



2012 Update On New ASTM Ultrafast 2887 Method

Proposed Standard Test Method for the
Boiling Range Distribution of Petroleum
Distillates w/FBP up to 538° C



Paper Discussion

- ***Why a new method?***
- ***Summary of the new method***
- ***Data from the new method***
- ***Current status***
- ***Next steps***

Why a New Method?

- **Simple - a need in the industry**
- **That need is speed!**
 - **Existing 2887 method analysis time is 15 min. plus.**
 - **New proposed method analysis time is 5 min. or less.**
- **D02.04H subcommittee agreed that this kind of speed was needed in the industry and a new method could be pursued if the GC could run the ASTM approved Reference Gas Oil with results equal to or better than the existing method.**
 - **Completed and presented to D02.04H in December 2010. D02.04H agreed to the pursuit and writing of the new method.**

Summary of the New Method

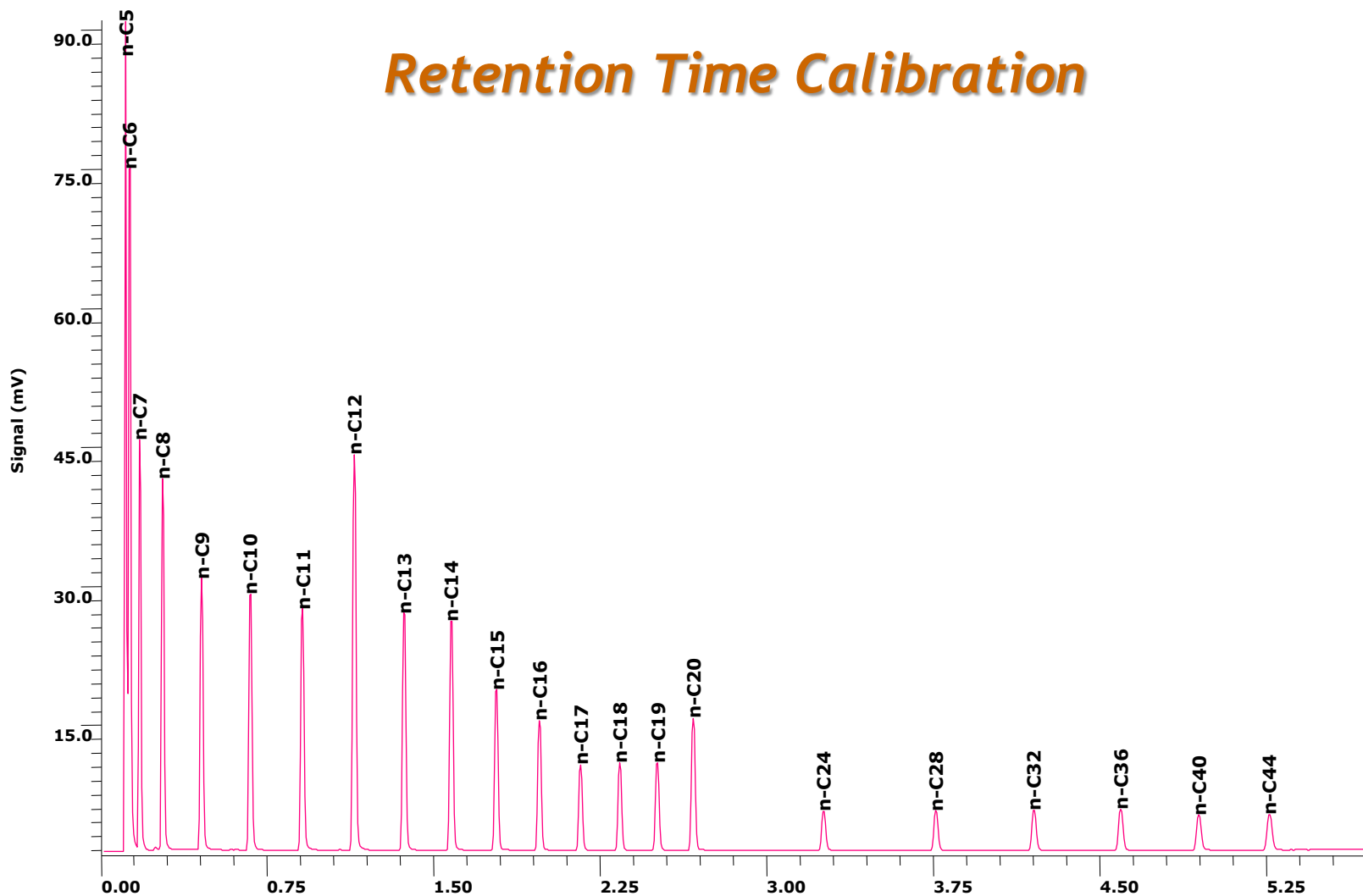
- **Gas Chromatograph**
 - *Sample Inject with temperature, pressure, flow, and sample volume control*
 - *A directly heated column (no analytical oven) with temperature, pressure, and flow control*
 - *FID detector with signal conversion, amplification, and fuel supply control*
- **Data Acquisition System**

Examples of UFGC Operating Conditions and Column Assembly Heating Types

Parameters	Instrument A	Instrument B	Instrument C
	Resistively heated columns	Resistively heated columns	Resistively heated columns
Inlet Temperature	Programmable TPI; 100°C to 360°C @ 300 °C/min- 1.0 min.	Split: Split ratio 50:1-150:1 350°C	Split/Splitless 0.4min purge delay
Auto sampler	Required	required	required
Data collection	100 Hz	100 Hz	100 Hz
Column	4-m-0.25mm 0.25 μ pdms	2m-0.32mm-0.20μ-pdms	5m-0.53mm-2.65u pdms
Inlet/FID Transfer Lines	360 ° C	350°C	340 ° C
Flow conditions	4 ml/min	1ml/min	9 ml/min
Make-up gas	25 ml/min		25 ml/min
Detector	Flame Ionization 400 °C	Flame Ionization; 350 °C	Flame Ionization 380 °C
Column program	40° to 360° at 160°C/min-1min	40°C-375°C at 60° C/min	40° (0.5min)to 240C° at 100°C/min-then 340°C at 100°C/min-0.5 min
Equilibration time	2min	1.5 min.	2min
Sample size	0.2μl	0.3-0.08 μl	0.2μl
Sample dilution	2% in CS ₂	2% in CS ₂ up to neat	neat
Calibration dilution	1% total solids in CS ₂	0.1wt/w% each component in CS ₂	1% total solids in CS ₂
Carrier	He	H ₂	He

Data from the new method

Retention Time Calibration



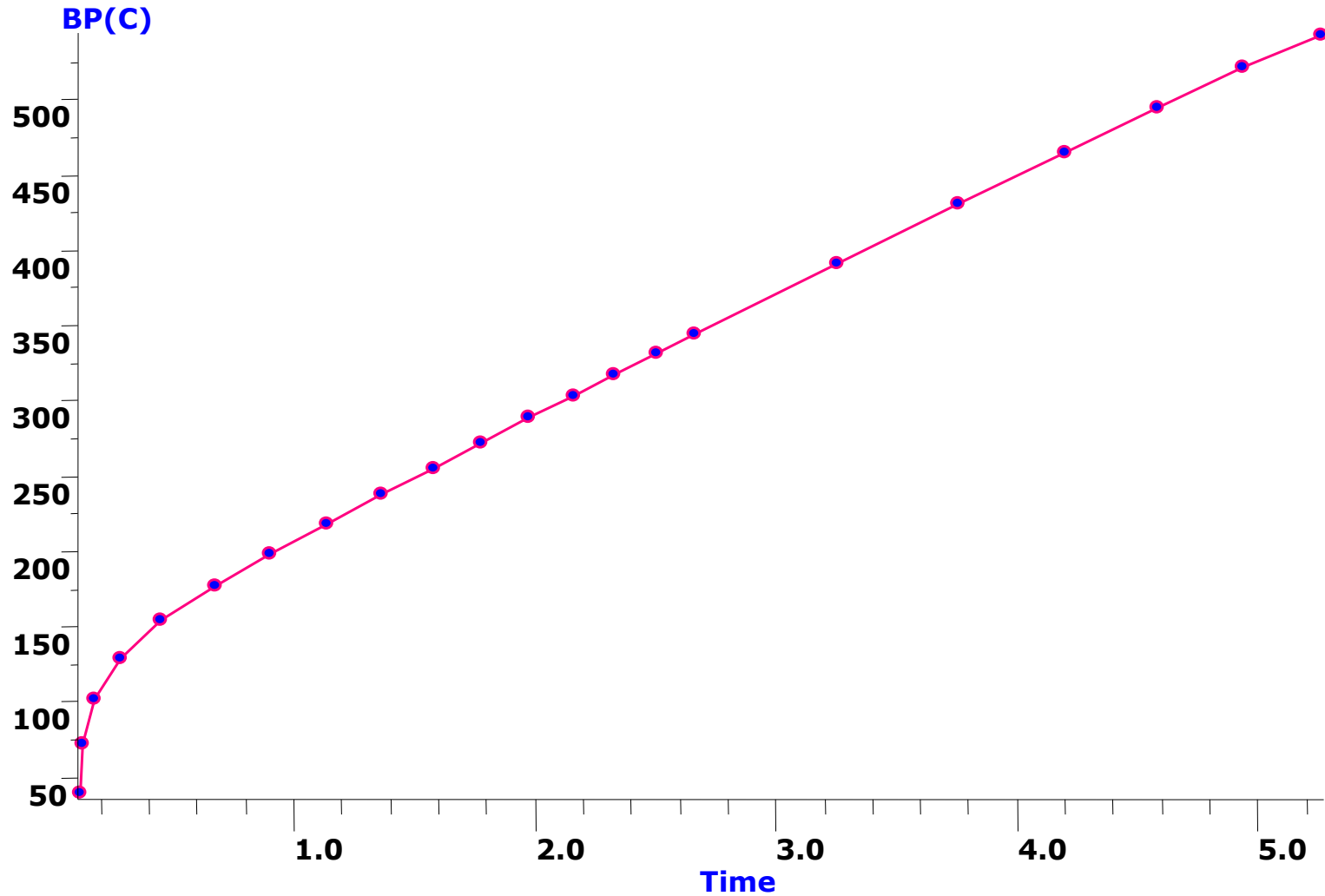
Peak Skewness & Resolution Calculations

Retention Time Calibration

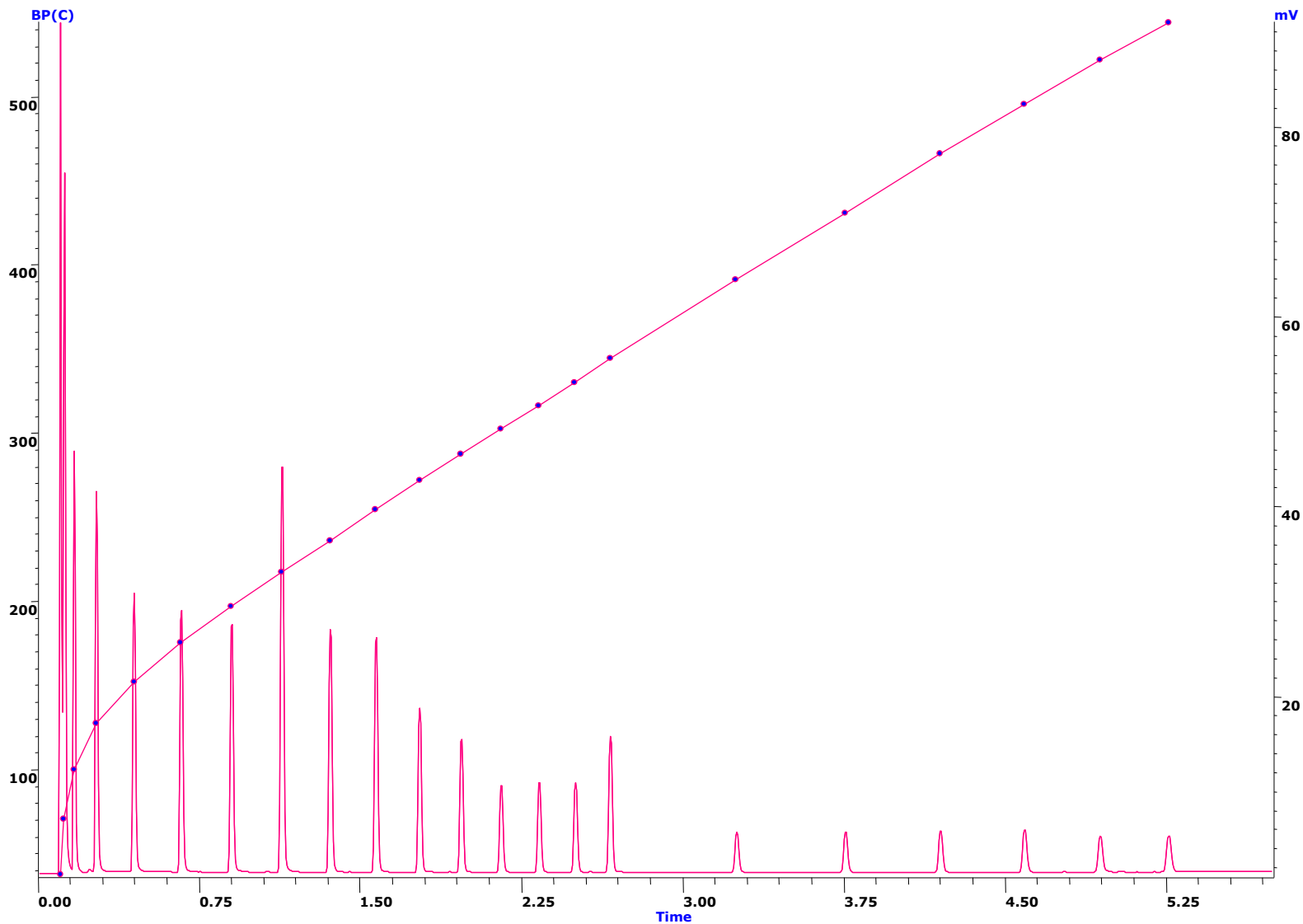
Component	Time	BP(C)	Skewness
n-C5	0.100	36.1	
n-C6	0.119	68.9	
n-C7	0.164	98.4	0.60
n-C8	0.268	126.1	0.72
n-C9	0.444	151.1	0.78
n-C10	0.664	174.1	0.83
n-C11	0.899	196.1	0.86
n-C12	1.134	216.3	0.97
n-C13	1.359	235.4	0.90
n-C14	1.572	253.9	0.93
n-C15	1.775	271.1	0.91
n-C16	1.969	287.2	0.86
n-C17	2.155	302.2	0.82
n-C18	2.332	316.1	0.83
n-C19	2.501	330.0	0.85
n-C20	2.664	343.9	0.87
n-C24	3.253	391.1	0.80
n-C28	3.760	431.1	0.81
n-C32	4.203	466.1	0.80
n-C36	4.595	496.1	0.81
n-C40	4.948	522.2	0.84
n-C44	5.266	545.0	0.82

File S:\1. Employee Files\Joaquin\FALCON_GC\110331.0036.CDF
Sample Id SS D2887
LIMS Id
Parameter File 110331
Column Resolution 16.0 [3.0, 30.0] [n-C16, n-C18]
Injection Date MAR 31, 2011 - 16:05:48

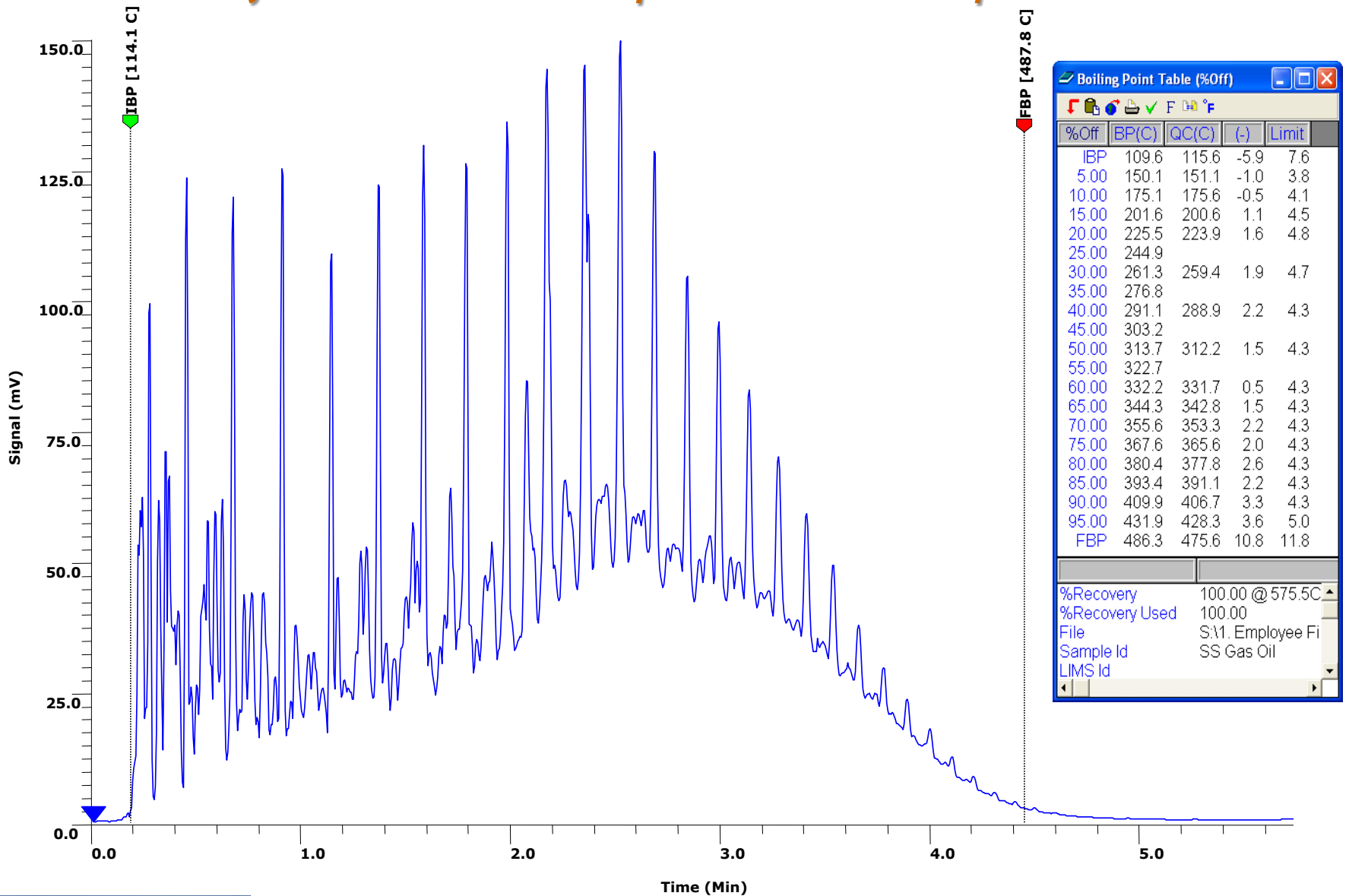
Retention Time Calibration Plot



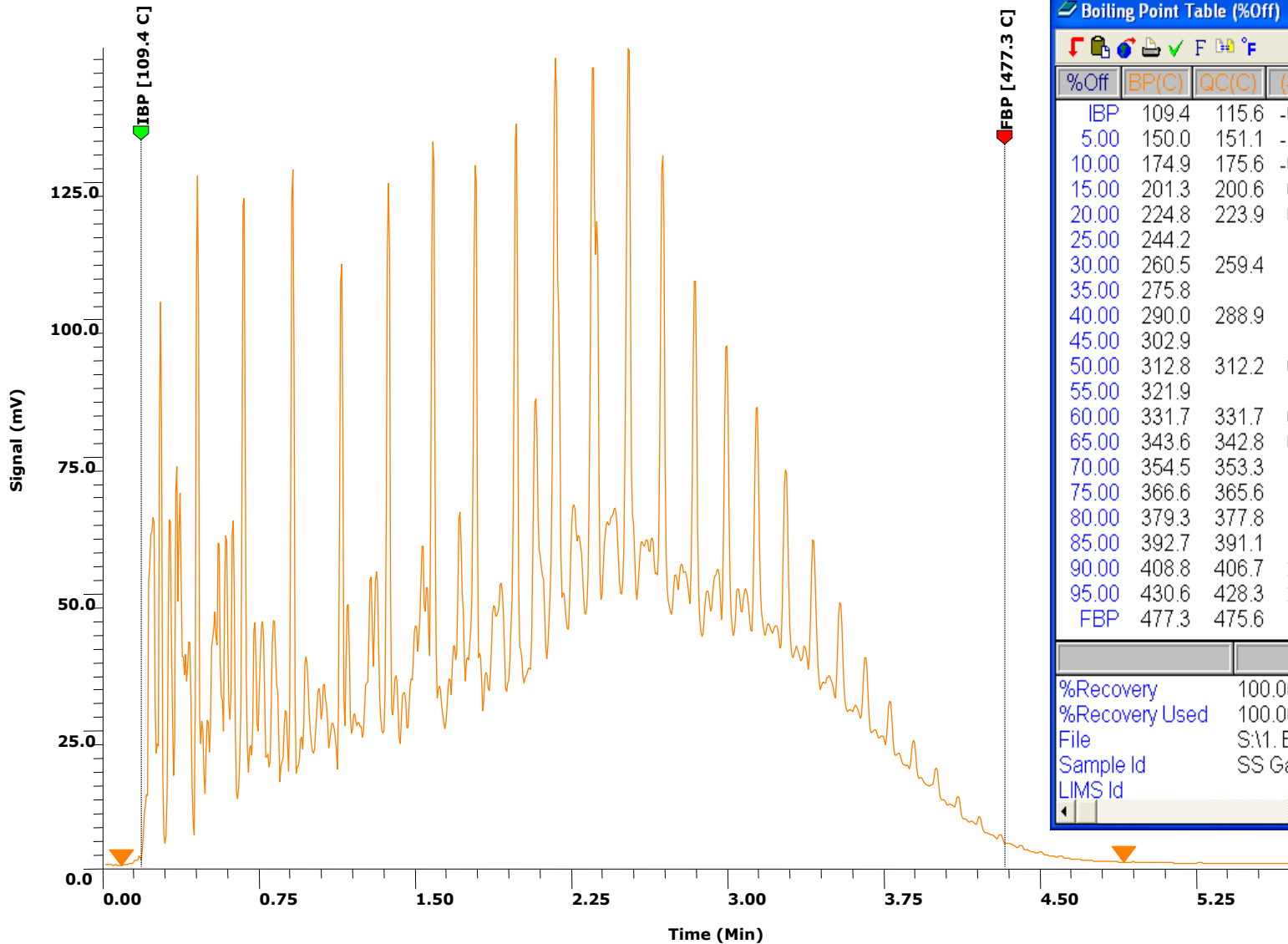
Retention Time Standard Overlaid the Retention Time Calibration Plot



ASTM Reference Gas Oil Comparison with Accepted Values



ASTM Reference Gas Oil Comparison with Accepted Values

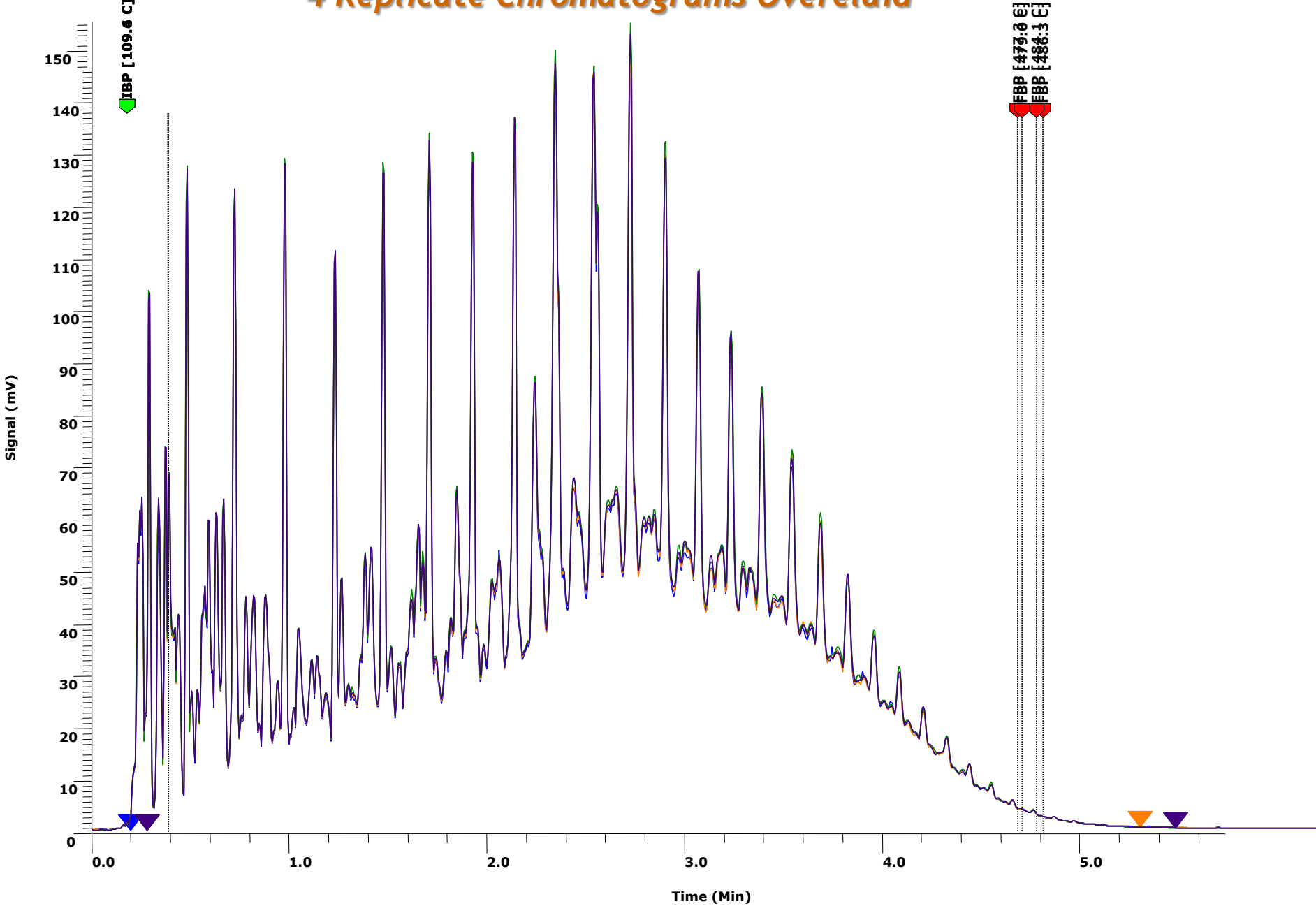


%Off	BP(C)	QC(C)	(-)	Limit
IBP	109.4	115.6	-6.2	7.6
5.00	150.0	151.1	-1.1	3.8
10.00	174.9	175.6	-0.7	4.1
15.00	201.3	200.6	0.8	4.5
20.00	224.8	223.9	0.9	4.8
25.00	244.2			
30.00	260.5	259.4	1.0	4.7
35.00	275.8			
40.00	290.0	288.9	1.1	4.3
45.00	302.9			
50.00	312.8	312.2	0.6	4.3
55.00	321.9			
60.00	331.7	331.7	0.0	4.3
65.00	343.6	342.8	0.8	4.3
70.00	354.5	353.3	1.1	4.3
75.00	366.6	366.6	1.0	4.3
80.00	379.3	377.8	1.5	4.3
85.00	392.7	391.1	1.6	4.3
90.00	408.8	406.7	2.1	4.3
95.00	430.6	428.3	2.3	5.0
FBP	477.3	475.6	1.7	11.8

%Recovery	100.00 @ 516.9C
%Recovery Used	100.00
File	S:\1. Employee File
Sample Id	SS Gas Oil
LIMS Id	



4 Replicate Chromatograms Overlaid

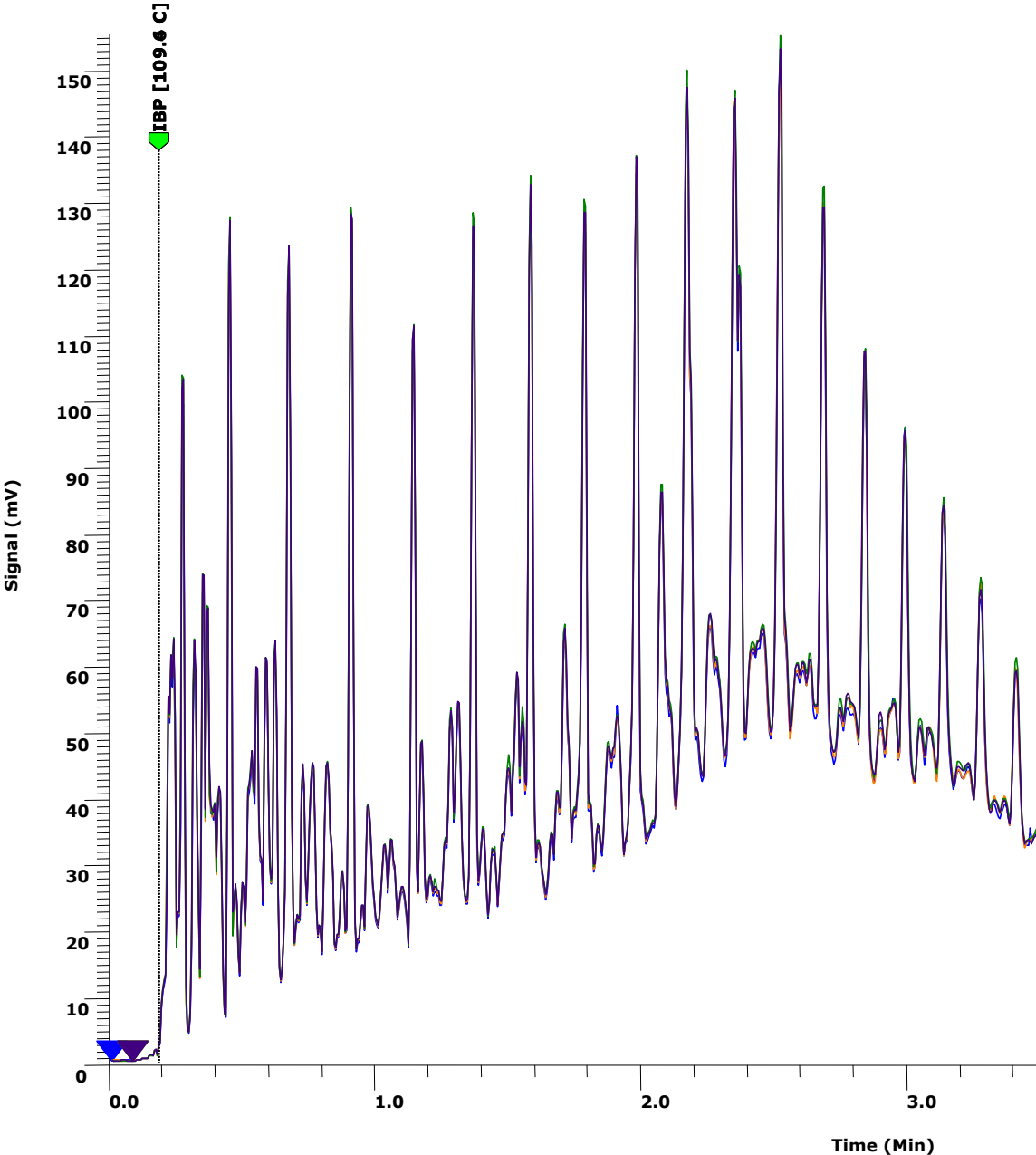


Reference Gas Oil Repeatability (single instrument)

%Off	BP(C)	BP(C)	BP(C)	BP(C)	AVERAGE	STD_DEV	REPEATABILITY	NUMBER OF
							LIMIT	RESULTS
IBP	109.4	109.4	109.6	111.6	110	1	2.77	4
5	150.1	150.1	150.1	146.1	149.09	1.32	3.6564	4
10	175	175.2	174.8	173.4	174.58	0.47	1.3019	4
15	201.5	201.7	201.2	196.4	200.19	1.26	3.4902	4
20	225	225.5	224.7	217.4	223.16	1.72	4.7644	4
25	244.4	245	244.1	236.7	242.57	1.61	4.4597	4
30	260.7	261.3	260.5	254.9	259.37	1.16	3.2132	4
35	276.1	276.7	275.9	271.8	275.13	0.81	2.2437	4
40	290.3	291	290.1	287.5	289.75	0.53	1.4681	4
45	303	303.2	303	299.8	302.25	0.53	1.4681	4
50	313	313.5	313	310.3	310.45	0.47	1.3019	4
55	322.1	322.5	322.1	319.8	321.62	0.38	1.0526	4
60	331.8	332.1	331.8	331	331.68	0.15	0.4155	4
65	343.9	344.2	343.8	341.1	343.25	0.42	1.1634	4
70	354.8	355.3	354.8	352.2	354.28	0.39	1.0803	4
75	367	367.3	366.9	364.5	366.42	0.36	0.9972	4
80	379.8	380.1	379.8	377.3	379.26	0.35	0.9695	4
85	393	393.2	393	391.3	392.61	0.23	0.6371	4
90	409.4	409.6	409.5	406.8	408.81	0.33	0.9141	4
95	431.5	431.6	431.6	428.8	430.88	0.33	0.9141	4
FBP	485.5	484.1	485.1	476.1	482.7	0.92	2.5484	4



ASTM Reference Gas Oil Boiling Point Repeatability



Boiling Point Table (%Off)

% Off	BP(C)	BP(C)	BP(C)	BP(C)	Avg	%SDV
IBP	109.6	109.4	109.4	109.6	109.49	0.12
5.00	150.1	150.0	150.1	150.1	150.08	0.03
10.00	175.1	174.9	175.2	174.8	174.97	0.10
15.00	201.6	201.3	201.7	201.1	201.43	0.13
20.00	225.5	224.8	225.5	224.5	225.08	0.23
25.00	244.9	244.2	245.0	243.9	244.50	0.23
30.00	261.3	260.5	261.3	260.3	260.87	0.21
35.00	276.8	275.8	276.7	275.7	276.26	0.22
40.00	291.1	290.0	291.0	289.9	290.52	0.22
45.00	303.2	302.9	303.2	302.9	303.05	0.05
50.00	313.7	312.8	313.5	312.8	313.21	0.15
55.00	322.7	321.9	322.5	321.9	322.23	0.13
60.00	332.2	331.7	332.1	331.7	331.92	0.08
65.00	344.3	343.6	344.2	343.6	343.92	0.11
70.00	355.6	354.5	355.3	354.6	354.95	0.15
75.00	367.6	366.6	367.3	366.6	367.04	0.14
80.00	380.4	379.3	380.1	379.5	379.82	0.13
85.00	393.4	392.7	393.2	392.8	392.99	0.08
90.00	409.9	408.8	409.6	409.0	409.31	0.13
95.00	431.9	430.6	431.6	430.9	431.26	0.14
FBP	486.3	477.3	484.1	479.0	481.67	0.88

	Sample Id	Start Time	End Time	%Recovery	%
■	SS Gas Oil	0.015	5.746	100.00	
■	SS Gas Oil	0.090	4.904	100.00	
■	SS Gas Oil	0.093	5.745	100.00	
■	SS Gas Oil	0.093	5.068	100.00	

Pre-shipment Results: Restek D-2887 Standard Overlaid Separation Systems Standard Gas Oil

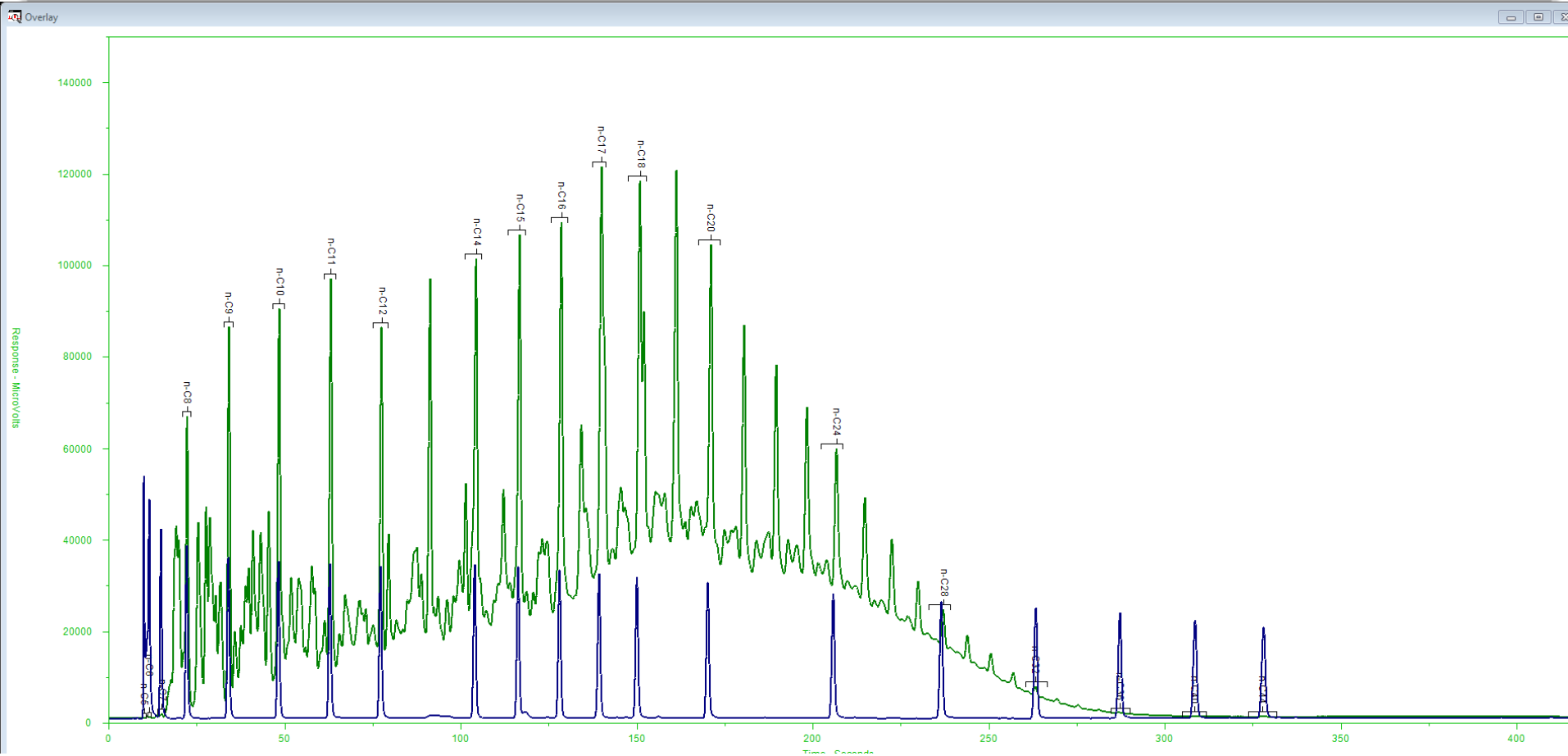
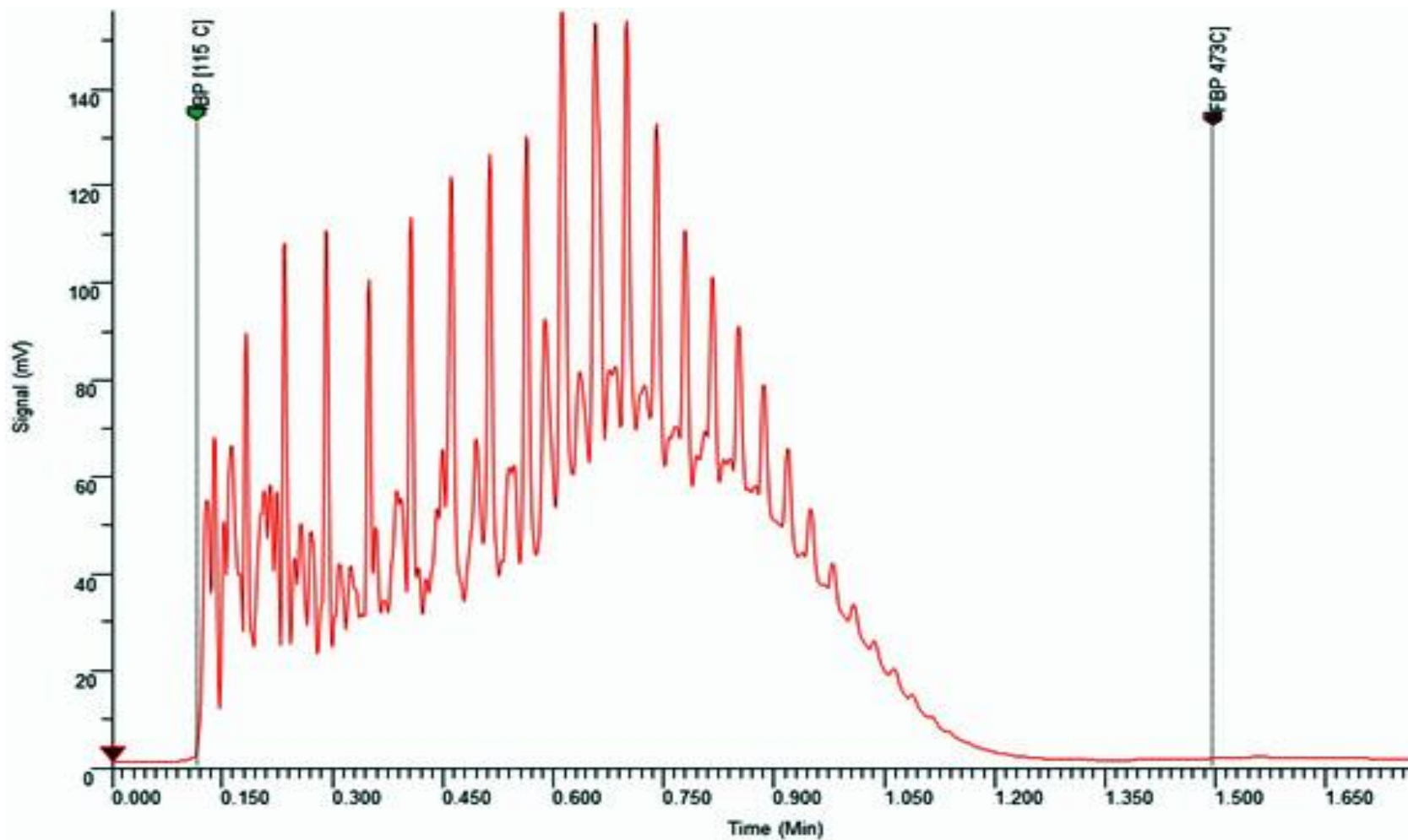


FIGURE 5B: CHROMATOGRAM OF THE REFERENCE GAS OIL OBTAINED WITH ULTRA FAST CHROMATOGRAPHIC CONDITIONS (INSTRUMENT B)



Seven Replicate Repeatability

BP Distribution	#23	#24	#25	#26	#27	#28	#29	AVG	STDEV	RSD
IBP	238.28	238.07	238.02	237.78	237.98	238.10	238.09	238.05	0.15	0.063%
5%	303.69	303.40	303.37	303.31	303.53	303.43	303.38	303.44	0.13	0.042%
10%	350.53	348.44	348.79	348.66	350.02	348.96	348.66	349.15	0.80	0.228%
15%	396.88	394.69	395.04	394.74	396.39	395.05	394.65	395.35	0.90	0.229%
20%	439.25	436.66	437.23	436.30	438.74	437.10	436.45	437.39	1.15	0.264%
25%	473.52	470.75	471.56	470.16	473.01	471.37	470.61	471.57	1.26	0.267%
30%	502.47	499.82	500.63	499.13	502.04	500.56	499.86	500.64	1.22	0.243%
35%	529.89	527.45	528.13	526.77	529.56	528.14	527.59	528.22	1.13	0.214%
40%	554.56	552.54	553.21	552.06	554.50	553.27	552.83	553.28	0.95	0.171%
45%	576.14	575.71	575.85	575.60	576.17	575.87	575.91	575.89	0.21	0.036%
50%	594.44	593.28	593.73	593.06	594.53	593.71	593.64	593.77	0.55	0.092%
55%	610.68	609.65	610.09	609.48	610.74	610.01	609.99	610.09	0.48	0.078%
60%	627.68	627.22	627.44	627.18	627.81	627.31	627.40	627.43	0.23	0.037%
65%	649.00	648.23	648.60	648.30	649.17	648.40	648.50	648.60	0.36	0.055%
70%	668.90	668.09	668.46	668.31	669.05	668.20	668.42	668.49	0.36	0.053%
75%	690.94	690.16	690.58	690.58	691.17	690.42	690.63	690.64	0.33	0.048%
80%	713.73	713.05	713.44	713.65	714.07	713.36	713.47	713.54	0.32	0.045%
85%	737.93	737.75	737.90	738.05	738.19	737.82	737.90	737.93	0.15	0.020%
90%	766.29	766.08	766.37	766.83	766.77	766.23	766.42	766.43	0.28	0.036%
95%	804.88	804.85	805.12	806.11	805.45	805.08	805.09	805.22	0.44	0.054%
FBP	880.67	880.59	880.92	886.22	881.04	880.80	880.99	881.60	2.04	0.232%
100%	914.03	913.87	913.87	934.74	913.37	913.68	913.92	916.78	7.92	0.864%

The average STDEV is < 1°F including FBP & 100%.
 Excluding both 100% and FBP (99.5%) it is ~0.6°F.
 This performance should enable very tight control
 limits in process.



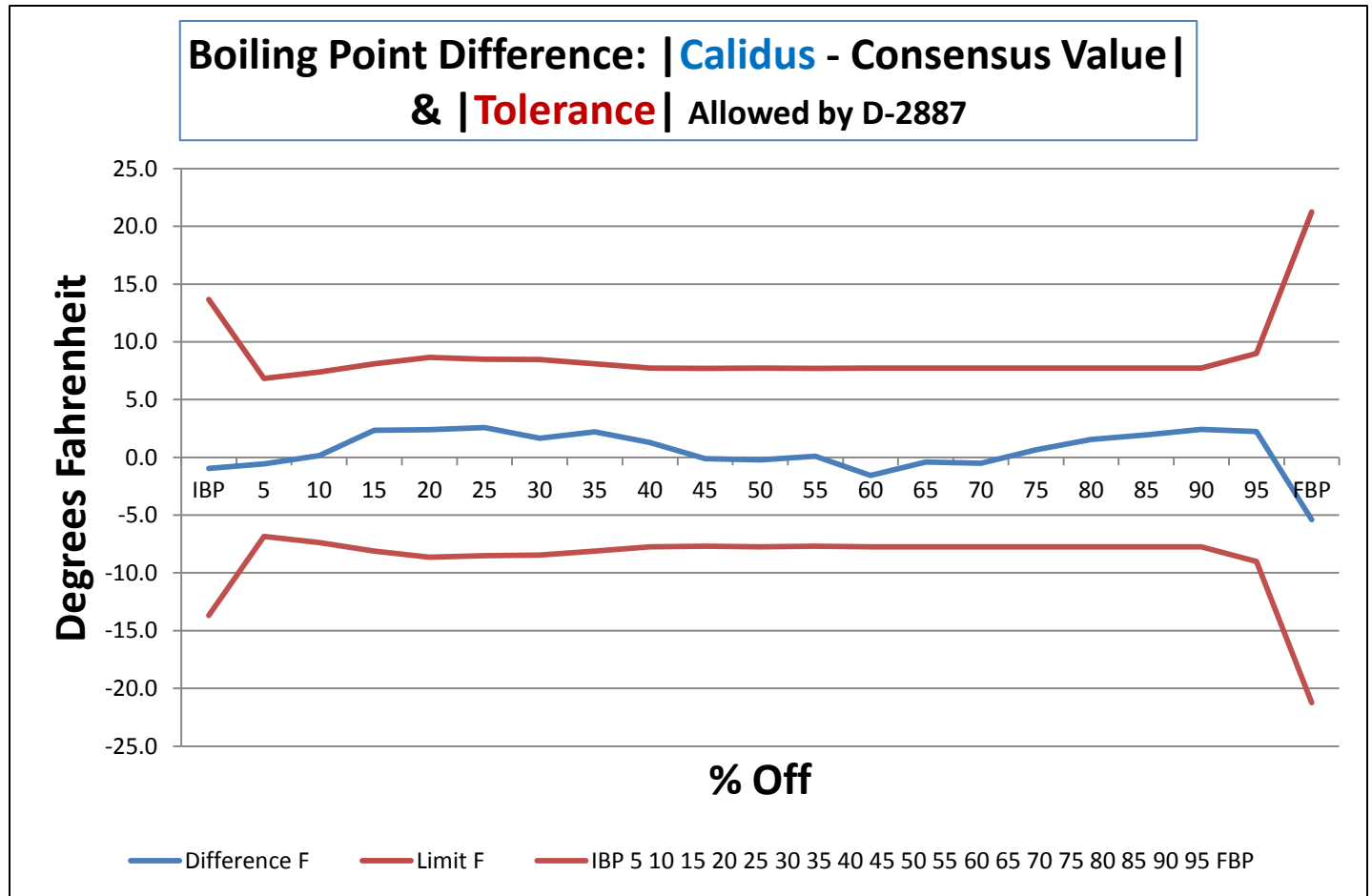
7 Replicate Comparison to Accepted Values

	Consensus	#23		#24		#25		#26		#27		#28		#29	
IBP	239	238.28	0.72	238.07	0.93	238.02	0.98	237.78	1.22	237.98	1.02	238.10	0.90	238.09	0.91
5%	304	303.69	0.31	303.40	0.60	303.37	0.63	303.31	0.69	303.53	0.47	303.43	0.57	303.38	0.62
10%	349	350.53	-1.53	348.44	0.56	348.79	0.21	348.66	0.34	350.02	-1.02	348.96	0.04	348.66	0.34
15%	393	396.88	-3.88	394.69	-1.69	395.04	-2.04	394.74	-1.74	396.39	-3.39	395.05	-2.05	394.65	-1.65
20%	435	439.25	-4.25	436.66	-1.66	437.23	-2.23	436.30	-1.30	438.74	-3.74	437.10	-2.10	436.45	-1.45
25%	469	473.52	-4.52	470.75	-1.75	471.56	-2.56	470.16	-1.16	473.01	-4.01	471.37	-2.37	470.61	-1.61
30%	499	502.47	-3.47	499.82	-0.82	500.63	-1.63	499.13	-0.13	502.04	-3.04	500.56	-1.56	499.86	-0.86
35%	526	529.89	-3.89	527.45	-1.45	528.13	-2.13	526.77	-0.77	529.56	-3.56	528.14	-2.14	527.59	-1.59
40%	552	554.56	-2.56	552.54	-0.54	553.21	-1.21	552.06	-0.06	554.50	-2.50	553.27	-1.27	552.83	-0.83
45%	576	576.14	-0.14	575.71	0.29	575.85	0.15	575.60	0.40	576.17	-0.17	575.87	0.13	575.91	0.09
50%	594	594.44	-0.44	593.28	0.72	593.73	0.27	593.06	0.94	594.53	-0.53	593.71	0.29	593.64	0.36
55%	610	610.68	-0.68	609.65	0.35	610.09	-0.09	609.48	0.52	610.74	-0.74	610.01	-0.01	609.99	0.01
60%	629	627.68	1.32	627.22	1.78	627.44	1.56	627.18	1.82	627.81	1.19	627.31	1.69	627.40	1.60
65%	649	649.00	0.00	648.23	0.77	648.60	0.40	648.30	0.70	649.17	-0.17	648.40	0.60	648.50	0.50
70%	669	668.90	0.10	668.09	0.91	668.46	0.54	668.31	0.69	669.05	-0.05	668.20	0.80	668.42	0.58
75%	690	690.94	-0.94	690.16	-0.16	690.58	-0.58	690.58	-0.58	691.17	-1.17	690.42	-0.42	690.63	-0.63
80%	712	713.73	-1.73	713.05	-1.05	713.44	-1.44	713.65	-1.65	714.07	-2.07	713.36	-1.36	713.47	-1.47
85%	736	737.93	-1.93	737.75	-1.75	737.90	-1.90	738.05	-2.05	738.19	-2.19	737.82	-1.82	737.90	-1.90
90%	764	766.29	-2.29	766.08	-2.08	766.37	-2.37	766.83	-2.83	766.77	-2.77	766.23	-2.23	766.42	-2.42
95%	803	804.88	-1.88	804.85	-1.85	805.12	-2.12	806.11	-3.11	805.45	-2.45	805.08	-2.08	805.09	-2.09
FBP	887	880.67	6.33	880.59	6.41	880.92	6.08	886.22	0.78	881.04	5.96	880.80	6.20	880.99	6.01
100%		914.03		913.87		913.87		934.74		913.37		913.68		913.92	

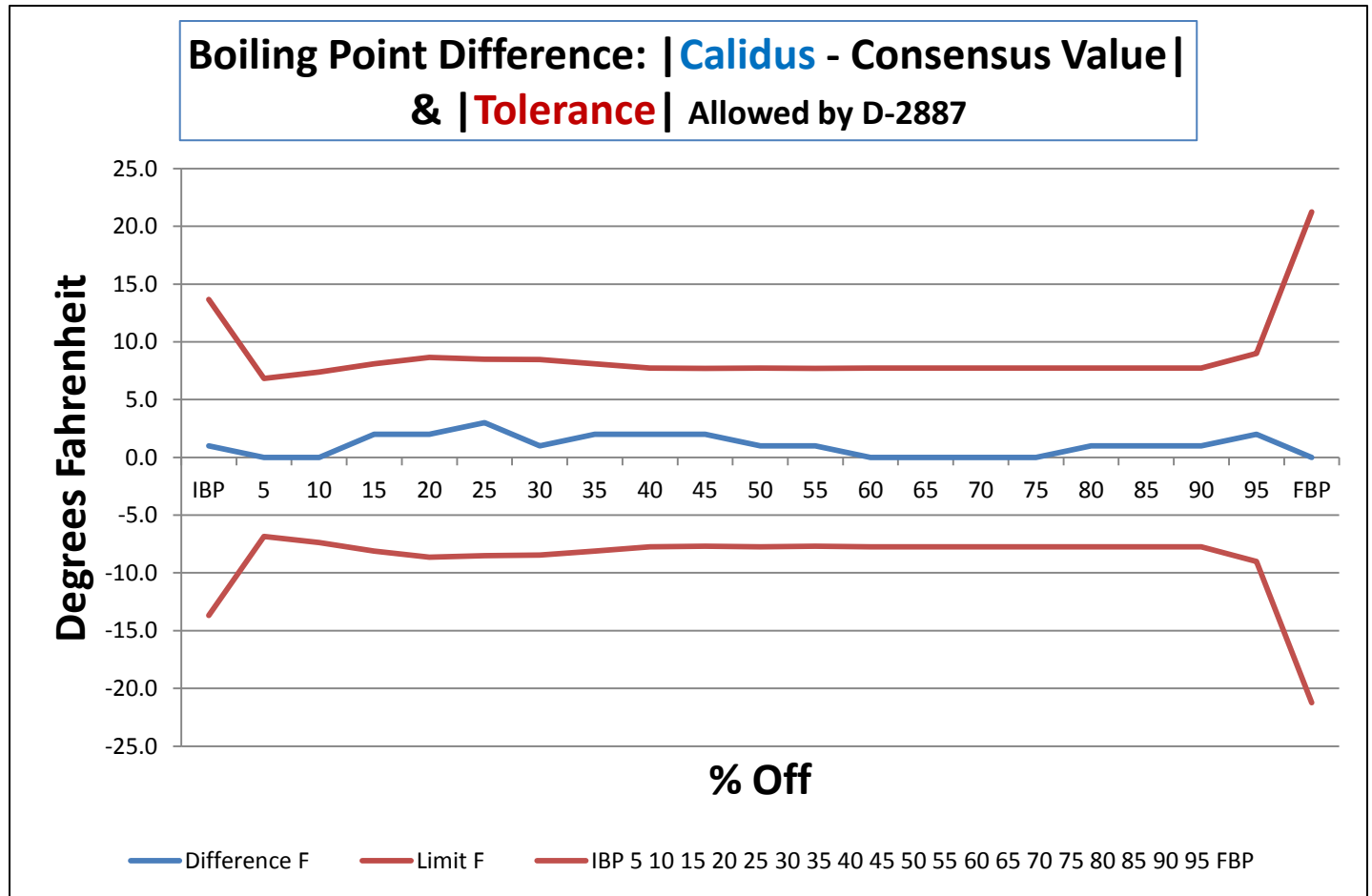
The average variance from the accepted values for all results is < 1.5°F including FBP & 100%. Excluding 100% and FBP (99.5%) reduces the average variance by only about 0.15°F.



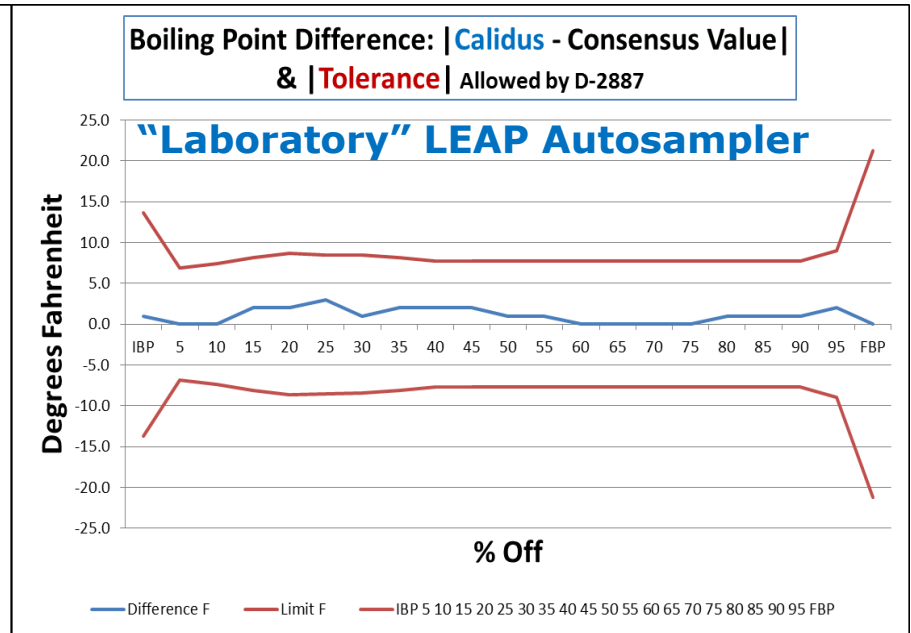
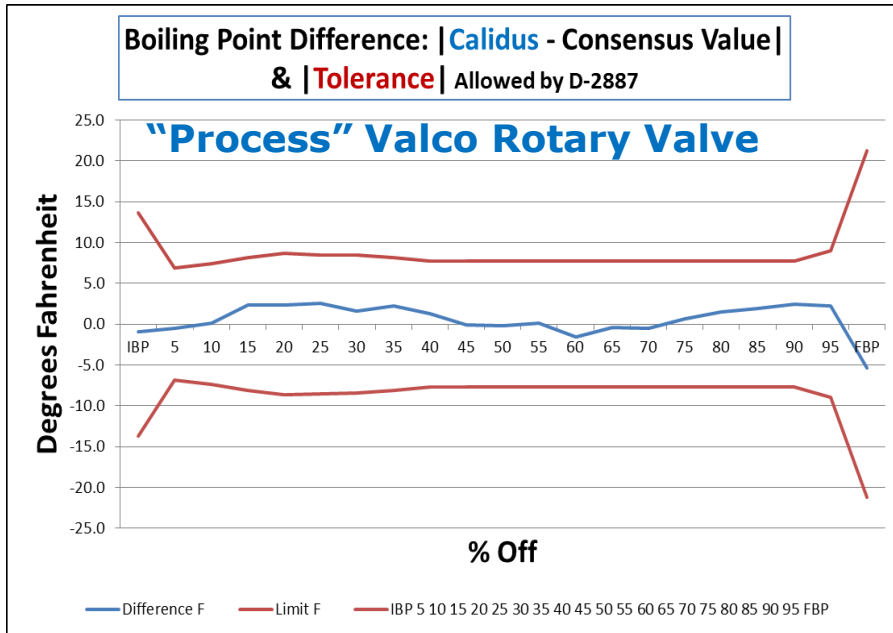
Rotary Sample Valve Graphical Comparison to Accepted Values



Syringe Automatic Sampler Graphical Comparison to Accepted Values



Rotary Sample Valve (left) VS Syringe (right) Performance



While the profiles are different both meet the requirements of the current D-2887 standard and compare favorably when thinking about the possibility of one substituting for the other.

Current status

- **Draft method submitted for subcommittee ballot in spring of 2011.**
 - **Received 2 negatives relating to incorrect paragraph references and typo's of some technical terms.**
 - **Negatives were voted as persuasive but were minor in nature.**
- **Subcommittee agreed to do a concurrent D02/o4H ballot in spring of 2012.**
 - **Passed subcommittee ballot but received 2 negatives on D02 ballot. Negative concerning form and style violation of terminology section voted persuasive.**
- **Re-balloting at D02 in fall of 2012**

Next Steps

- *Fall ballot results by end of November 2012.(Fully expect to pass).*
- *Begin preparation for the Interlaboratory Study (ILS) to determine precision and bias of the method. This is mandatory and is required within 5 years of method approval. Will begin spring of 2013.*
- *ILS requires acceptable test results from a minimum of six laboratories on at least six materials representing different test levels.*
- *Write a Research Report (RR) to support the ILS.*