Run RT Statistics (no outliers rejected)							
	Methane	**Ethane**	**Propane**	**Butane**	**Pentane**	**Hexane**	
Average	0.100218	0.145572	0.321795	0.625310101	0.939598	1.23237	
Std. Dev.	7.96E-05	0.000103	0.000137	0.000242224	0.000407	0.000812	**AVG**
%RSD	0.0794%	0.0705%	0.0427%	0.0387%	0.0433%	0.0659%	**0.057%**



100 Run Area Statistics (no outliers rejected)							
	Methane	**Ethane**	**Propane**	**Butane**	**Pentane**	**Hexane**	
Average	2117.64	4253.89	6282.28	8363.68	10325.85	12459.9	
Std. Dev.	16.467	36.48464	51.6748	131.788542	96.32881	102.4173	**AVG**
%RSD	0.7776%	0.8577%	0.8225%	1.5757%	0.9329%	0.8220%	**0.965%**

Featured Application: UltraFast D-2887 for High Throughput Analysis



- Refiners need boiling range distributions
  - Laboratory
  - At-line
  - Online
- Older GC technology
  - Too slow
  - Too big
  - Can't meet the T-rating requirements in plant economically
- Thus, valuable data is not available for realtime process control
  - Fingerprinting
  - Yield
  - Operating parameters
- All leads to the need for easier, smaller, smarter, faster & greener analytical chemistry –
  Calidus 101-HT, IntraFlow^{tm} NeSSI, Infometrix Chemometrics

Purchased RT Calibration Standard

- Standard GC
  - Capillary column
  - 40 minute run time

RESTEK

Certificate of Composition

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

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 Date[1]: 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)

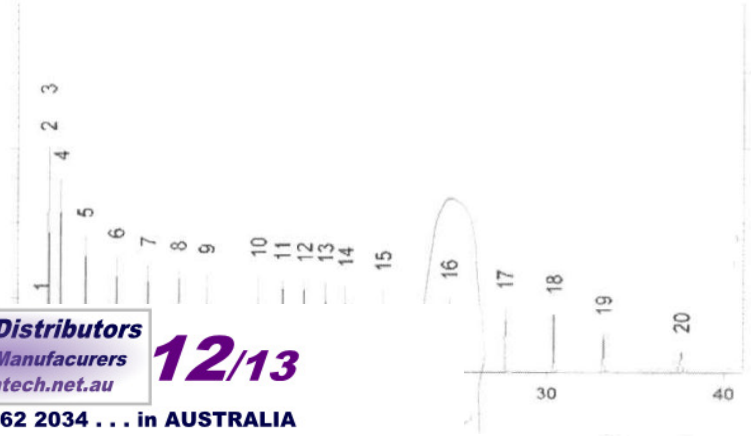
Carrier Gas:
hydrogen-constant pressure 10 psi.

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

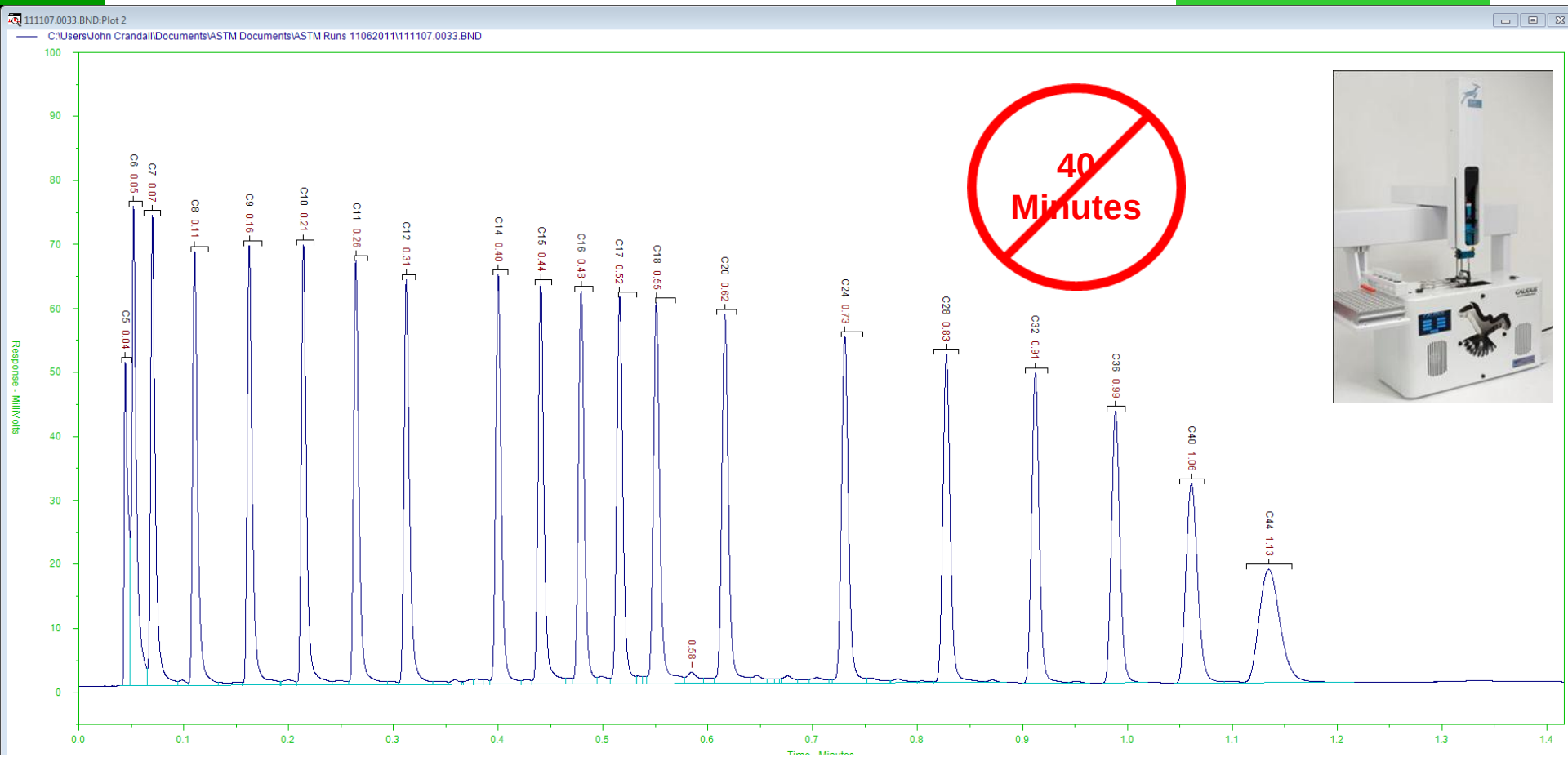
Inj. Temp:
250°C

Det. Temp:
330°C

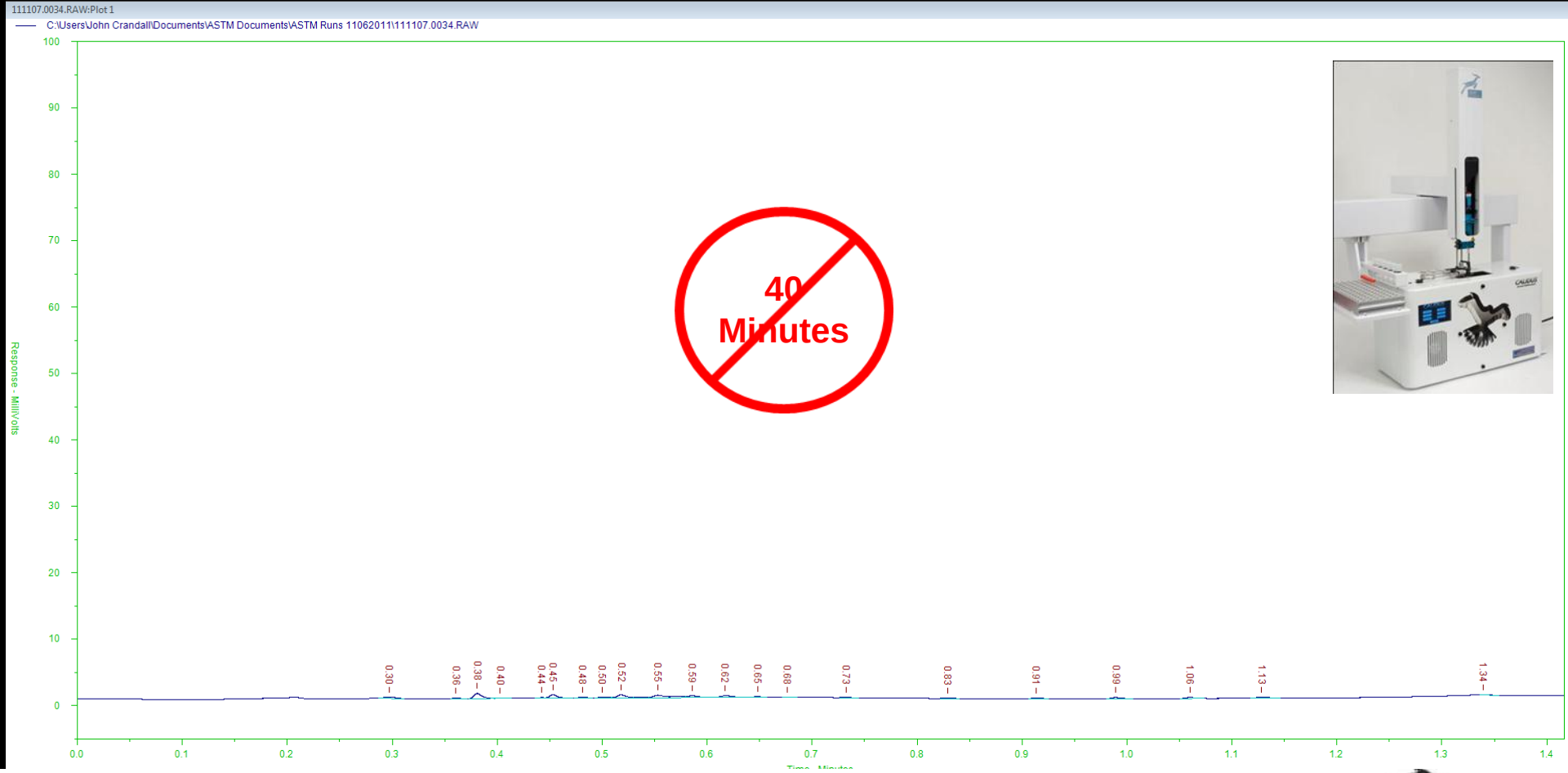
Det. Type:



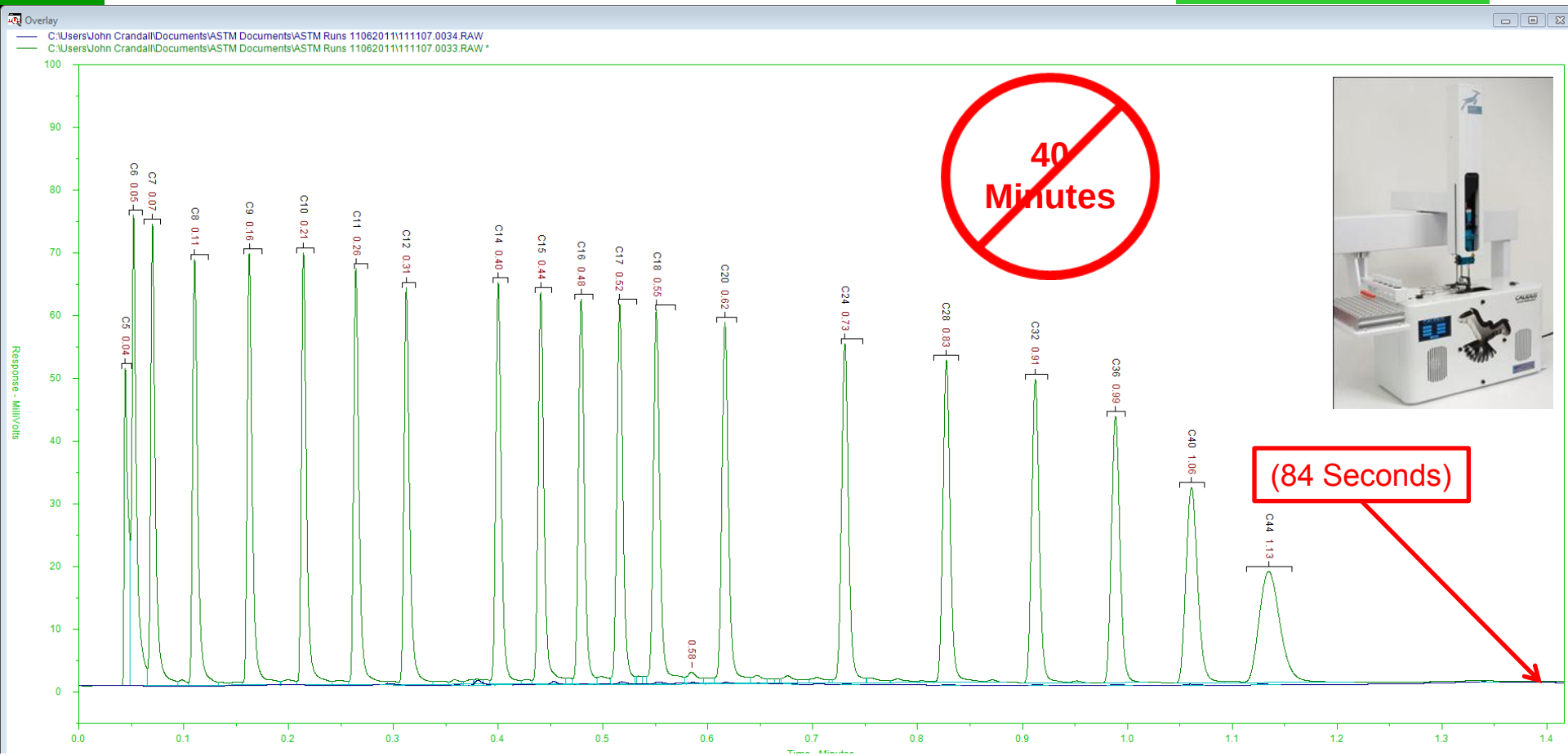
Calidus 101-HT Purchased Restek D-2887 Standard, Analysis Time 84 Seconds



Calidus 101-HT “Non-injection” Blank



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



Purchased Standard Gas Oil

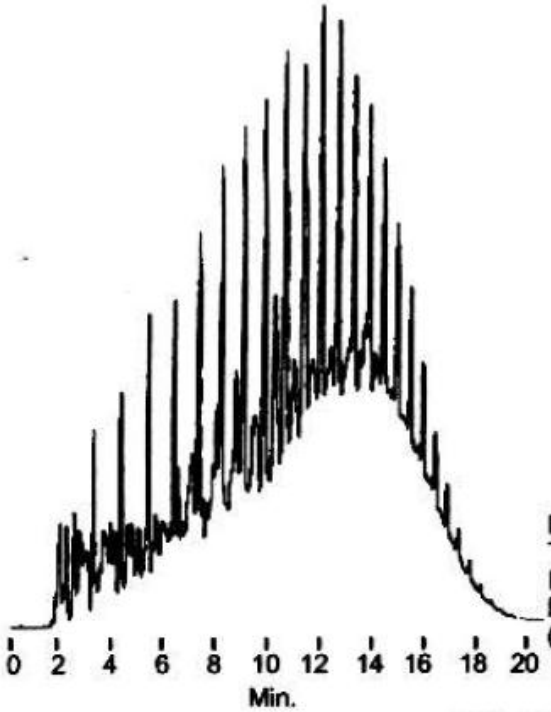
- Standard GC
  - Packed column
  - 20 minute run time
  - Certificate of analysis follows

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.



Petrocol™ B column, 20" x 1/8" SS, Col. Temp.: -25°C to 350°C at 15°C/min., Inj. Temp.: 350°C, Det. Temp.: 375°C, Flow Rate: 30mL/min., He, Det.: FID (128 x 10^{-10} AFS), Sample: 0.1µl.

712-0413

DS97983C

SUPELCO
Bellefonte, PA

Purchased Standard Gas Oil

Chevron Phillips Chemical Company LP

48873 LB86400V

ASTM D2887 Reference Gas Oil No. 1
Lot 2

- Certificate of analysis
  - Consensus values
  - 30 participating laboratories

ASTM D-2887 REFERENCE GAS OIL NO. 1

LOT NO. 2
Consensus Analysis*

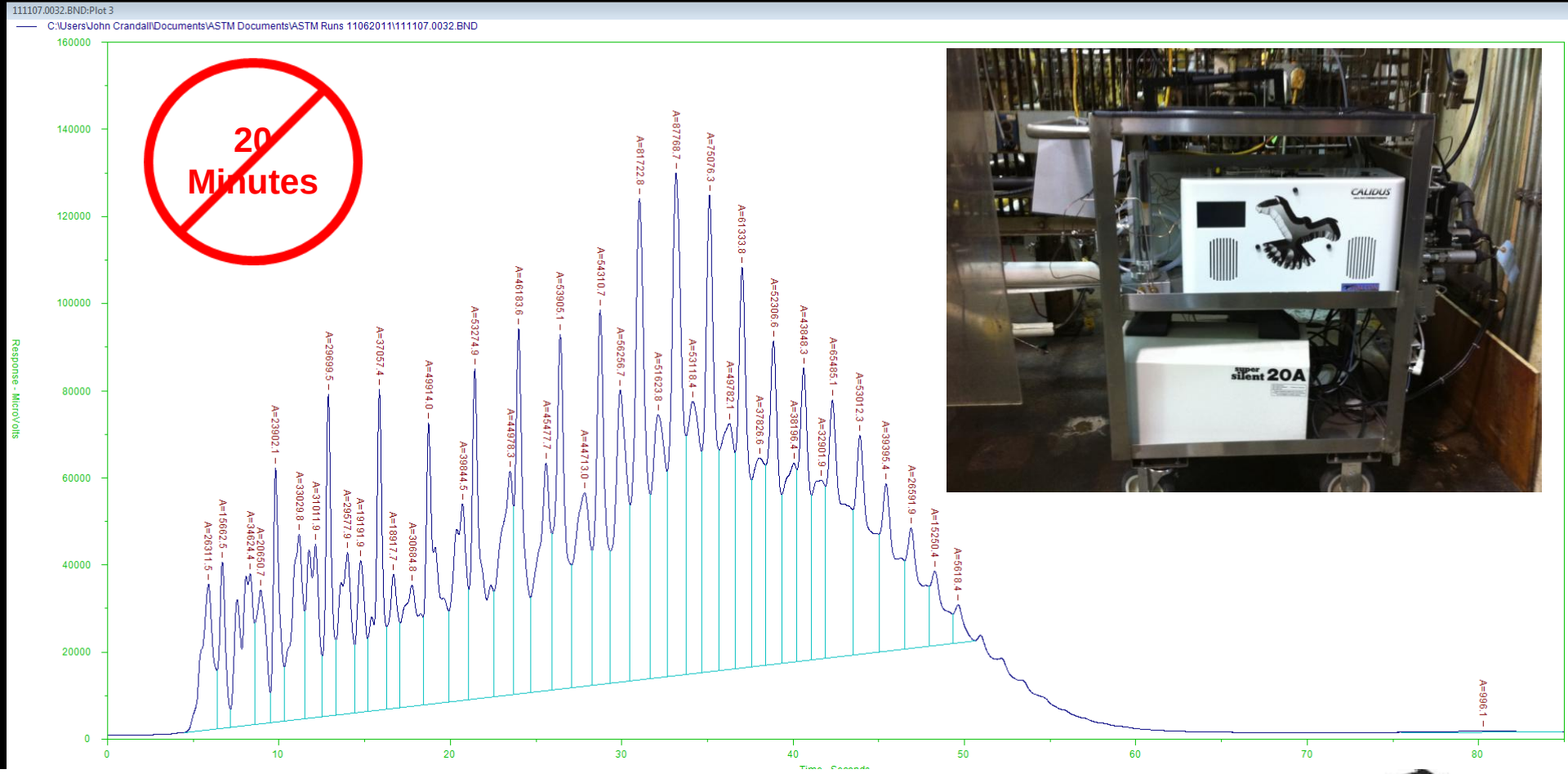
	Batch 2 °F	95% conf. °F	Batch 2 °C	95% conf. °C
IBP	239	+/-1	115	+/- 0.6
5%	304	+/-0.7	151	+/- 0.4
10	349	+/-1.2	176	+/- 0.7
15	393	+/-1.5	201	+/- 0.8
20	435	+/-1.7	224	+/- 0.9
25	469	+/-1.7	243	+/- 0.9
30	499	+/-1.6	259	+/- 0.9
35	526	+/-1.6	275	+/- 0.9
40	552	+/-1.2	289	+/- 0.7
45	576	+/-0.9	302	+/- 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 D4, Section H.

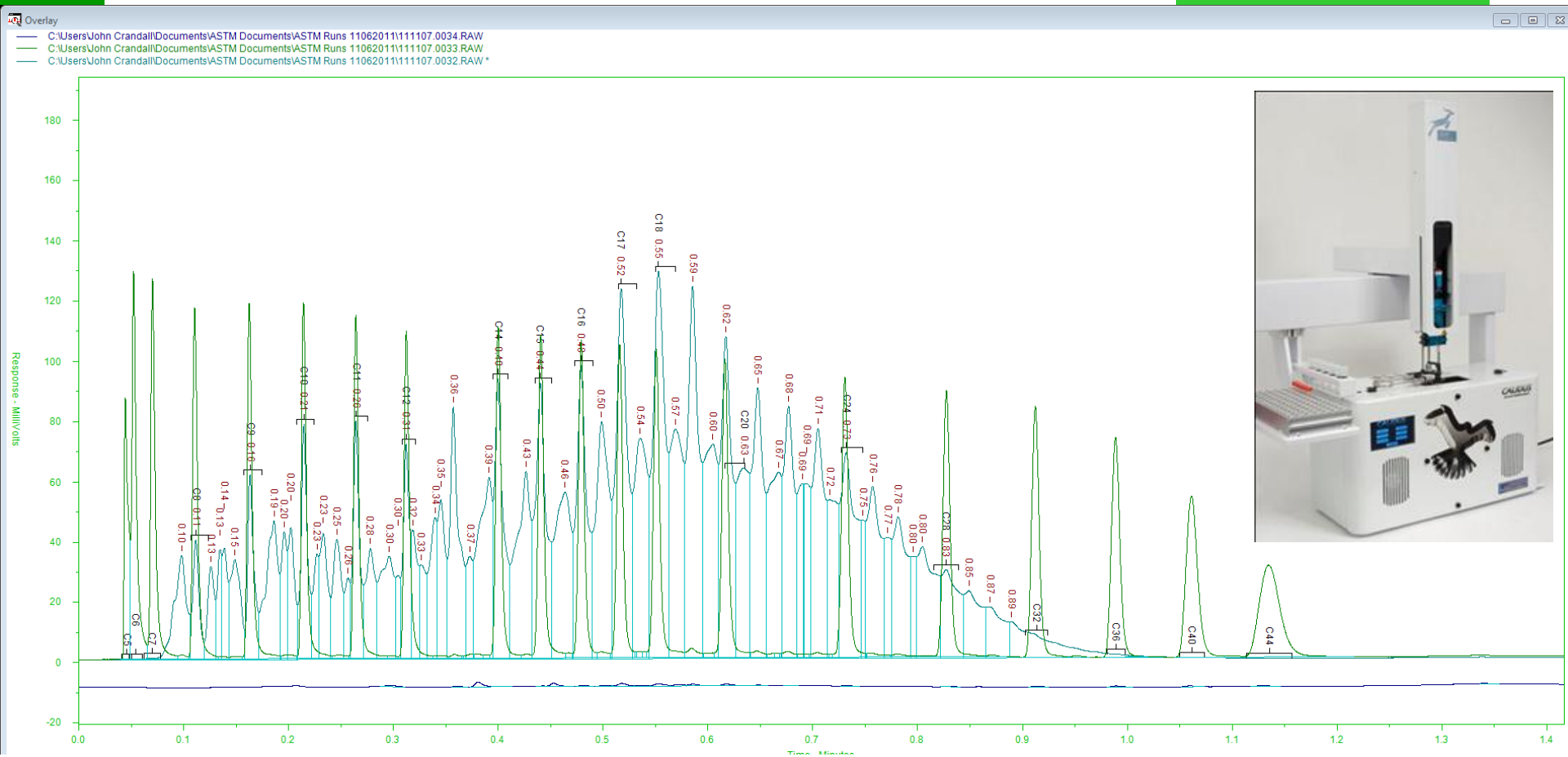
NOTE: This sample is nitrogen blanketed. If transferred to other containers for storage, nitrogen blanketing is recommended. Store in a cool, dark place. Be sure the sample is at room temperature and well mixed before use. The wax point on this product is 55 °F.

ab Team Leader

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 11062011\111107.0032.CDF

Blank File: C:\Users\John Crandall\Documents\ASTM Documents\ASTM Runs 11062011\111107.0034.CDF

Calib File: C:\Users\wayne\Documents\Falcon D2887 Demos\Marathon\111107.0033.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**

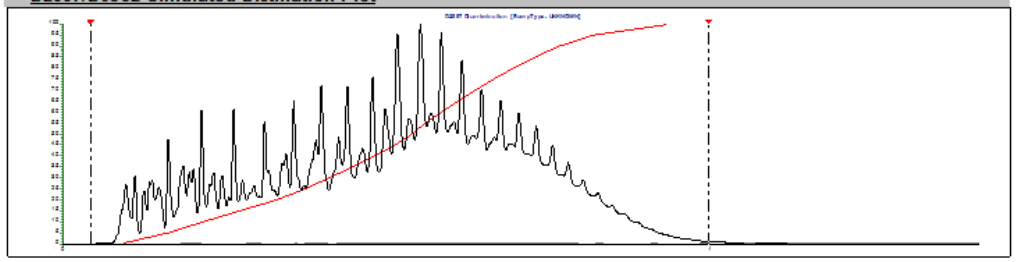
SOM Thrsh: **(0.00001000%)** EOM Thrsh: **(0.00032000%)** Solvent Weight (g): **0.0000**

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

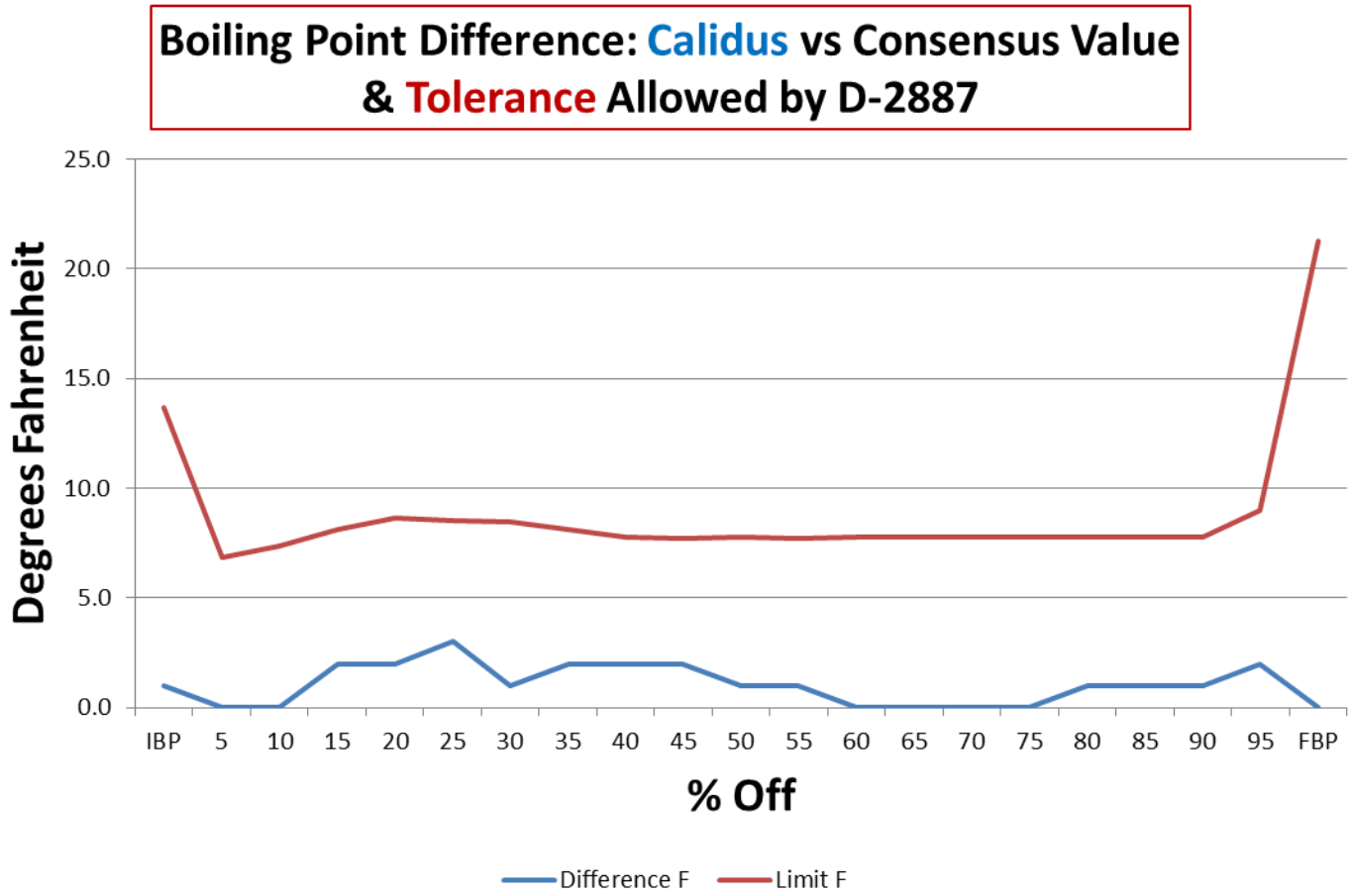
IBP ... 239.34	80.00% ... 710.94
5.00% ... 302.95	85.00% ... 735.05
10.00% ... 347.64	90.00% ... 763.54
15.00% ... 393.12	95.00% ... 803.32
20.00% ... 434.54	FBP ... 885.16
25.00% ... 468.80	
30.00% ... 497.77	
35.00% ... 525.00	
40.00% ... 551.77	
45.00% ... 575.14	
50.00% ... 592.50	
55.00% ... 608.68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

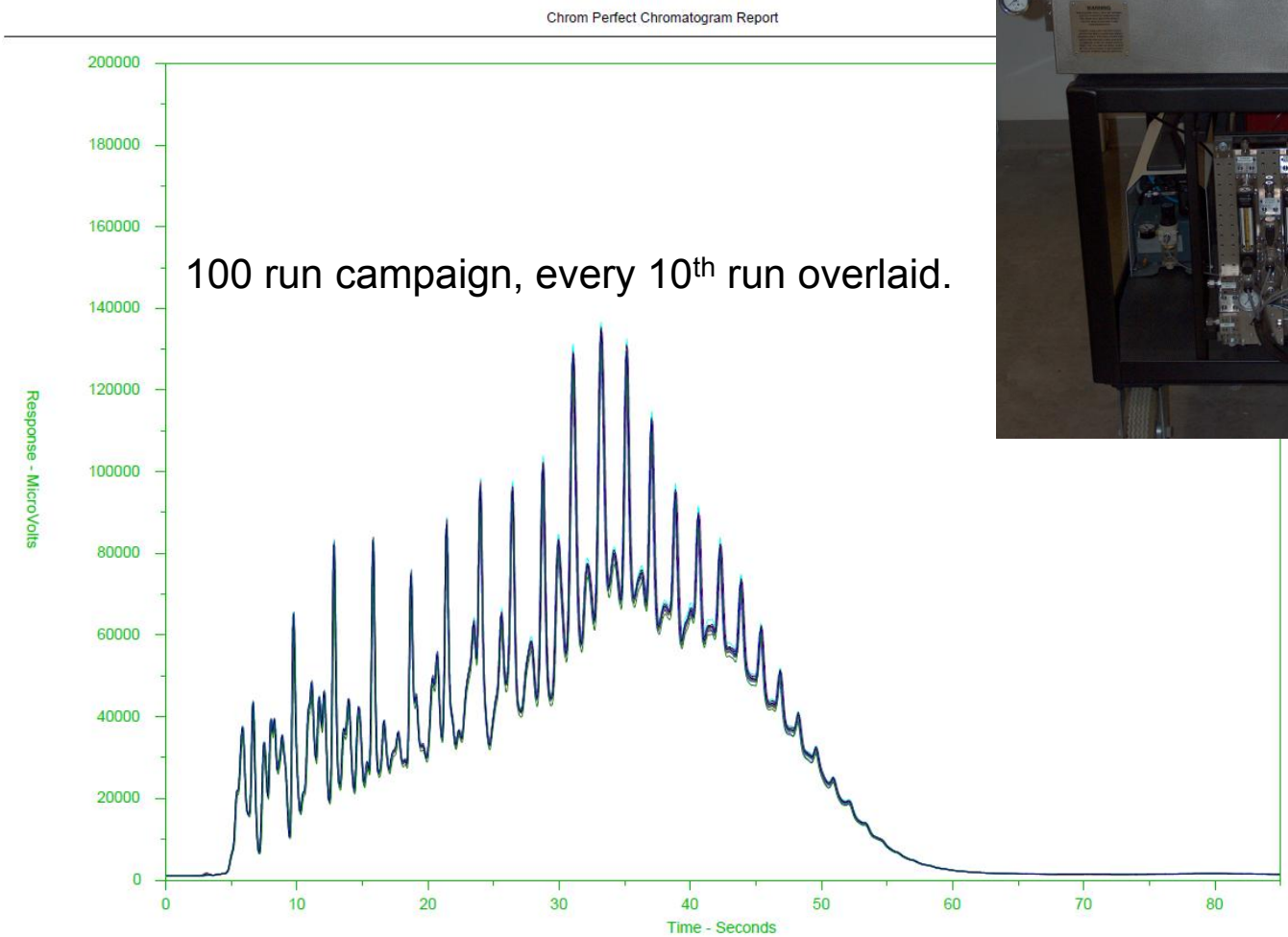
Degrees I	Measured	Accepted	Difference F	Limit F
IBP	240	239	1.0	13.7
5	304	304	0.0	6.8
10	349	349	0.0	7.4
15	395	393	2.0	8.1
20	437	435	2.0	8.6
25	472	469	3.0	8.5
30	500	499	1.0	8.5
35	528	526	2.0	8.1
40	554	552	2.0	7.7
45	578	576	2.0	7.7
50	595	594	1.0	7.7
55	611	610	1.0	7.7
60	629	629	0.0	7.7
65	649	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
  - Extend maintenance interval time
  - Elevate confidence in the results

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

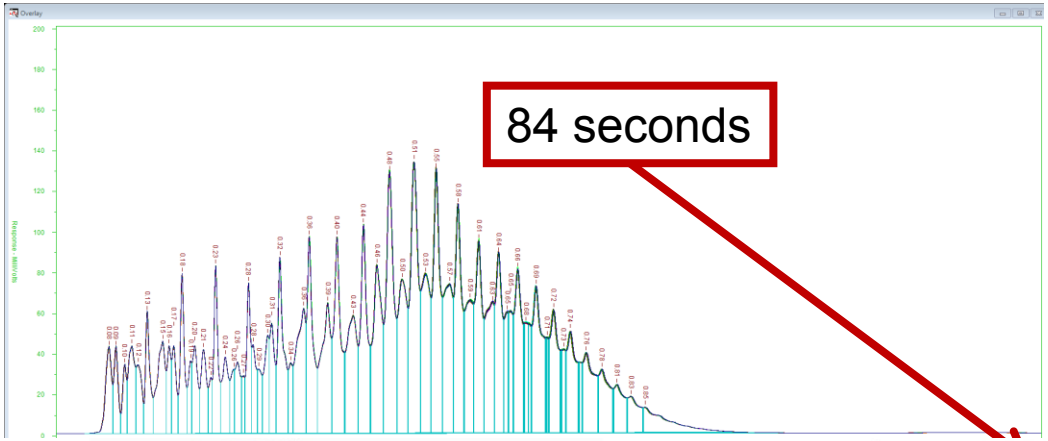


What about Repeatability?



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%
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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**
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
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%**
Consensus	**239**	**304**	**349**	**393**	**435**	**469**	**499**	**526**	**552**	**576**	**594**	**610**	**629**	**649**	**669**	**690**	**712**	**736**	**764**
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

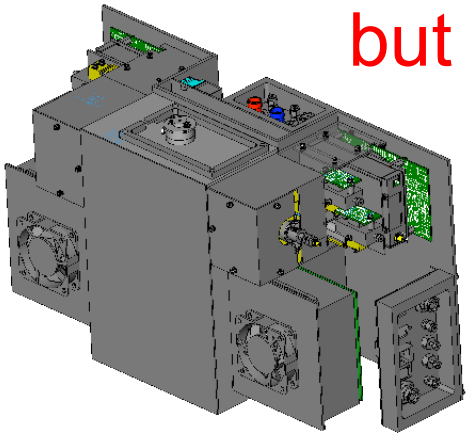


- Initial BP = 241°F
- Final BP = 886°F
- Ave. Sdev = **0.30°F**
- Ave. RSD = **0.054%**
- Ave. Difference = **0.99°F**

Clearly: The Approach Works – fixed gases to C-60

- Automation makes it easier
- Modular components make it a smaller GC
- Data handling makes it smarter
- Low thermal mass makes it faster and
- …Makes it greener… < 300 Watts

but what makes it a process GC?

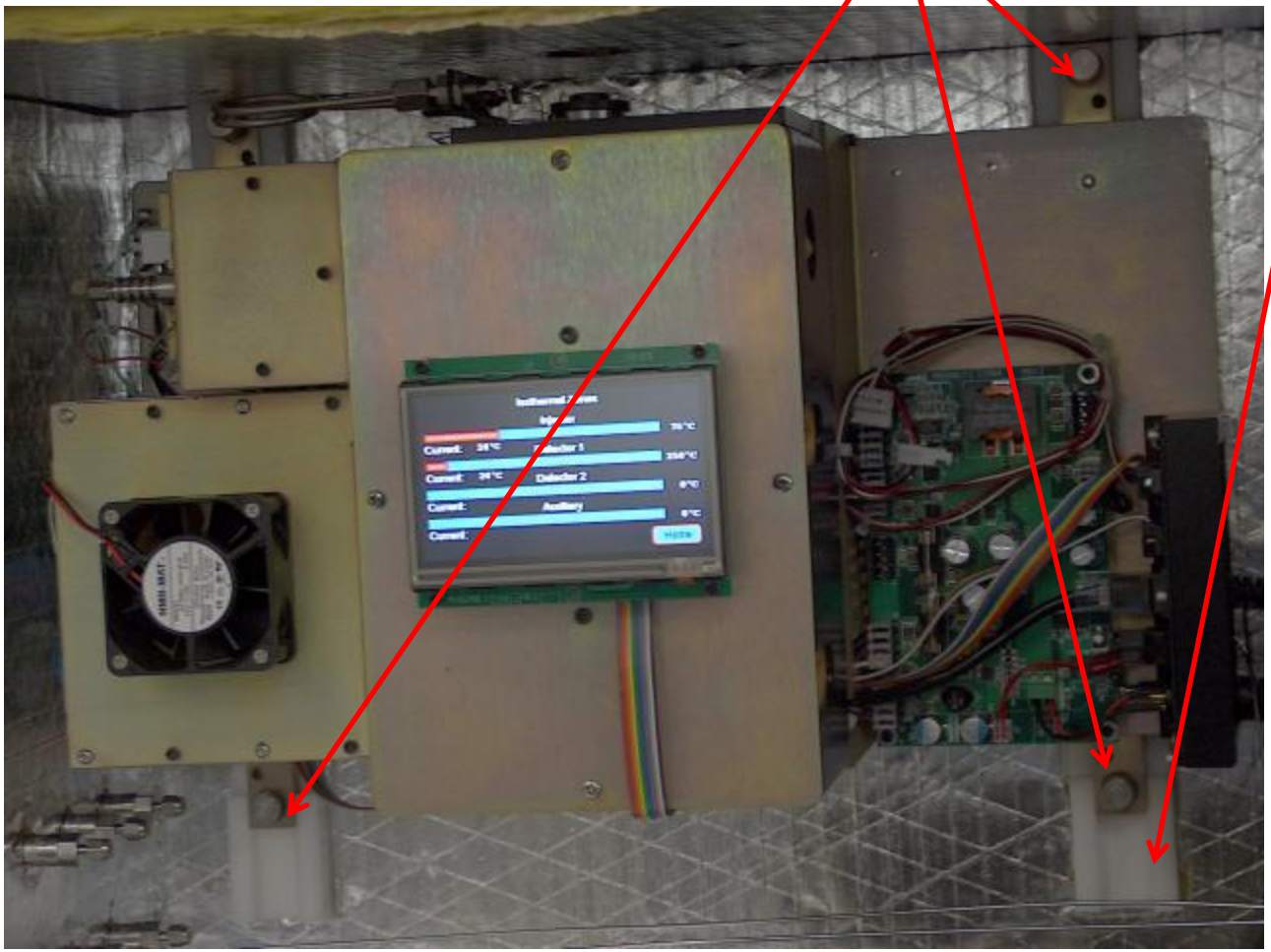


Modularity

Calidus Process GC with NeSSi Sample System on Transportable Cart

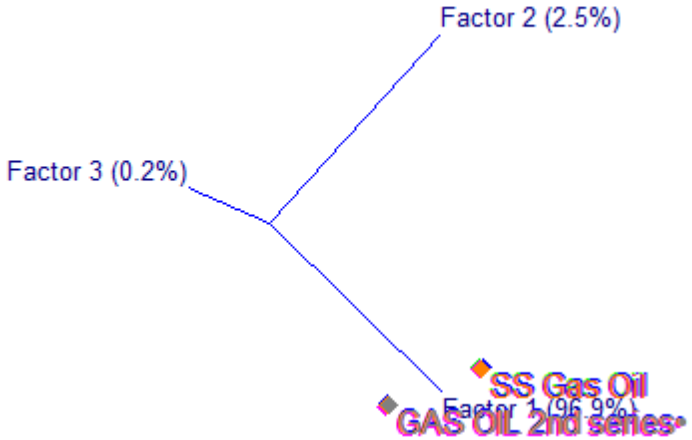
- Environmental
  - 0°-130° F
  - Rain/sun cover
  - Suitable for Class 1, Division II sites
- Interior
  - Thermoelectric temperature control
  - Maintains 60°F
- Plug & Play
  - Column modules or
  - The entire micro GC

Calidus “Plug & Play Connectors & Sliders



Pull & twist connectors, slide Calidus 101 Module down & out.

Smaller, Smarter, Faster, Easier, Greener



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