Boiling Range Distributions: In the Lab In the Process

Joe Perron, Ned Roques, John Crandall

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Abstract

Boiling Range Distributions: In the Lab, In the Process - 3:20-3:40
Joe Perron, Ned Roques, John Crandall, Falcon Analytical

Fast GC brings multiple benefits to simulated distillation analysis. Boiling range information is an important part of producing appropriate fuel blend components and fuels themselves. Many are attempting to use spectroscopy of one type or another to predict boiling range distribution at significantly higher capital cost instead of a real separation process, gas chromatography. One reason is the need for timely analysis cycles. While spectroscopy seems to be an appropriate answer to the need for speed, Fast GC brings not only the speed but also better precision than prediction based technologies.

This paper will discuss the operational parameters for both lab based and online process control based fast GC. The work considers the differences in results from liquid syringe autosampler based inlets used in laboratories to rotary valve based inlets required in the process. Data will show the capabilities and limitations for samples ranging up to C44 or 535°C.

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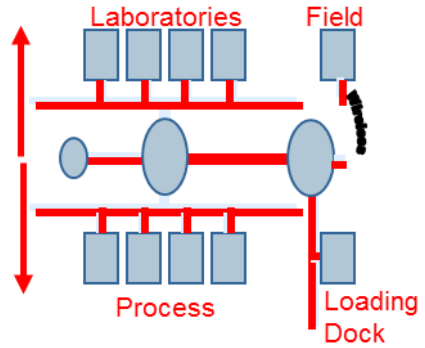
Lab Instruments & Process Analyzers Are Different

- Installation sites mandate design differences
  - Explosion hazard mitigation
    - Arc & spark
    - Hot surfaces
  - Instrument survival criteria in the
    - Nasty process environment vs
    - Nice laboratory setting
- All of these mandated technique differences
  - Maximum surface temperature limits (T-ratings)
  - Use of high thermal mass for temperature stability
  - Column switching vs programmed temperature operation



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What if They Could Be Exactly The Same?
Data Equivalency… Regardless of Location

LAB

PROCESS

TRANSPORTABLE

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Lab Use

Injections With An Autosampler

Boiling Point Analysis With Dragon SimDist

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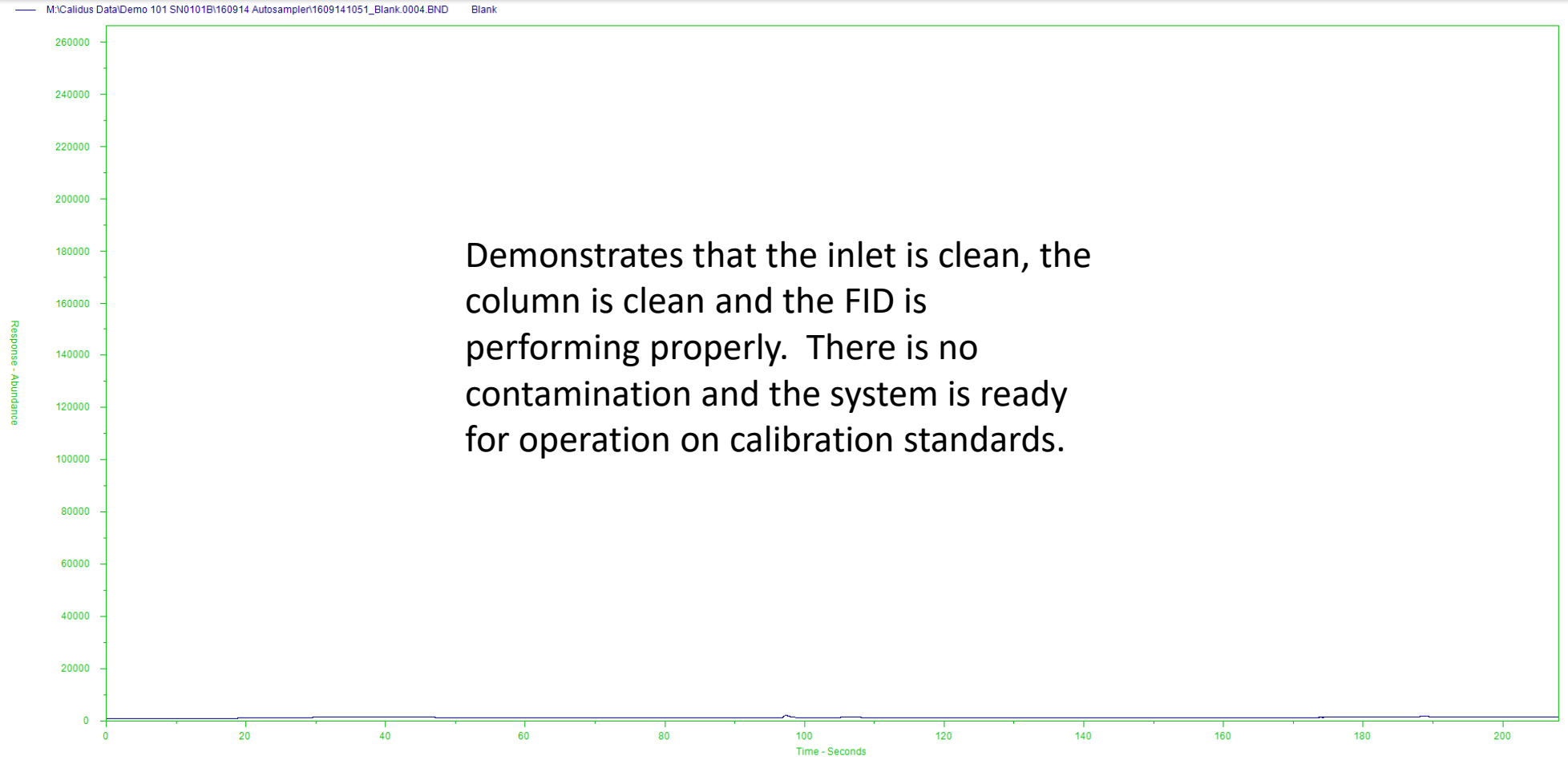
Non-injection Blank *(Autosampler - performs the injection into a waste vial and starts the PTGC cycle)*



Demonstrates that the inlet is clean, the column is clean and the FID is performing properly. There is no contamination and the system is ready for operation on calibration standards.

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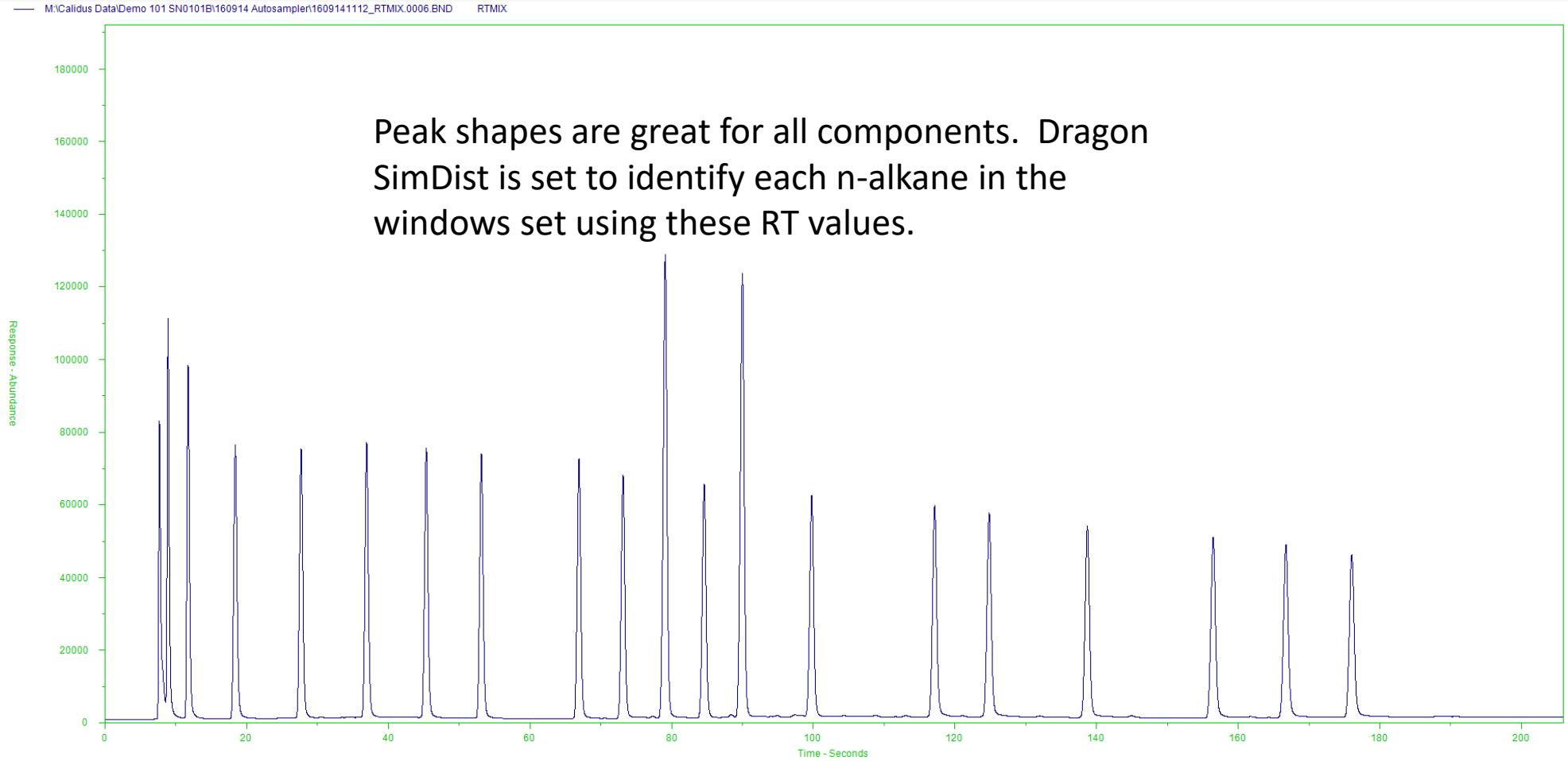
RTMIX *(Autosampler - injects the retention time standard mix, C_5 to C_{44})*



Peak shapes are great for all components. Dragon SimDist is set to identify each n-alkane in the windows set using these RT values.

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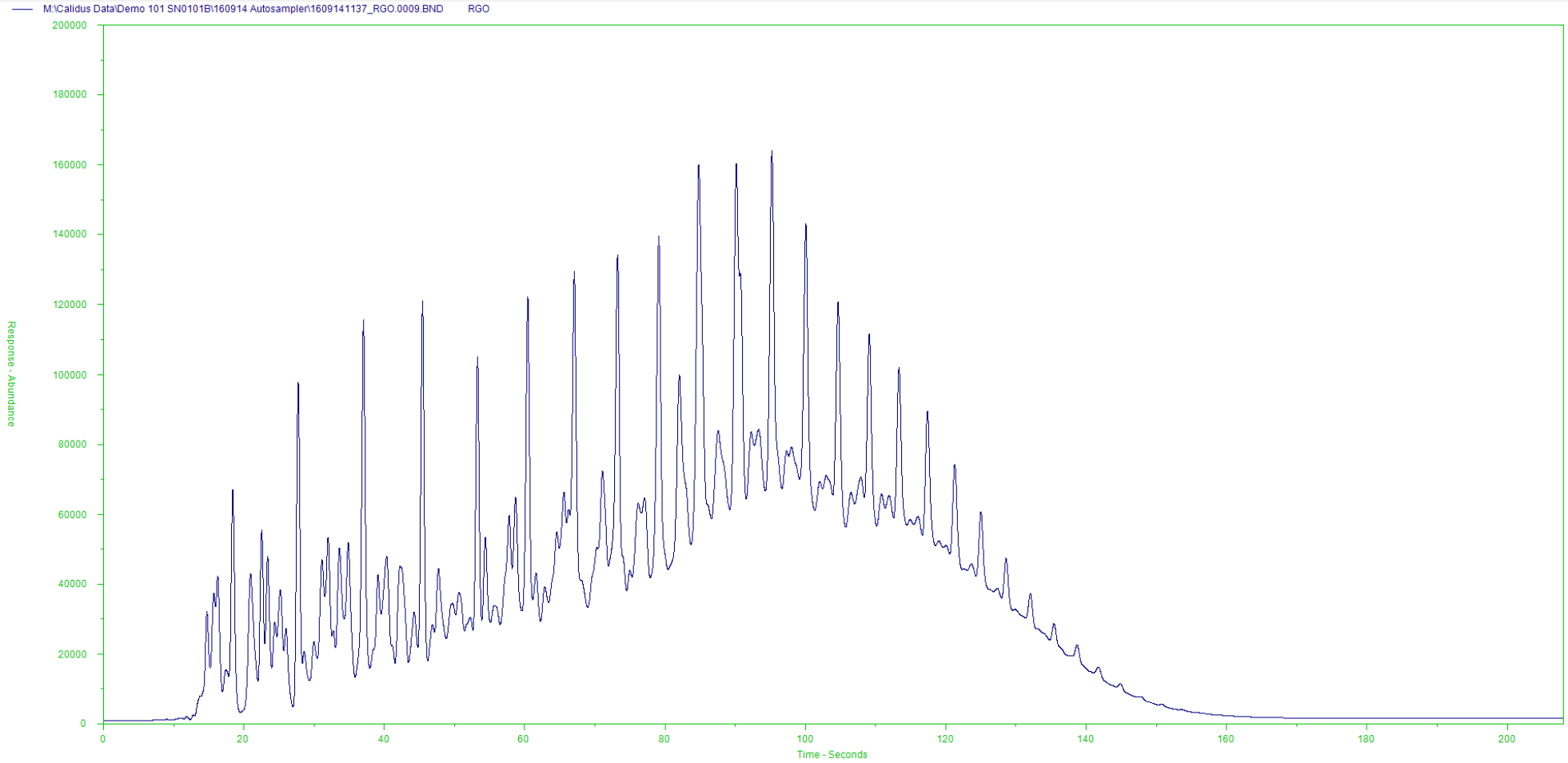
RGO (Autosampler - injects the Reference Gas Oil sample)



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RGO SimDist Result using the Autosampler

All boiling points are within the tolerance of ASTM D-7798.

RGO (deg. F)				
% OFF	Accepted	Measured	Difference	Tolerance
IBP	239	236.4	-2.6	12.6
10	349	346.1	-2.9	8
20	435	434.3	-0.7	9
30	499	498.3	-0.7	8.6
40	552	552.2	0.2	7.7
50	594	593.8	-0.2	7.7
60	629	628.7	-0.3	7.7
70	669	669.3	0.3	7.7
80	712	713.6	1.6	7.7
90	764	767.1	3.1	7.7
FBP	887	897.9	10.9	21.2

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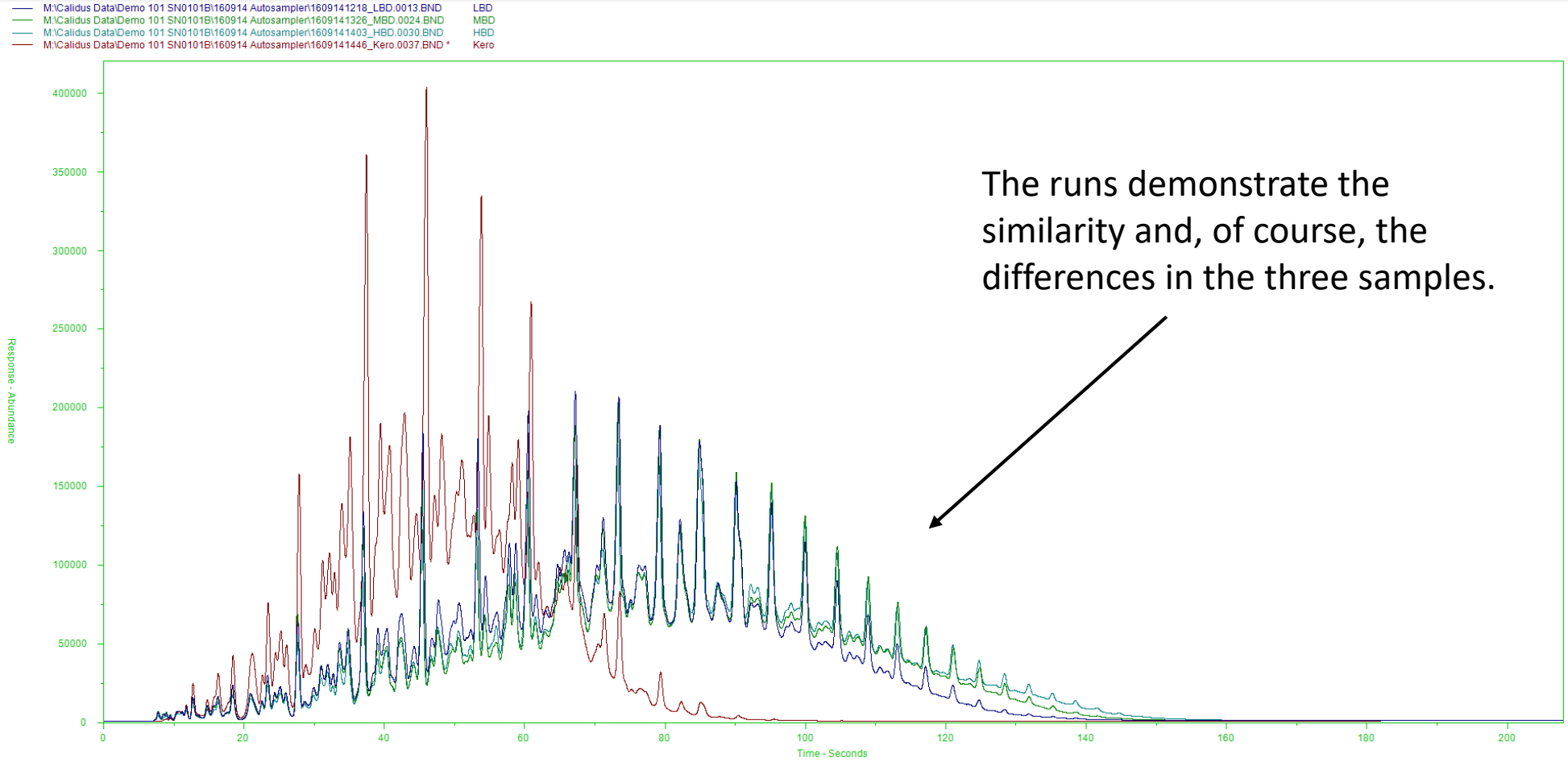
Samples (LBD, MBD, HBD, Kero) Run with Autosampler



The runs demonstrate the similarity and, of course, the differences in the three samples.

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Process Use

Injections With A Vici Liquid Injection Valve

Boiling Point Analysis With Dragon SimDist

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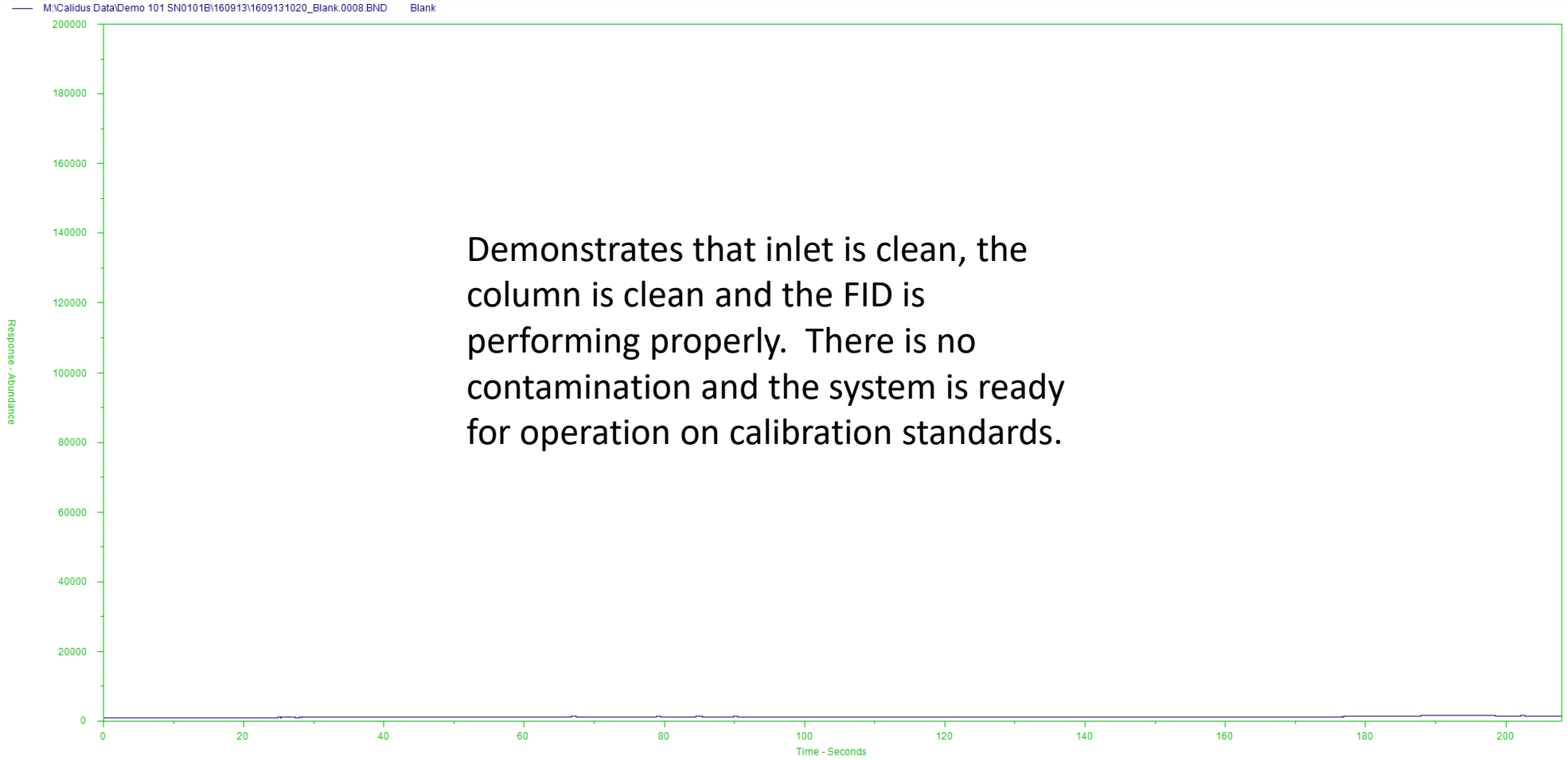
Non-injection Blank *(Valco valve - actuator is turned off and the PTGC cycle is started)*



Demonstrates that inlet is clean, the column is clean and the FID is performing properly. There is no contamination and the system is ready for operation on calibration standards.

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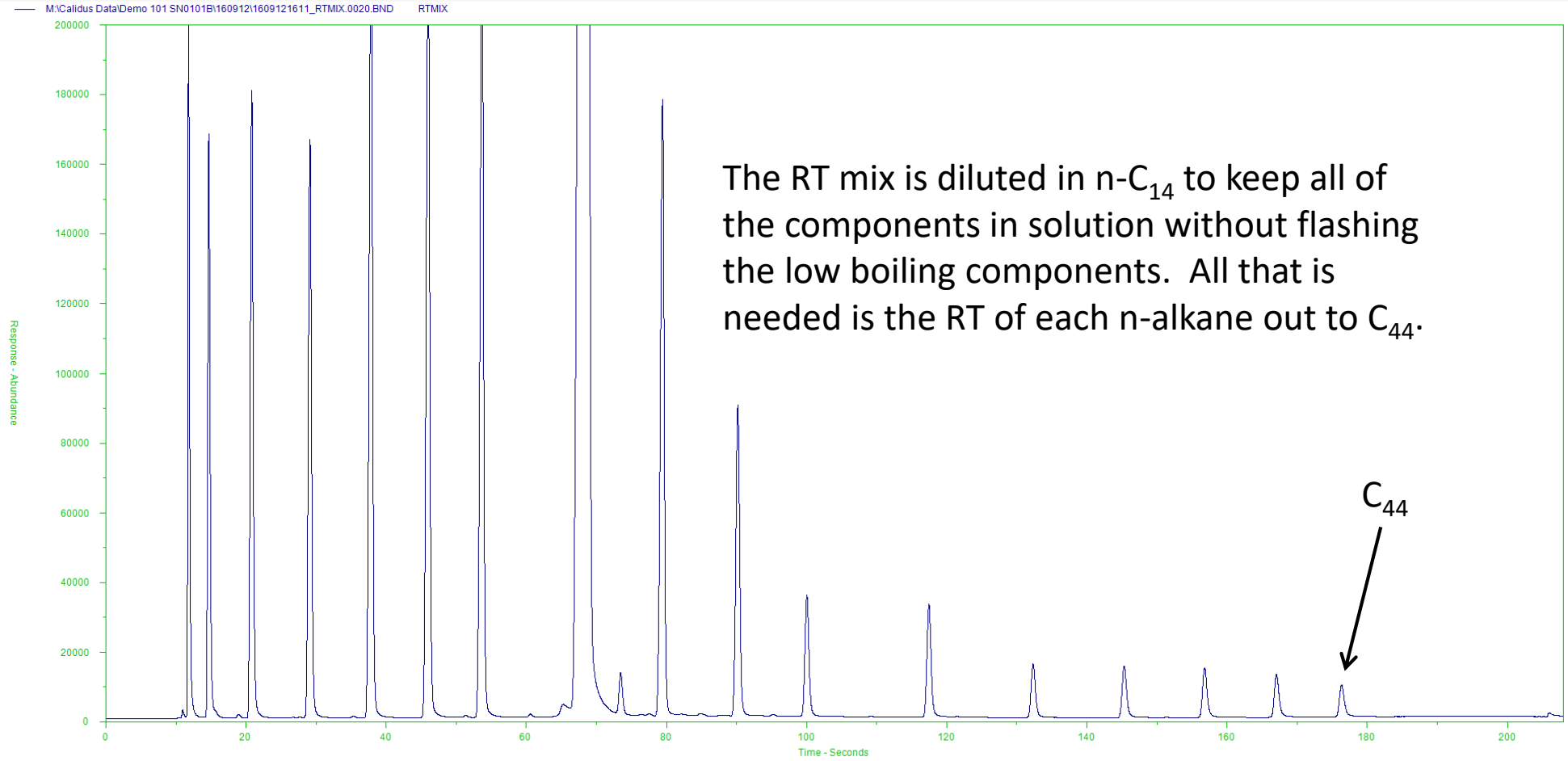
RTMIX *(Valco Valve - cleaned and loaded using a syringe with enough backpressure to keep components from flashing too soon)*



The RT mix is diluted in n-C_{14} to keep all of the components in solution without flashing the low boiling components. All that is needed is the RT of each n-alkane out to C_{44}.

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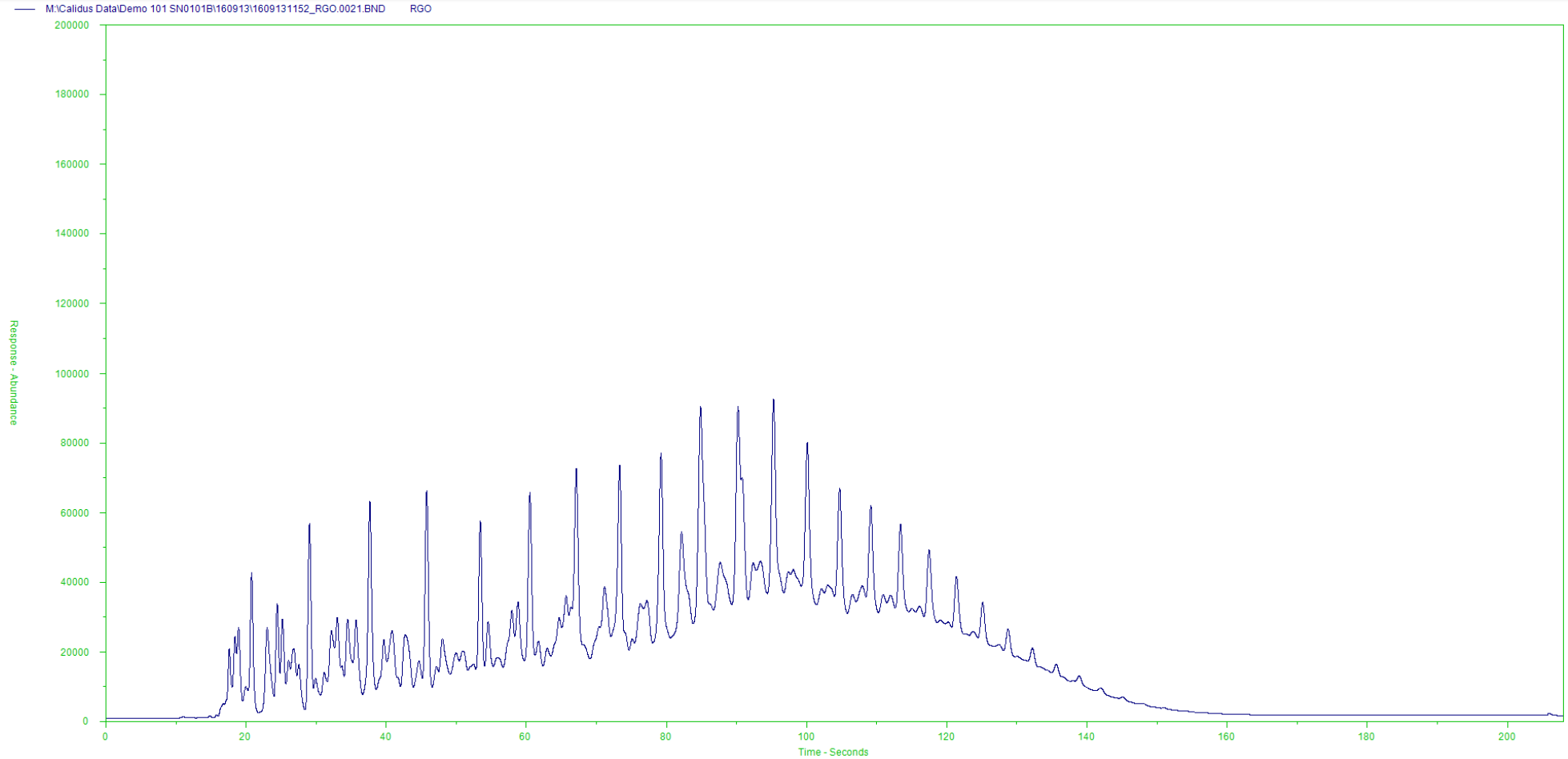
RGO (Valco Valve)



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RGO SimDist Results (Valco Valve)

All boiling points are within the tolerance of ASTM D-7798

RGO (deg. F)				
% OFF	Accepted Value	Measured Value	Difference	Tolerance
IBP	239	237.2	-1.8	12.6
10	349	347.1	-1.9	8
20	435	437.1	2.1	9
30	499	496.9	-2.1	8.6
40	552	556.5	4.5	7.7
50	594	596.6	2.6	7.7
60	629	629.9	0.9	7.7
70	669	671.0	2.0	7.7
80	712	714.5	2.5	7.7
90	764	767.0	3.0	7.7
FBP	887	889.0	2.0	21.2

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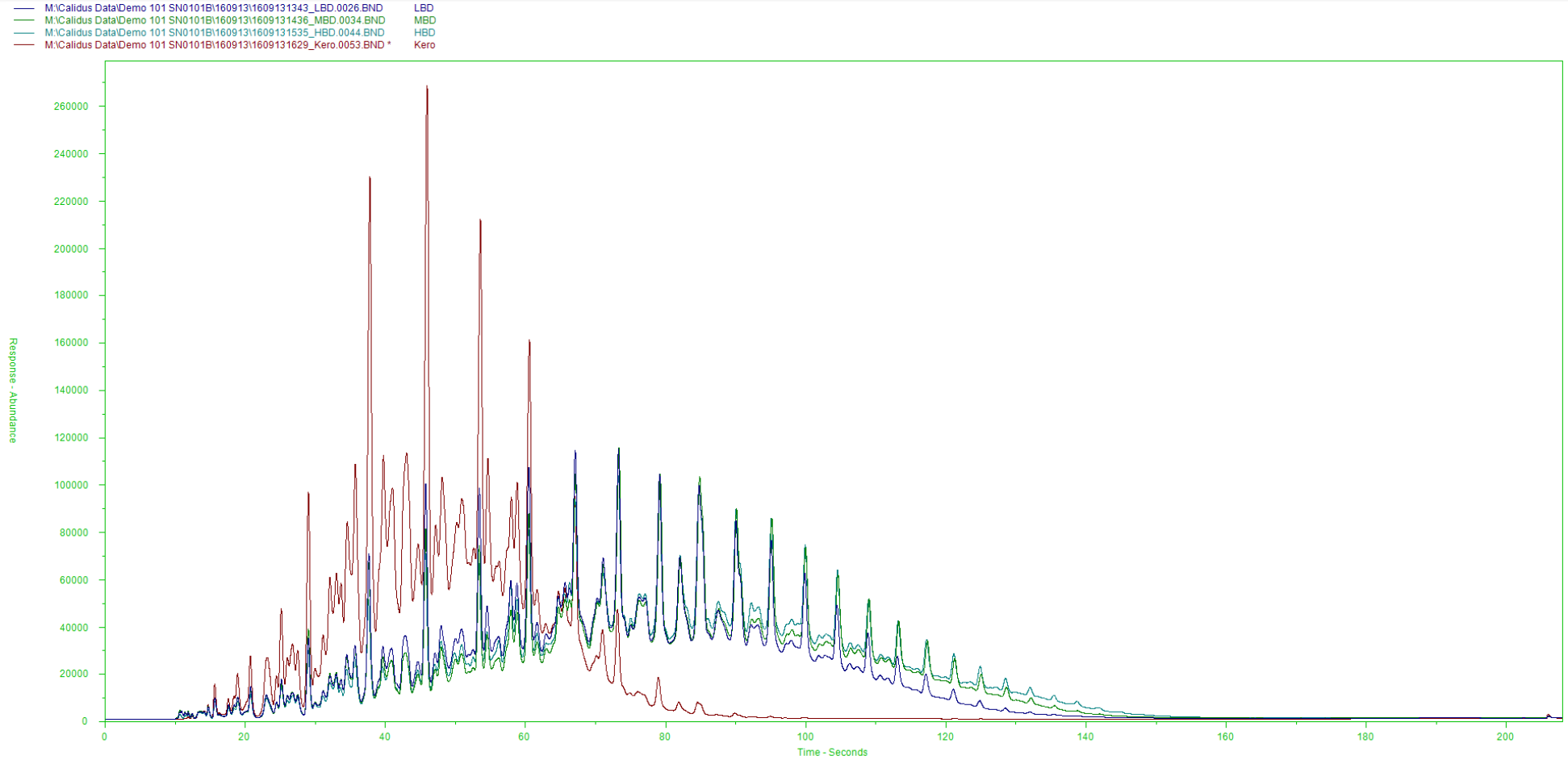
Samples: LBD, MBD, HBD, Kero (Valco Valve)



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Lab And Process Comparison

Autosampler and Valve Comparison

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RGO (Autosampler to Valco Valve)

RGO Autosampler		RGO Valve		
% OFF	BP(F)	% OFF	BP(F)	Difference
IBP	236.4	IBP	237.2	0.8
10	346.1	10	347.1	1.0
20	434.3	20	437.1	2.8
30	498.3	30	496.9	-1.4
40	552.2	40	556.5	4.3
50	593.8	50	596.6	2.8
60	628.7	60	629.9	1.2
70	669.3	70	671	1.7
80	713.6	80	714.5	0.9
90	767.1	90	767	-0.1
FBP	897.9	FBP	889	-8.9

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Autosampler to Valco Valve Differences

Note: 8 replicates of each sample type were run with each injection method. These results were averaged to obtain the data in this table

% OFF	Autosampler - Valve LBD Difference	Autosampler – Valve MBD Difference	Autosampler – Valve HBD Difference	Autosampler – Valve Kero Difference
IBP	-0.4	0.6	-2.0	-2.3
10	0.2	0.2	-1.4	-0.2
20	-1.5	0.0	0.8	0.8
30	-0.8	-0.9	-1.3	1.1
40	-1.2	-0.4	1.9	1.9
50	-0.2	3.4	1.8	1.8
60	3.9	4.8	5.4	2.2
70	3.7	4.6	4.7	2.4
80	7.3	2.6	4.1	2.1
90	4.9	0.2	-0.6	2.9
FBP	4.9	-0.5	-3.2	2.8

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4 Samples, 8 Replicate Statistics
(Valve and Liquid Syringe AS)

Autosampler								
	LBD		MBD		HBD		Kero	
% OFF	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
IBP	228.0	0.5	225.7	0.2	238.0	0.2	224.8	0.3
5	329.1	0.1	329.5	0.1	339.9	0.3	292.5	0.1
10	363.3	0.2	370.1	0.1	384.3	0.2	319.4	0.1
15	391.1	0.2	404.0	0.1	415.6	0.4	333.0	0.1
20	416.3	0.2	432.5	0.1	442.4	0.4	345.5	0.0
25	435.7	0.2	456.6	0.1	462.8	0.5	353.6	0.1
30	455.4	0.2	480.2	0.1	485.0	0.6	362.8	0.1
35	473.5	0.2	495.1	0.1	503.3	0.7	373.3	0.1
40	489.1	0.2	514.2	0.1	520.5	0.7	384.4	0.1
45	505.4	0.2	529.8	0.1	538.1	0.8	389.3	0.1
50	520.7	0.2	548.2	0.0	555.7	1.0	398.8	0.1
55	536.7	0.2	565.0	0.1	575.0	1.0	409.2	0.1
60	551.9	0.2	579.7	0.1	589.7	1.1	419.0	0.1
65	571.1	0.3	598.9	0.1	605.7	1.3	425.7	0.1
70	585.4	0.3	616.0	0.2	626.3	1.3	436.2	0.1
75	603.0	0.2	636.1	0.2	647.2	1.4	447.6	0.1
80	624.4	0.3	658.0	0.2	669.2	1.5	458.4	0.1
85	647.5	0.3	682.7	0.2	694.7	1.6	471.2	0.1
90	673.9	0.2	712.3	0.2	726.4	1.7	488.9	0.1
95	711.0	0.3	751.9	0.3	773.3	1.9	511.3	0.1
FBP	793.1	1.3	828.6	1.1	856.2	2.3	576.7	0.2
Avg. Std. Dev.		0.1		1.0		0.2		0.3

Valve								
	LBD		MBD		HBD		Kero	
% OFF	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
IBP	228.3	2.4	225.1	3.5	239.9	0.3	227.1	0.5
5	329.0	0.2	329.3	0.7	341.4	0.4	292.7	0.3
10	364.8	0.6	370.1	1.0	383.6	0.1	318.6	0.2
15	391.9	0.3	404.9	1.4	416.9	0.5	331.8	0.3
20	417.5	0.2	432.9	1.5	440.6	0.3	343.6	0.2
25	435.9	0.2	453.2	0.7	461.0	0.6	351.8	0.4
30	451.4	0.1	475.5	0.8	479.7	0.3	360.6	0.3
35	469.7	0.1	490.5	1.5	498.6	0.5	370.9	0.3
40	481.9	0.1	511.6	1.1	516.4	0.5	382.2	0.5
45	500.4	0.3	529.6	1.0	538.8	0.7	386.4	0.4
50	515.8	0.3	548.6	0.5	559.0	0.6	396.0	0.5
55	536.6	0.4	567.0	0.9	575.1	0.4	406.5	0.5
60	554.9	0.7	581.4	0.9	591.8	0.6	416.4	0.6
65	573.2	0.4	600.7	0.3	608.6	0.7	422.2	0.5
70	587.7	0.6	619.4	0.9	627.2	0.5	431.8	0.7
75	604.3	0.7	639.8	0.9	649.4	0.5	442.1	0.6
80	625.8	0.5	661.7	1.0	671.7	0.6	451.5	0.4
85	649.6	0.7	686.2	1.2	696.1	0.7	463.9	1.3
90	675.8	1.7	715.2	1.0	730.1	1.2	479.8	0.7
95	714.9	1.9	755.0	1.9	775.9	2.0	504.2	3.2
FBP	806.9	8.9	841.1	12.7	869.3	12.3	593.2	15.2
Avg. Std. Dev.		1.0		1.7		1.2		1.2

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4 Sample, All 14 Replicates Combined Statistics
(Valve and Liquid Syringe AS)

	Combined							
	LBD		MBD		HBD		Kero	
% OFF	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
IBP	228.1	1.7	225.4	2.4	238.9	1.0	225.9	1.3
5	329.0	0.2	329.4	0.5	340.7	0.8	292.6	0.3
10	364.1	0.9	370.1	0.7	384.0	0.4	319.0	0.4
15	391.5	0.5	404.4	1.1	416.2	0.8	332.4	0.6
20	416.9	0.7	432.7	1.1	441.5	1.0	344.6	1.0
25	435.8	0.2	454.9	1.8	461.9	1.1	352.7	1.0
30	453.4	2.0	477.8	2.5	482.4	2.8	361.7	1.2
35	471.6	1.9	492.8	2.6	500.9	2.5	372.1	1.3
40	485.5	3.8	512.9	1.5	518.4	2.2	383.3	1.2
45	502.9	2.6	529.7	0.7	538.4	0.8	387.8	1.5
50	518.3	2.6	548.4	0.4	557.3	1.9	397.4	1.5
55	536.7	0.3	566.0	1.2	575.1	0.7	407.8	1.5
60	553.4	1.6	580.5	1.1	590.8	1.4	417.7	1.4
65	572.1	1.1	599.8	1.0	607.1	1.8	424.0	1.9
70	586.6	1.3	617.7	1.8	626.8	1.1	434.0	2.3
75	603.6	0.8	638.0	2.0	648.3	1.6	444.9	2.9
80	625.1	0.8	659.8	2.1	670.4	1.7	454.9	3.6
85	648.6	1.2	684.4	2.0	695.4	1.4	467.5	3.9
90	674.9	1.5	713.7	1.6	728.3	2.4	484.3	4.7
95	712.9	2.4	753.5	2.1	774.6	2.3	507.8	4.3
FBP	800.0	9.4	834.8	10.8	862.7	10.9	585.0	11.1
Avg. Std. Deviation		1.8		1.9		1.9		2.3

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Infometrix LineUp and Pirouette Chemometrics

Autosampler and Valve Comparison

Line Up and Pirouette Were Used for the Correction of Retention Time Differences and Area Normalization

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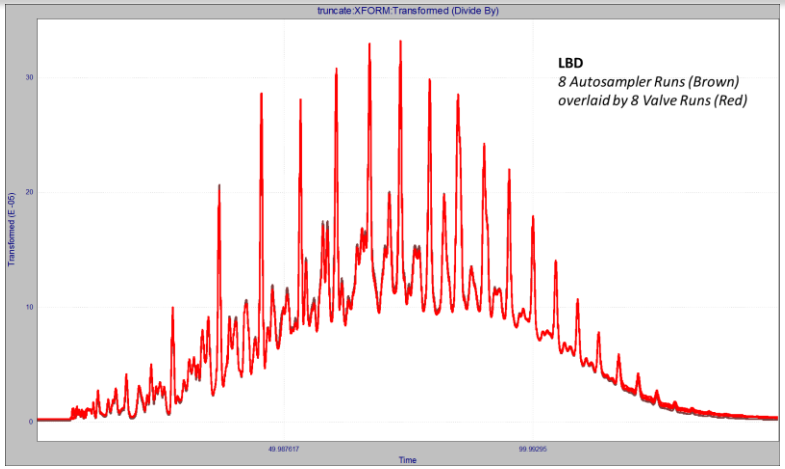
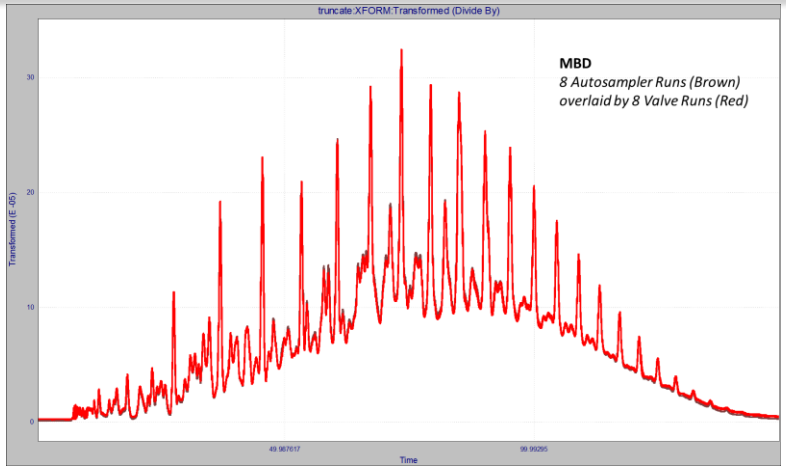
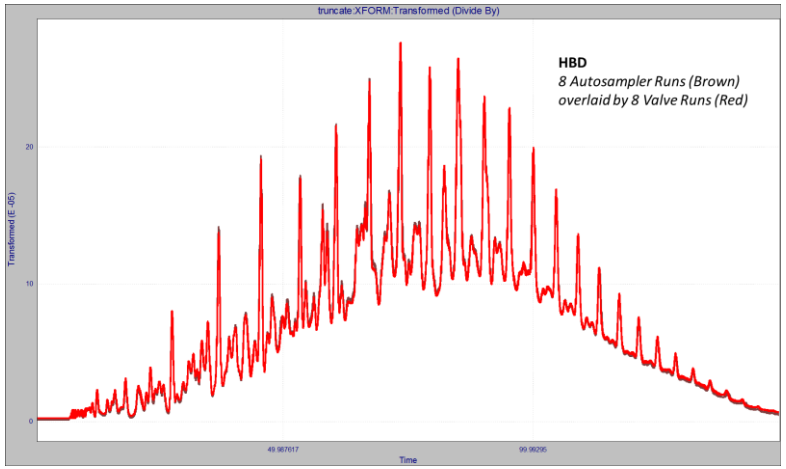
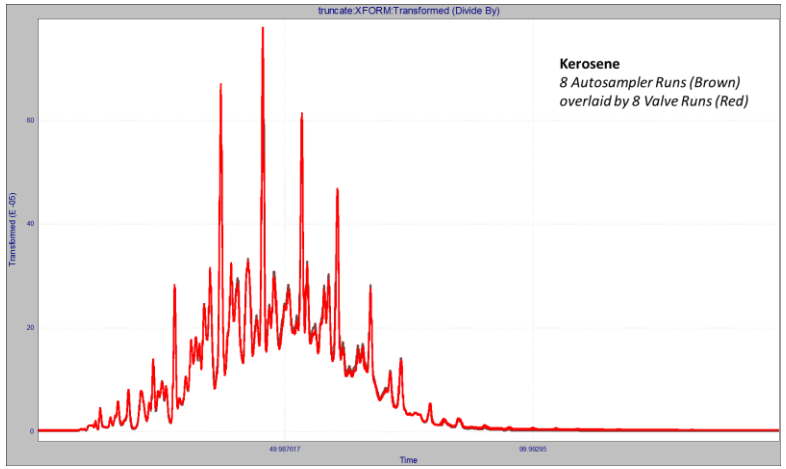
All Autosampler and Valve Results Overlaid After LineUp and Normalization









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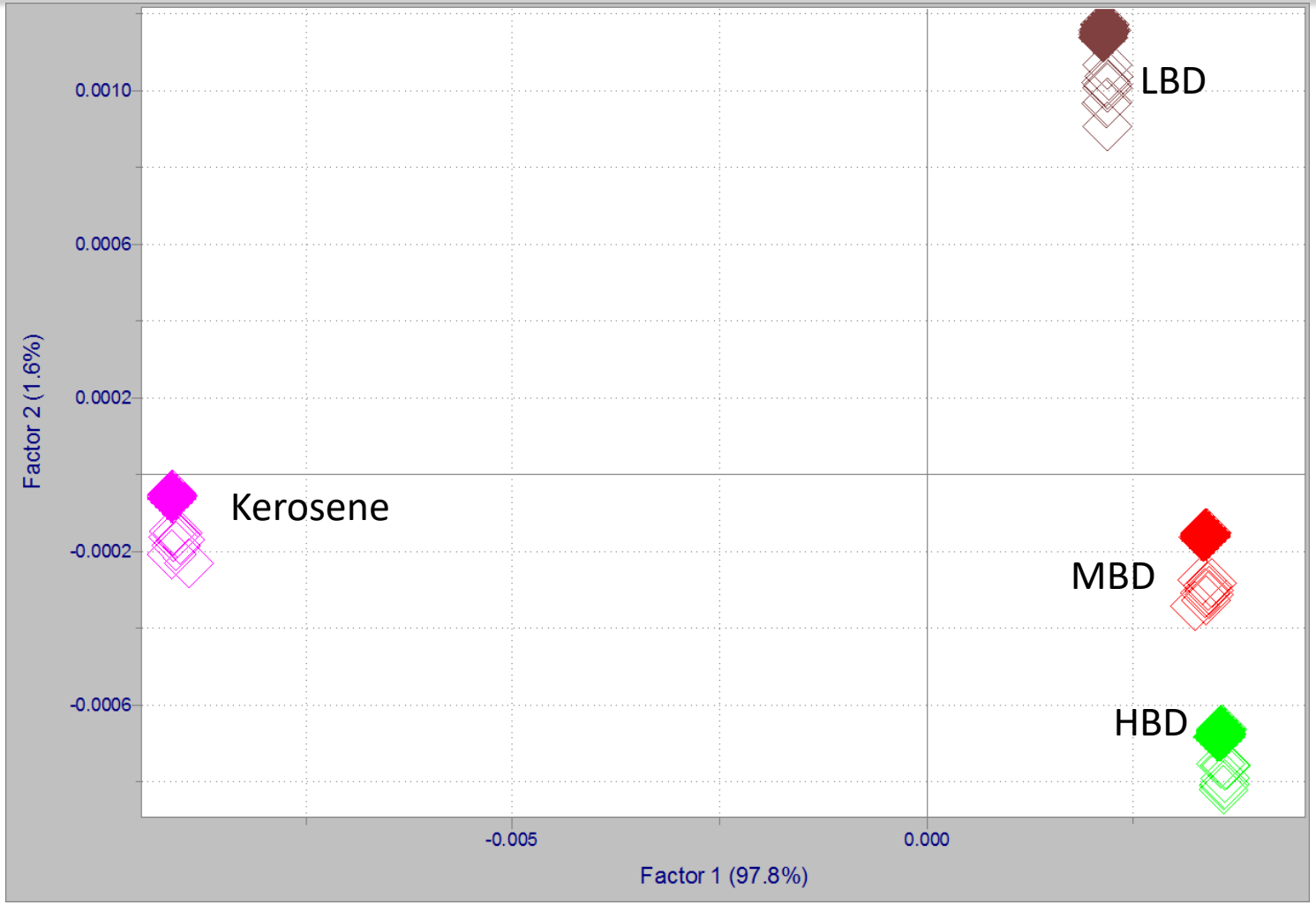
PCA Scores Plot - 16 Runs Per Sample Type (8 Valve and 8 Autosampler)



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Data Equivalency…Regardless of Location

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Questions??

Thank you for your attention

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