Fully Automated Fast & Micro Gas Chromatography for UltraFast Fuel Characterizations from C_5 to C_{44}: Significance & Performance Employing the New ASTM D7798 Method

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GC System Used In Accordance With ASTM D7798

- Calidus Model 101-HT micro Gas Chromatograph configured as follows:
  - Sample Size: 0.3 – 0.08 µl
  - Split Ratio: 50:1 – 150:1 350°C
  - Sample: neat
  - Inlet FID Transfer Lines 350°C
  - Carrier: H_2
  - Detector: FID; 350°C
  - Column: MXT – 1 – HT 320 micron ID, 0.2 micron film thickness, 2 M length
  - Column Program: 40°C – 375°C @ 60°C/min.
  - Column is stainless steel resistively heated
- PC running on Windows With:
  - ChromPerfect chromatography data system software
  - SimDist 2000 software for liquid hydrocarbon characterization by boiling range and reports defined in ASTM D7798
- Leap Auto Sample

Automation Makes An Analytical System

Performance

- Data from 2 US refineries demonstrates the accuracy of the Calidus Model 101-HT

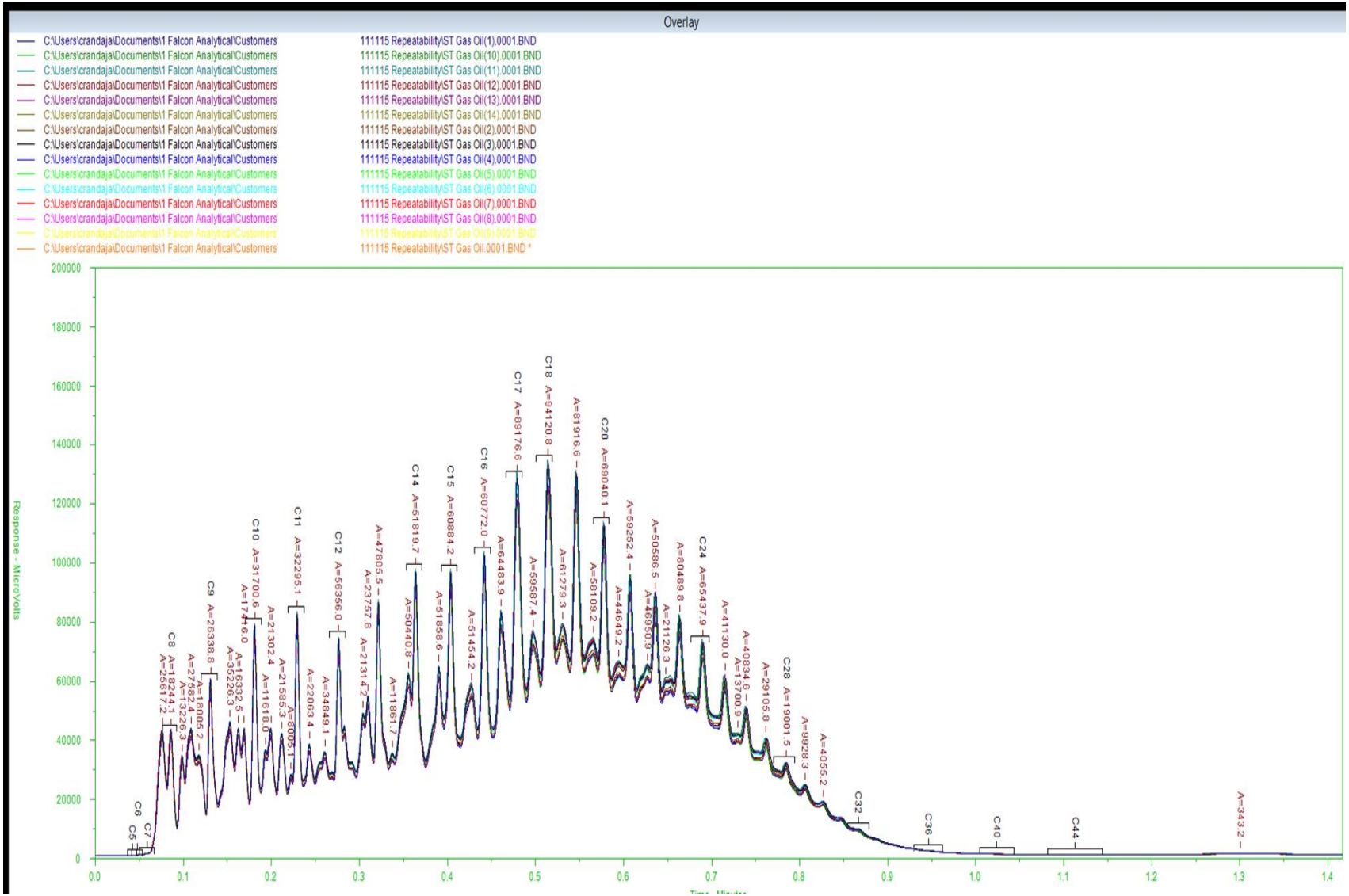
Note

The Inter Laboratory Study (ILS) to determine precision and bias for ASTM method D7798 and D6708 Bias Study between D2887 –A, D2887-B and D7798 to begin fall of 2013.

US Refinery # 1

- 1-set RGO run by same operator 15 replicates
- Fall of 2011
- Shows Average BP, Average Sdev., Average RSD, and average difference from consensus value for boiling points 0.5%, 5%, 10%, 15%,…95% and 99.5%
- Performance with cycle times of 3 min. well within the performance of the 9-18 min. cycle times of the D2887 –A and B.

15 RGO Replicates overlaid



US Refinery # 1
Boiling Point

Rep #	0.5%	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%	90%	95%	99.5%
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*

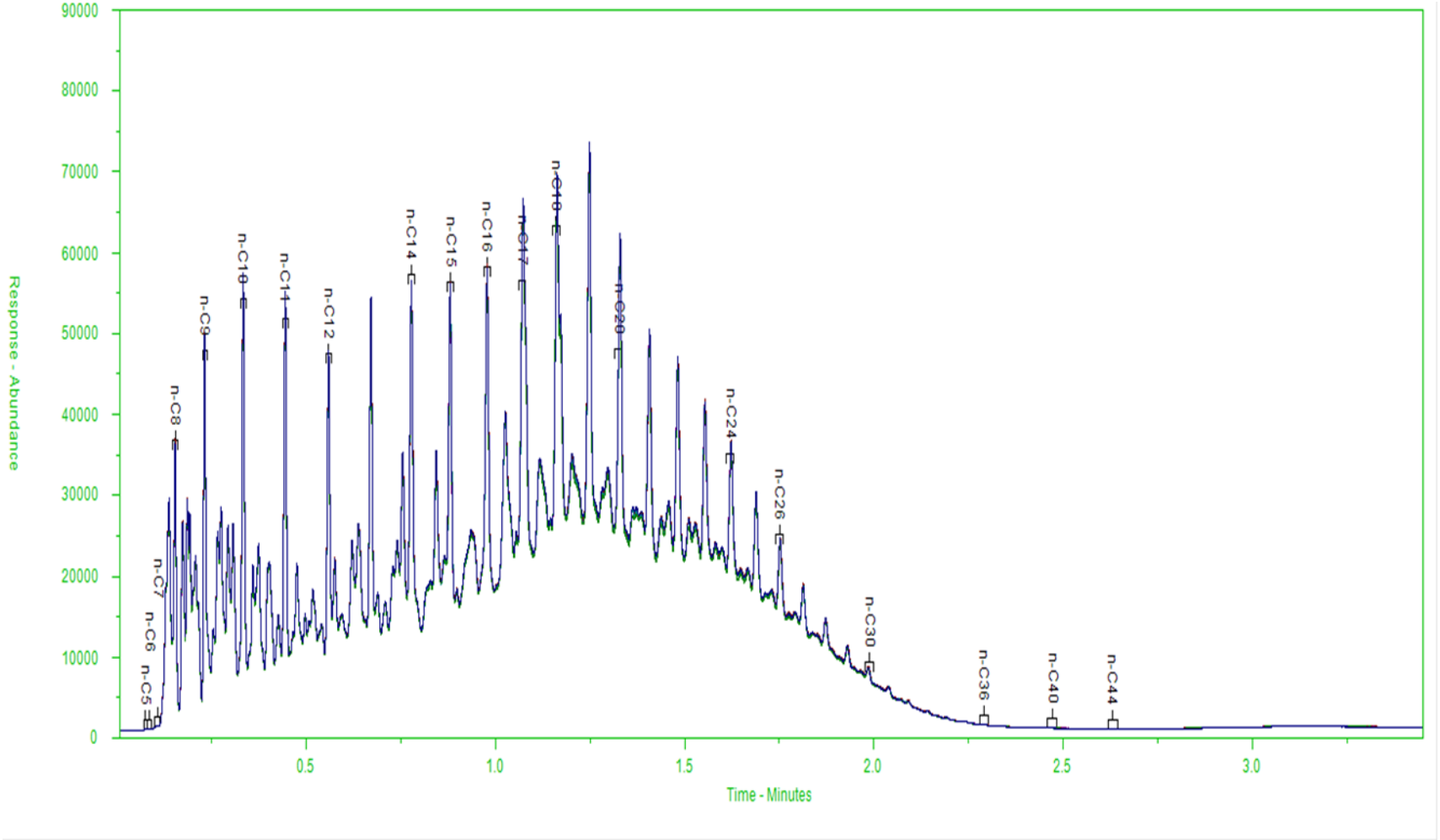
Ave. Sdev = 0.3°F *Ave. RSD = 0.05%*

Ave. Difference from Consensus Value = 1.0°F

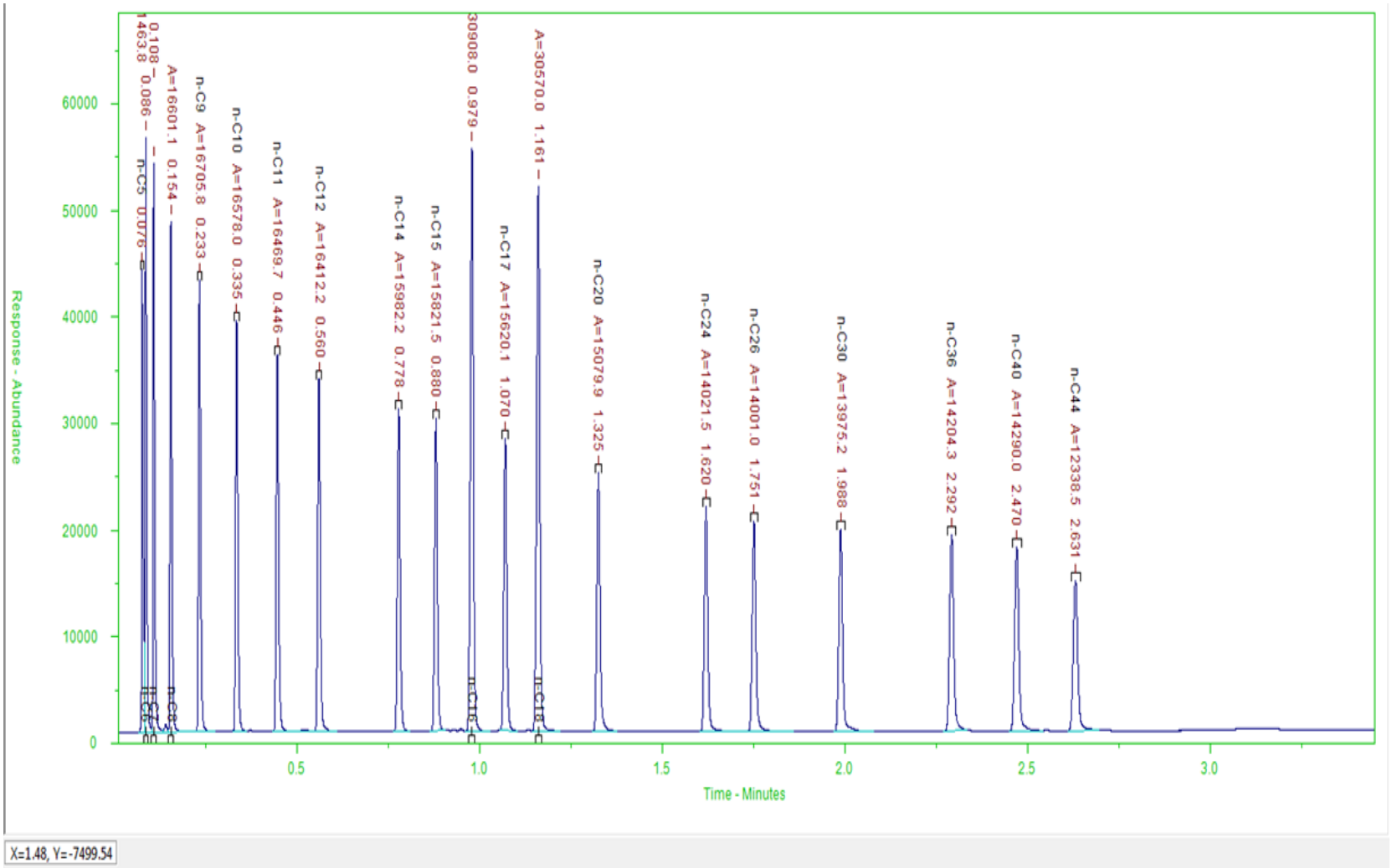
US Refinery # 2

- 5 Consecutive RGO standards run by same operator
- ASTM D2887 Retention Time Calibration Standard
- Replicates of 4 different streams run by same operator
- Average analysis time 210 seconds, average cycle time < 5 min.
- Run during August & September of 2013

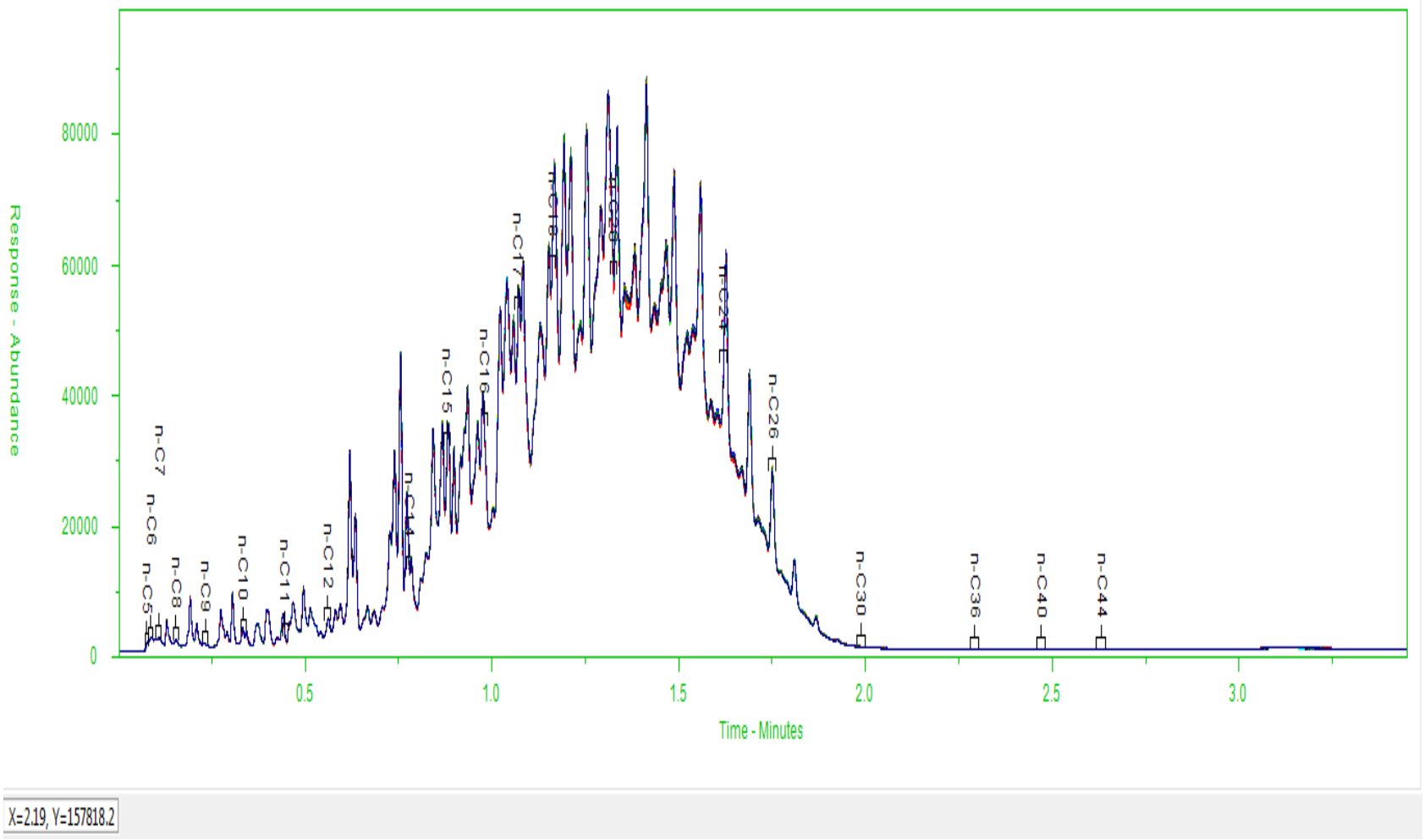
5 Consecutive Reference Gas Oil Standards



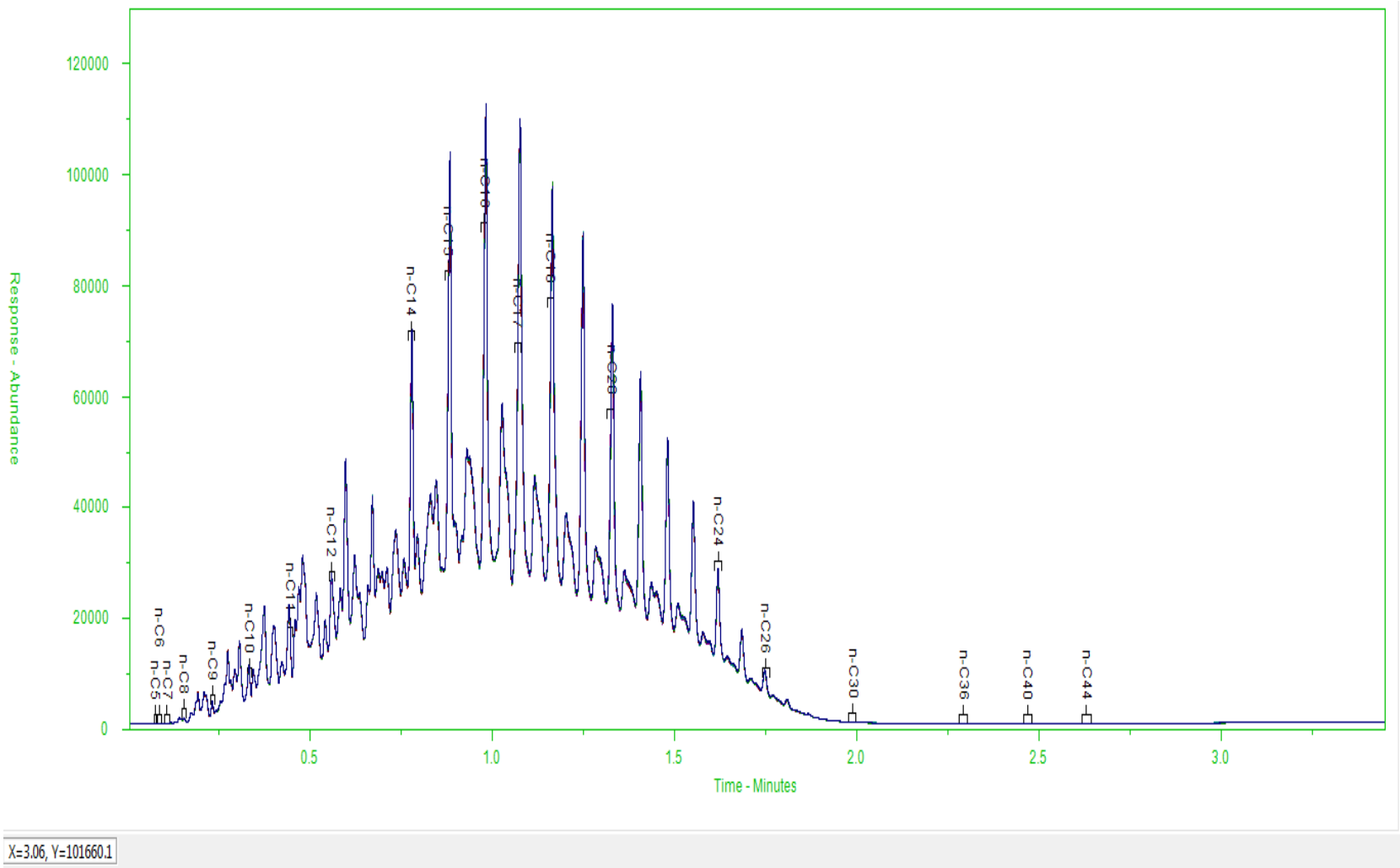
ASTM D-2887 Retention Time Cal. Standard



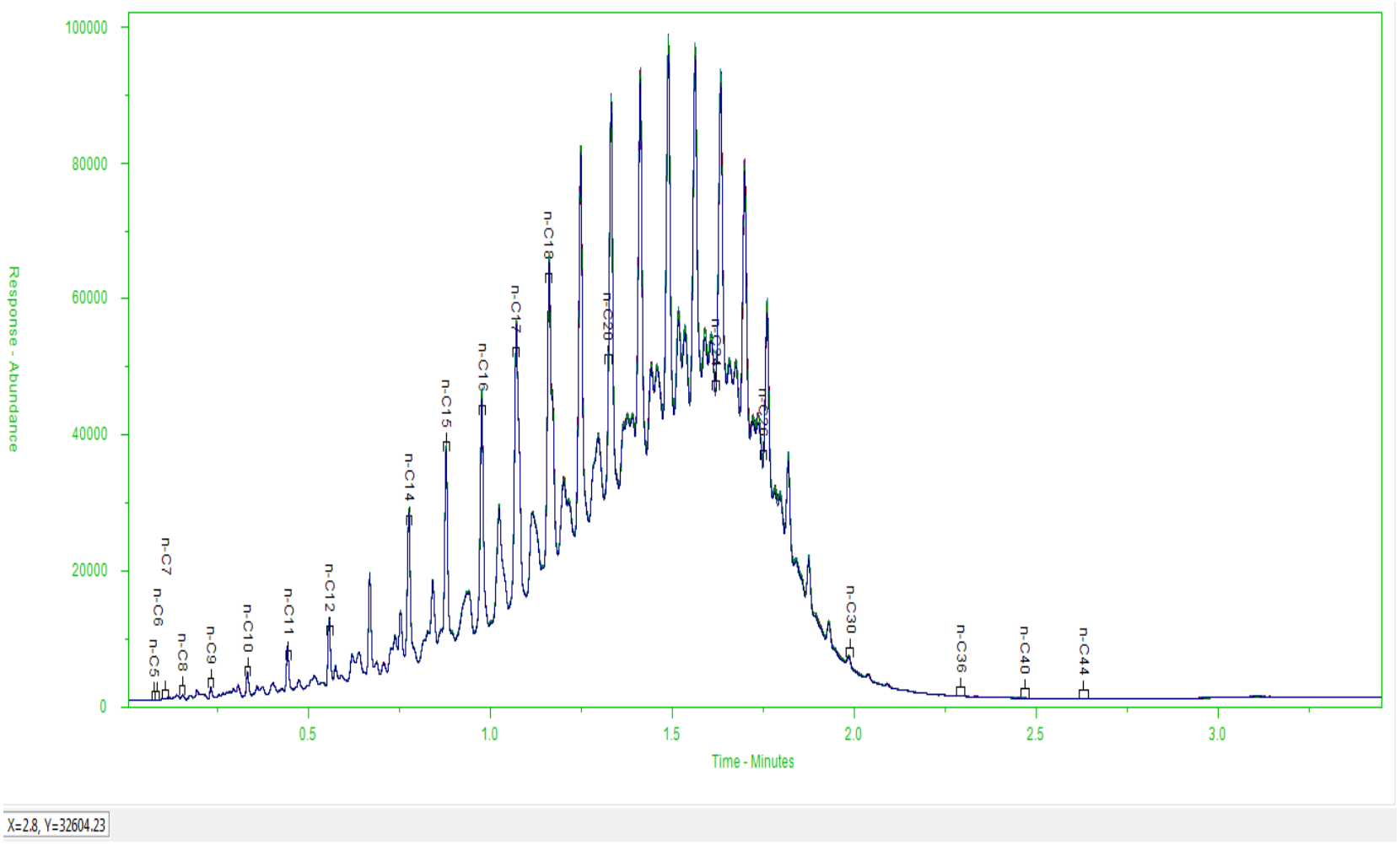
Replicates of Stream 1



Replicates of Stream 2



Replicates of Stream 3



Example Stream X Statistics

% Off	BP (F)	BP (F)	BP (F)	BP (F)	BP (F)		Average	Std Dev	RSD	95% confidence
0.5	227.49	227.36	227.4	227.87	227.13		227.45	0.27	0.12	0.75
5	284.56	284.68	284.83	284.77	284.51		284.67	0.14	0.05	0.38
10	317.16	317.23	317.18	317.33	317.11		317.20	0.08	0.03	0.23
15	330.22	330.27	330.39	330.38	330.17		330.29	0.10	0.03	0.27
20	346.02	346.17	346.54	346.35	346.05		346.23	0.22	0.06	0.60
25	365.99	366.07	366.38	366.3	365.95		366.14	0.19	0.05	0.53
30	386.86	386.78	387.38	387.04	386.81		386.97	0.25	0.06	0.69
35	402.99	403.08	403.61	403.41	402.99		403.22	0.28	0.07	0.78
40	425	425.09	425.82	425.61	424.92		425.29	0.40	0.09	1.11
45	441.85	441.96	442.51	442.44	441.78		442.11	0.34	0.08	0.95
50	462.98	462.86	463.92	463.68	462.51		463.19	0.59	0.13	1.63
55	480.16	480.13	480.48	480.52	480.02		480.26	0.22	0.05	0.62
60	494.49	494.18	495.11	494.91	493.72		494.48	0.56	0.11	1.55
65	512.74	512.56	513.1	513.05	512.29		512.75	0.34	0.07	0.94
70	528.01	527.91	528.47	528.27	527.4		528.01	0.41	0.08	1.13
75	545.15	544.98	545.27	545.33	544.64		545.07	0.28	0.05	0.77
80	568.74	568.34	569.13	568.9	567.79		568.58	0.53	0.09	1.46
85	591.06	590.65	591.86	591.41	590.02		591.00	0.71	0.12	1.96
90	619.48	619.22	619.83	619.79	618.97		619.46	0.37	0.06	1.02
95	655.75	655.28	656.35	655.7	654.66		655.55	0.63	0.10	1.73
99.5	715.87	714.28	718.55	713.63	713		715.07	2.22	0.31	6.15

Example Stream Y Statistics

% Off	BP (F)	BP (F)	BP (F)	BP (F)	BP (F)		Average	Std Dev	RSD	95% confidence
0.5	298.85	298.56	298.73	298.55	298.59		298.66	0.13	0.04	0.36
5	397.43	396.9	396.49	396.71	396.97		396.90	0.35	0.09	0.97
10	442.33	441.98	441.59	442.01	441.98		441.98	0.26	0.06	0.73
15	475.81	475.49	475.04	475.39	475.38		475.42	0.28	0.06	0.76
20	499.5	499.23	498.79	499.04	498.95		499.10	0.27	0.05	0.76
25	517.99	517.54	517.39	517.44	517.27		517.53	0.28	0.05	0.77
30	540.07	539.28	539.29	539.31	539.08		539.41	0.38	0.07	1.06
35	556.7	556.25	556.29	556.13	555.98		556.27	0.27	0.05	0.75
40	571.88	571.54	571.65	571.48	571.28		571.57	0.22	0.04	0.61
45	583.17	582.72	582.97	582.47	582.42		582.75	0.32	0.06	0.89
50	595.99	595.52	595.84	595.37	595.25		595.59	0.31	0.05	0.87
55	605.04	604.68	605.01	604.18	604.21		604.62	0.42	0.07	1.15
60	617.86	617.32	617.8	617.04	617.02		617.41	0.40	0.07	1.12
65	626.9	626.55	626.85	626.22	626.34		626.57	0.30	0.05	0.83
70	638.82	638.39	638.64	637.89	637.99		638.35	0.40	0.06	1.11
75	649.11	648.9	648.97	648.46	648.58		648.80	0.27	0.04	0.76
80	658.37	657.75	658.11	657.17	657.26		657.73	0.52	0.08	1.45
85	669.18	668.6	668.83	668.01	668.09		668.54	0.50	0.07	1.37
90	678.31	677.42	677.76	676.69	676.88		677.41	0.66	0.10	1.82
95	692.34	691.5	691.96	690.86	691.04		691.54	0.62	0.09	1.71
99.5	752.59	721.23	734.1	718.28	718.47		728.93	14.74	2.02	40.82

Example Stream Z Statistics

% Off	BP (F)	BP (F)	BP (F)	BP (F)	BP (F)		Average	Std Dev	RSD	95% confidence
0.5	359	358.04	359.08	357.86	357.8		358.36	0.63	0.18	1.75
5	489.64	489.29	489.74	489.33	489.45		489.49	0.20	0.04	0.54
10	540.98	539.97	540.5	539.99	540.38		540.36	0.42	0.08	1.15
15	575.1	574.63	574.93	574.62	574.76		574.81	0.21	0.04	0.57
20	598.3	597	597.75	597.15	597.41		597.52	0.52	0.09	1.44
25	616.79	615.77	616.44	615.91	616.06		616.19	0.42	0.07	1.15
30	633.64	632.68	633.14	632.71	632.92		633.02	0.39	0.06	1.09
35	651.9	651.25	651.63	651.29	651.37		651.49	0.27	0.04	0.76
40	665.21	664.19	664.75	664.55	664.55		664.65	0.37	0.06	1.03
45	677.51	677.06	677.31	677.13	677.23		677.25	0.17	0.03	0.48
50	690.57	689.58	690.12	689.96	689.92		690.03	0.36	0.05	1.00
55	701.07	700.41	700.82	700.79	700.7		700.76	0.24	0.03	0.66
60	713.48	712.39	713.07	712.93	712.76		712.93	0.40	0.06	1.11
65	723.63	722.64	723.16	723.07	722.75		723.05	0.39	0.05	1.08
70	735.94	734.68	735.65	735.26	734.93		735.29	0.51	0.07	1.42
75	746.48	745.12	745.93	745.83	745.35		745.74	0.53	0.07	1.47
80	759.31	758.41	759.06	758.81	758.54		758.83	0.37	0.05	1.02
85	772.96	771.49	772.26	771.92	771.7		772.07	0.58	0.07	1.59
90	789.02	787.01	787.98	787.77	787.55		787.87	0.74	0.09	2.05
95	813.75	810.57	811.87	811.62	811.4		811.84	1.17	0.14	3.25
99.5	902.52	884.52	890.83	892.84	892.89		892.72	6.46	0.72	17.89

Example Stream N Statistics

% Off	BP (F)	BP (F)	BP (F)	BP (F)	BP (F)		Average	Std Dev	RSD	95% confidence
0.5	242.69	243	243.55	243.35	243.89		243.30	0.47	0.19	1.30
5	494.33	496.66	495.1	497.25	496.68		496.00	1.23	0.25	3.41
10	578.44	579.86	578.98	580.26	580.1		579.53	0.78	0.14	2.17
15	626	626.99	626.47	627.15	627.07		626.74	0.49	0.08	1.36
20	656.89	658.55	657.85	659.09	658.93		658.26	0.90	0.14	2.50
25	679.61	680.92	680.39	681.48	681.29		680.74	0.76	0.11	2.09
30	697.75	698.39	698.09	698.75	698.65		698.33	0.41	0.06	1.14
35	711.99	712.91	712.55	713.25	713.3		712.80	0.54	0.08	1.51
40	723.47	724.39	723.85	724.59	724.49		724.16	0.48	0.07	1.33
45	735.39	736.26	735.76	736.66	736.42		736.10	0.52	0.07	1.43
50	744.98	745.95	745.38	746.09	746.02		745.68	0.48	0.06	1.34
55	755.98	757.04	756.35	757.21	757.15		756.75	0.55	0.07	1.52
60	765.56	766.82	766	766.99	766.78		766.43	0.62	0.08	1.71
65	776.71	777.81	777.24	777.99	777.83		777.52	0.53	0.07	1.48
70	786.94	788.34	787.65	788.53	788.28		787.95	0.65	0.08	1.81
75	798.35	799.72	799.17	799.78	799.6		799.32	0.59	0.07	1.65
80	811.81	813.1	812.43	813.04	812.73		812.62	0.53	0.06	1.46
85	826.87	828.31	827.63	828.2	827.91		827.78	0.58	0.07	1.59
90	846	847.75	846.87	847.61	847.13		847.07	0.70	0.08	1.93
95	876.46	878.41	877.3	877.86	876.97		877.40	0.76	0.09	2.11
99.5	960.89	965.64	964.58	965.33	957.25		962.74	3.61	0.37	9.99

Performance Summary

- Precision is excellent across the board
  - Broad range of samples
  - Several replicates each
  - Over period of 10’s of day
- Reproducibility is excellent

Significance

Given the performance and the analysis cycle times of the Calidus Model 101-HT and using the following assumptions we can easily determine significance in throughput and cost savings employing this method.

Significance

Assumptions:

Cost per hour = $80

D2887 – B run time 9 min.

# of analysis per Hr. = 6

cost per analysis = $13

D7798 run time = 3 min.

# of analysis per Hr. = 20

cost per analysis = $4

Significance

- At the end of the day laboratory testing cost does not add to the bottom line.
- The flip side of that coin is that erroneous laboratory results can cost you dearly.

Significance

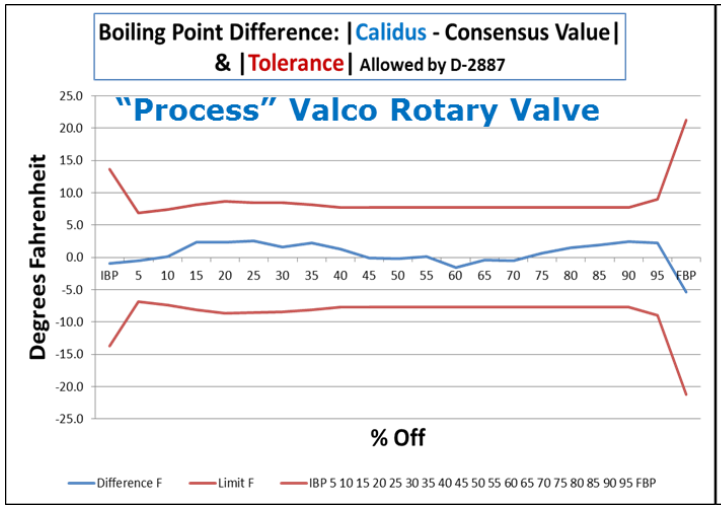
- If an on-line instrument and the laboratory instrument are of the same type then the lab job becomes the validation of the on-line measurement.
- Don’t forget the cost per square foot of laboratory bench space.

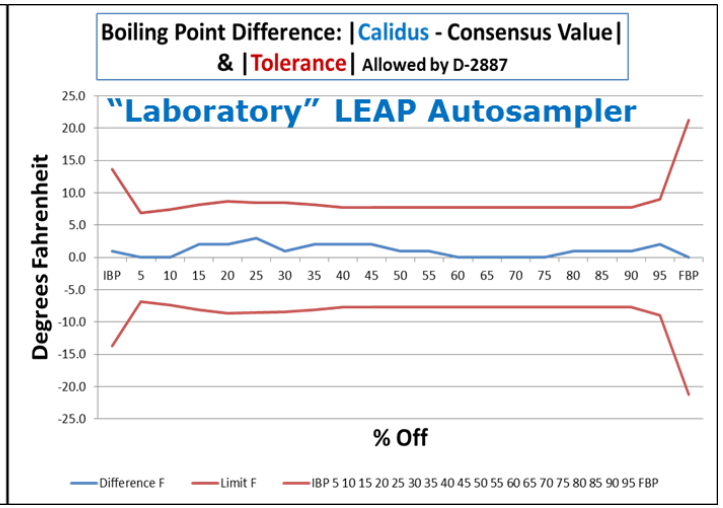
Benefits of Hydrogen Carrier

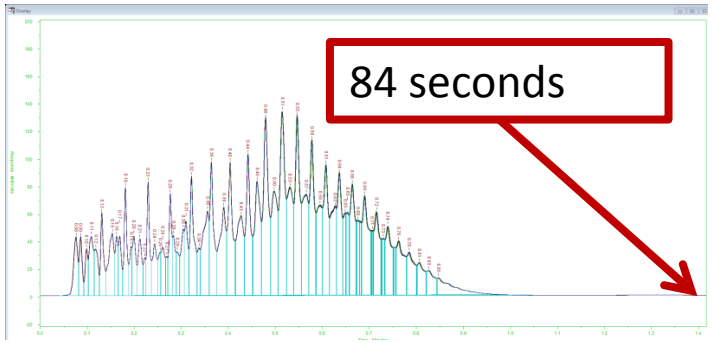
- Cost of Helium
- Cost of Hydrogen
- Chromatography benefits of Hydrogen
  - About 1/3 faster than Helium
  - Flow rates are low at < 2 ml/min
  - Hydrogen required for the detector anyhow
  - Reduces gas utilities by one kind

The Results Are… THE SAME

regardless of installation site







Conclusion

- No risk in performance by using ASTM D7798
- Significant increase in lab throughput
- Significant reduction in cost
- Equals big profits