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In the Lab…

In the Process

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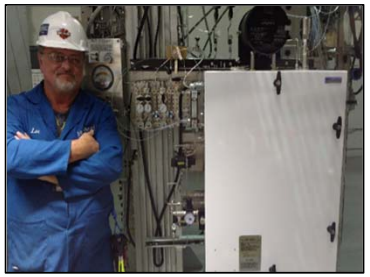

Data Equivalency Leads to Fluid Free Online Analyzer Calibrations

John Crandall, presenter, Joe Perron, Steve Bostic

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Brian Rohrback

InfoMetrix

Abstract

Data Equivalency Leads to Fluid Free Analyzer Calibrations

John Crandall, presenter, Joe Perron, Steve Bostic – Falcon Analytical
Brian Rohrback - Infometrix

The age old arguments between process GC analyzer and lab GC instrument results can be mitigated by using the same kind of instrument, same method and attention to the details in both locations. Of course, the sample taken out of the process GC system is really not the same by the time it is introduced to the lab GC system. But striving to make the two units deliver "the same" result has benefits beyond settling the squabble of "who is right."

A recent implementation in one refinery shows how to use laboratory GC as a way to calibrate the process GC using data files, not calibration fluids. This is achieved by using ASTM D7798 standard methods on both units. Expensive calibration standards and Reference Gas oil are used on the lab GC only. The resulting calibration data files from the lab GC are transferred to the process GC server. Validation occurs by use of a lab GC analyzed process sample to verify the results on the process GC. This eliminates painful operations handling cylinders of expensive calibration standards on the process GC.

Modern Processing Plant Architecture

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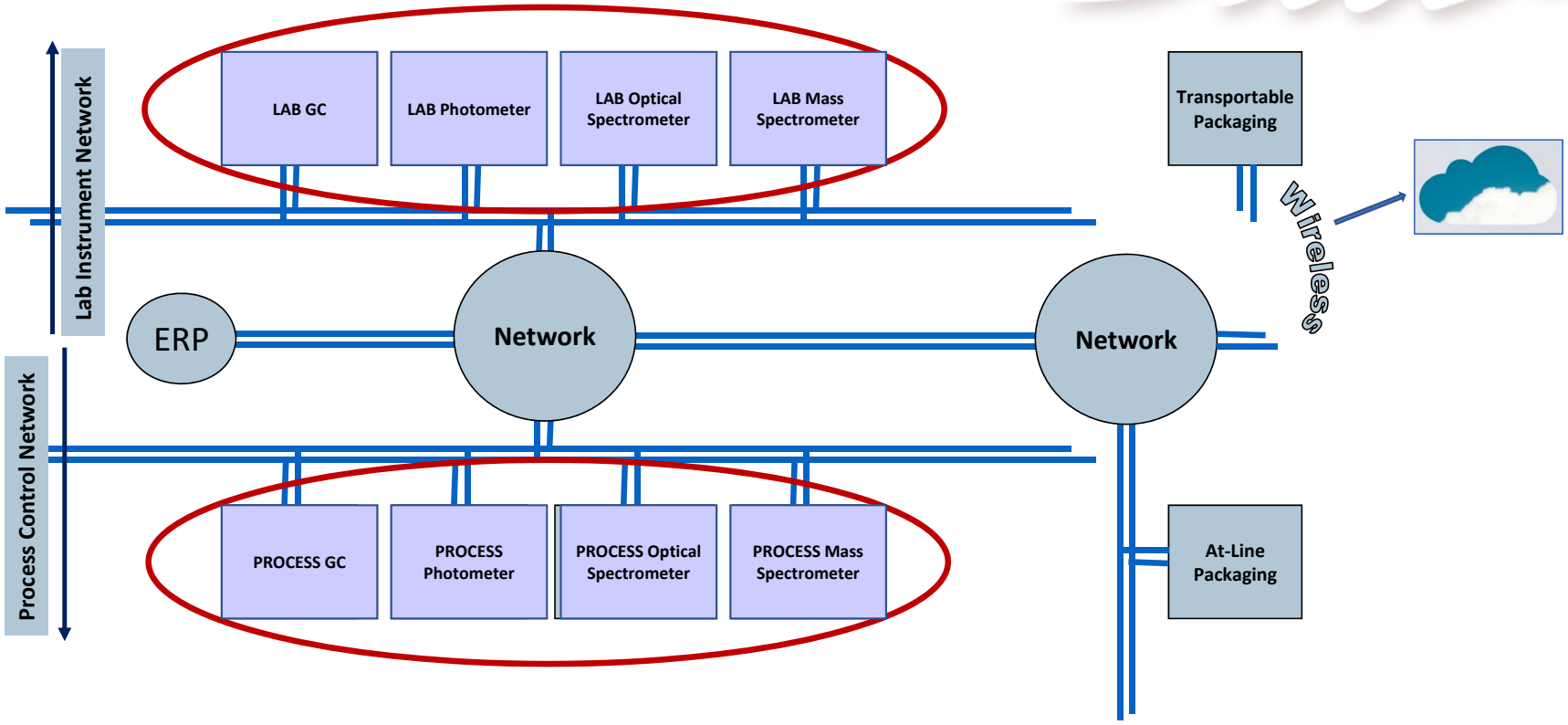
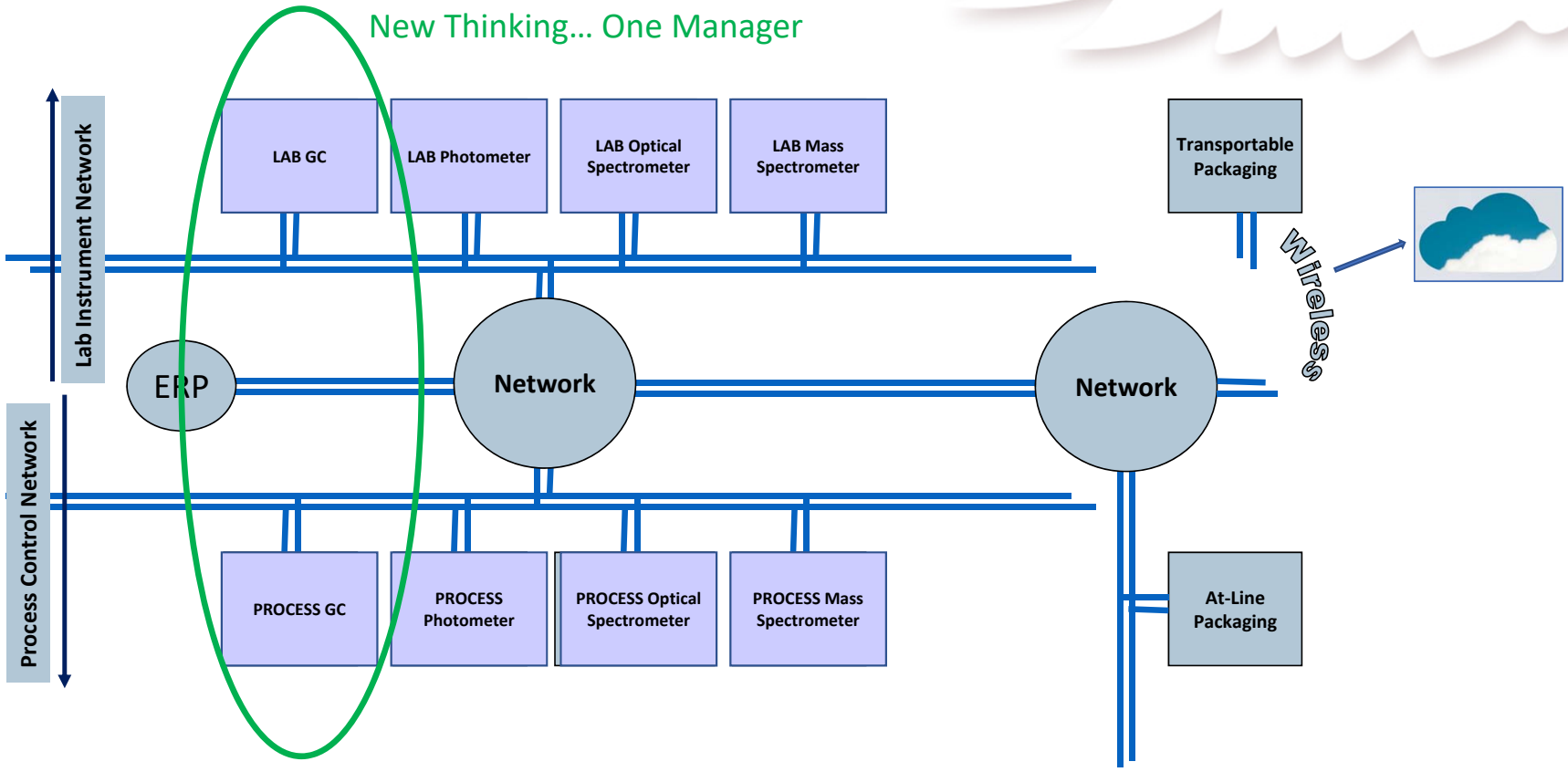
Old School…two managers

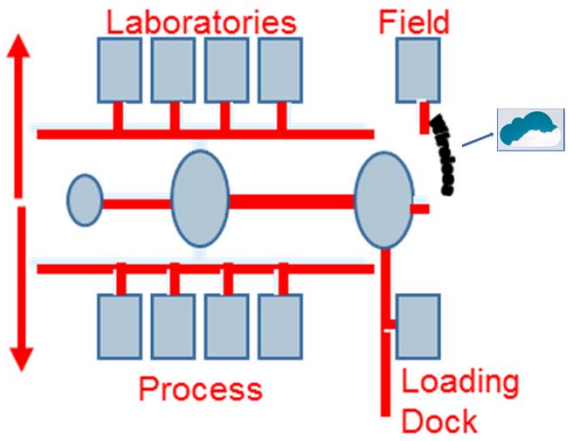


Modern Processing Plant Architecture



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



What if They Could Be Exactly The Same?

Data Equivalency… Regardless of Location

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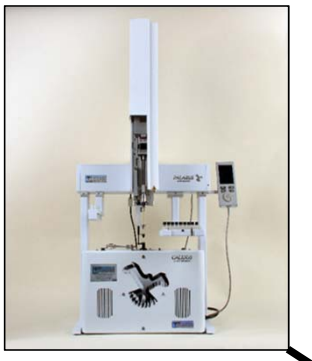
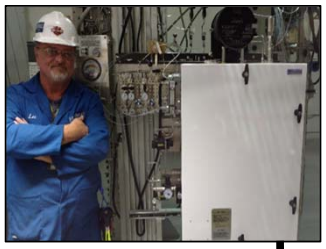
LAB



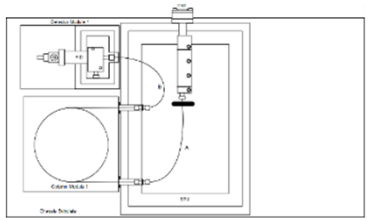
PROCESS



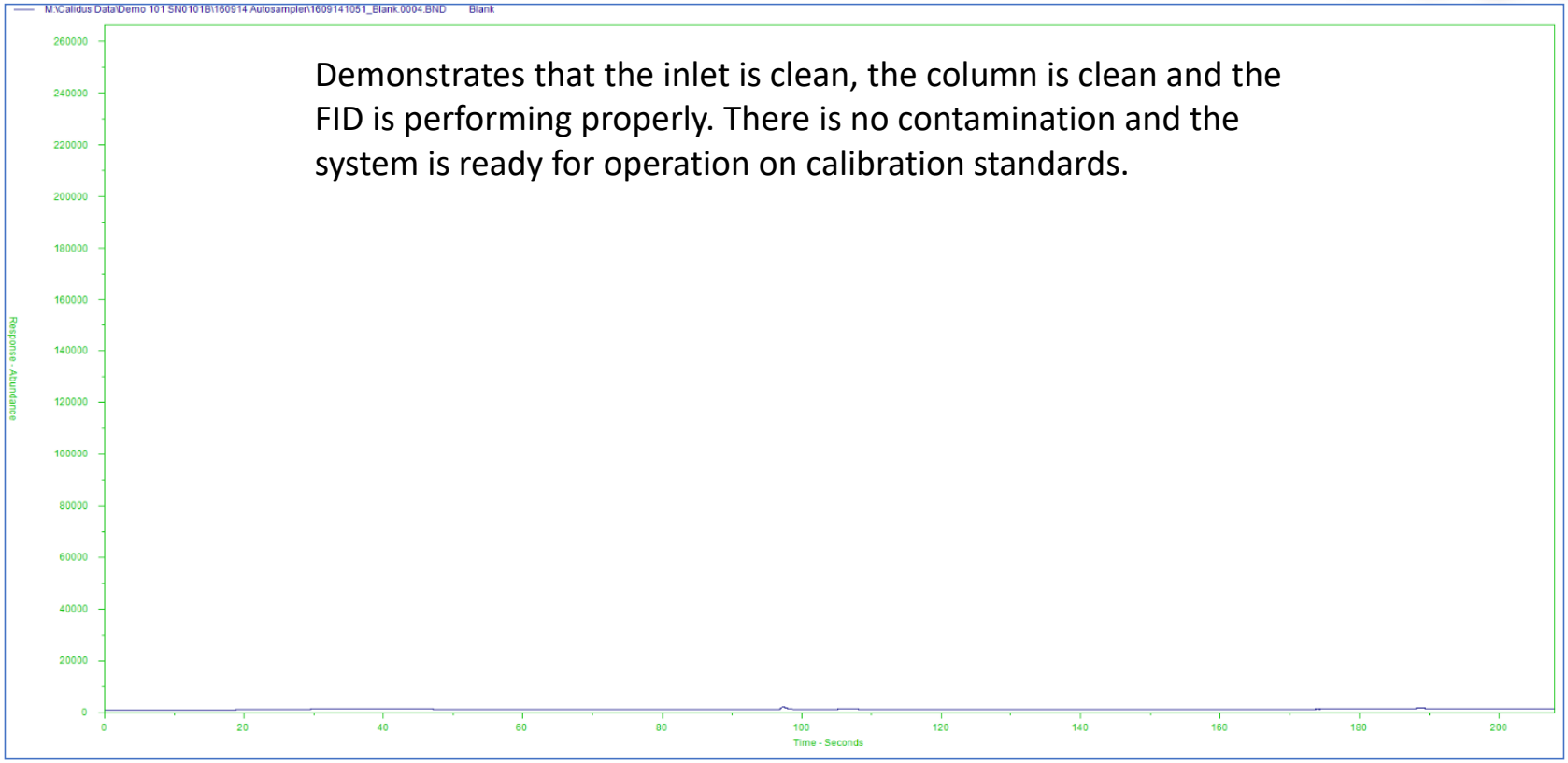
TRANSPORTABLE

Calidus 101-HT with Liquid Syringe Autosampler

- ASTM D7798 was followed
  - Split injection
    - 350°C
    - 70 nanoliter sample injected
    - Split ratio ~ 50:1
  - FID at 350°C
  - MXT-1 HT resistively heated capillary stainless steel column module
    - 320 micron ID x 0.2 micron film x 2 meter length
    - Initial temperature 40°C
    - Programmed temperature rate 2°C per second
    - Final temperature 385°C
  - Injection to injection cycle time <5 minutes

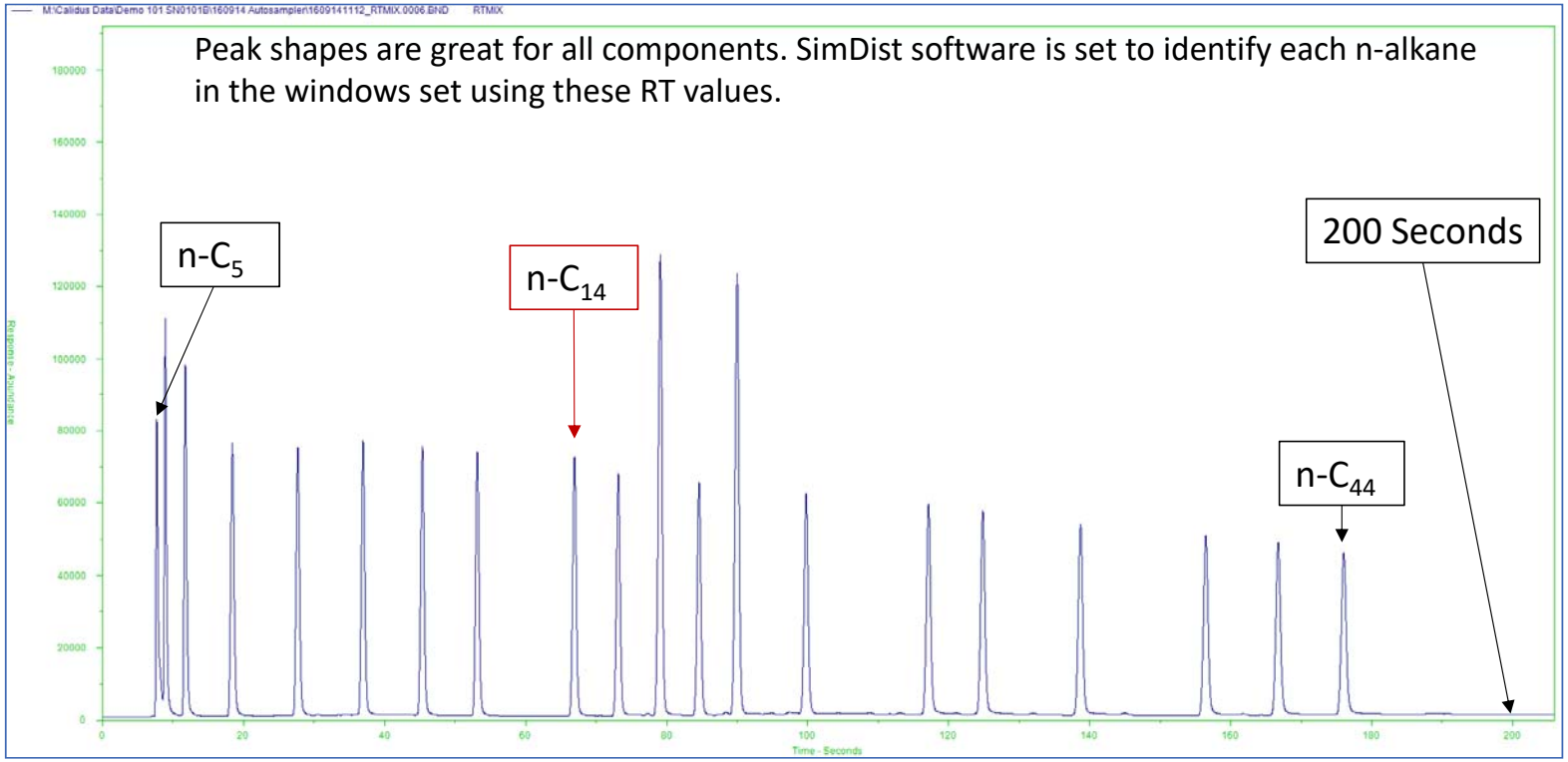


Non-injection Blank (Autosampler - performs the injection into a waste vial and starts the PTGC cycle)

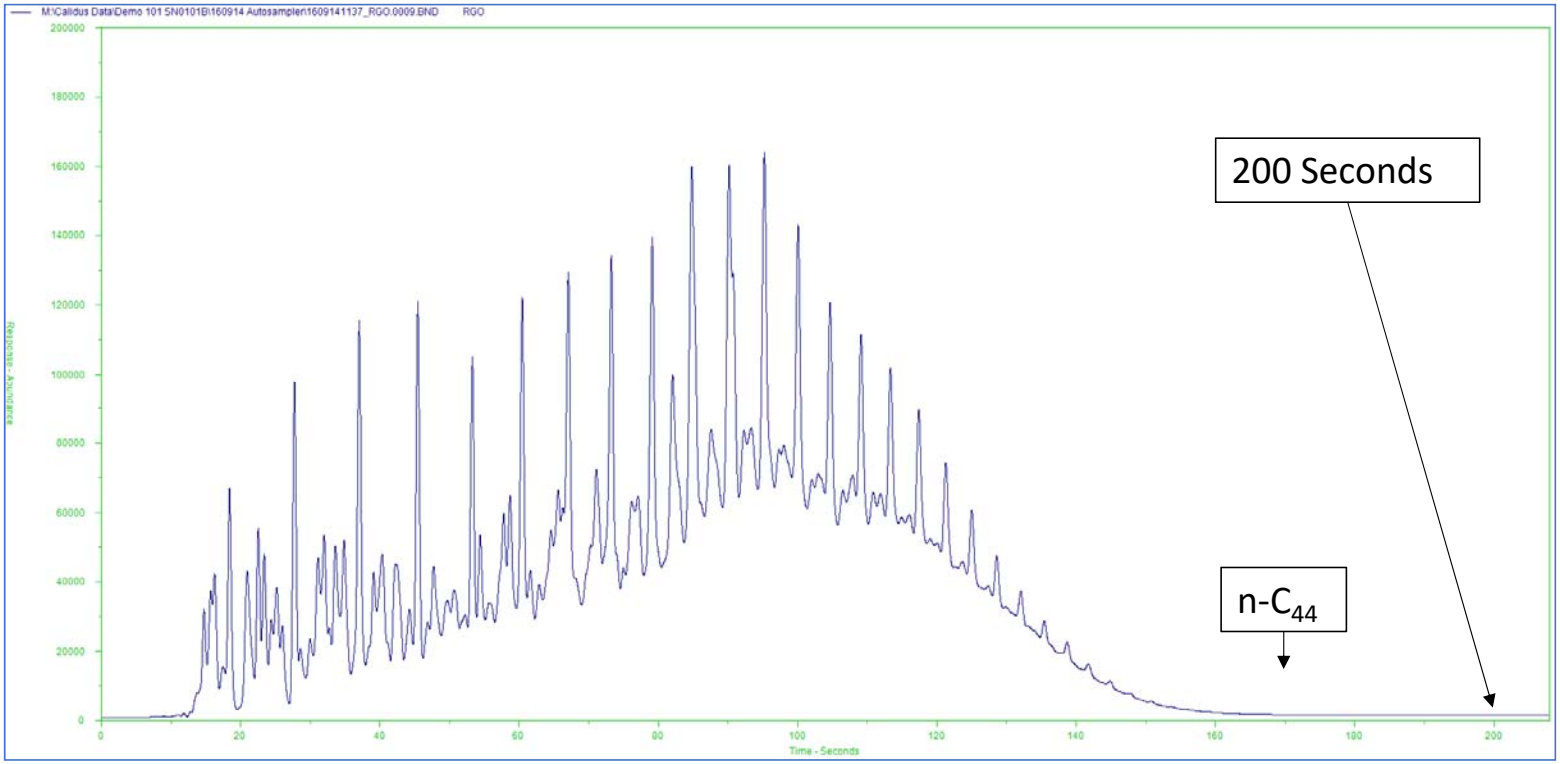


Demonstrates that the inlet is clean, the column is clean and the FID is performing properly. There is no contamination and the system is ready for operation on calibration standards.

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



RGO (Autosampler - injects the Reference Gas Oil sample)



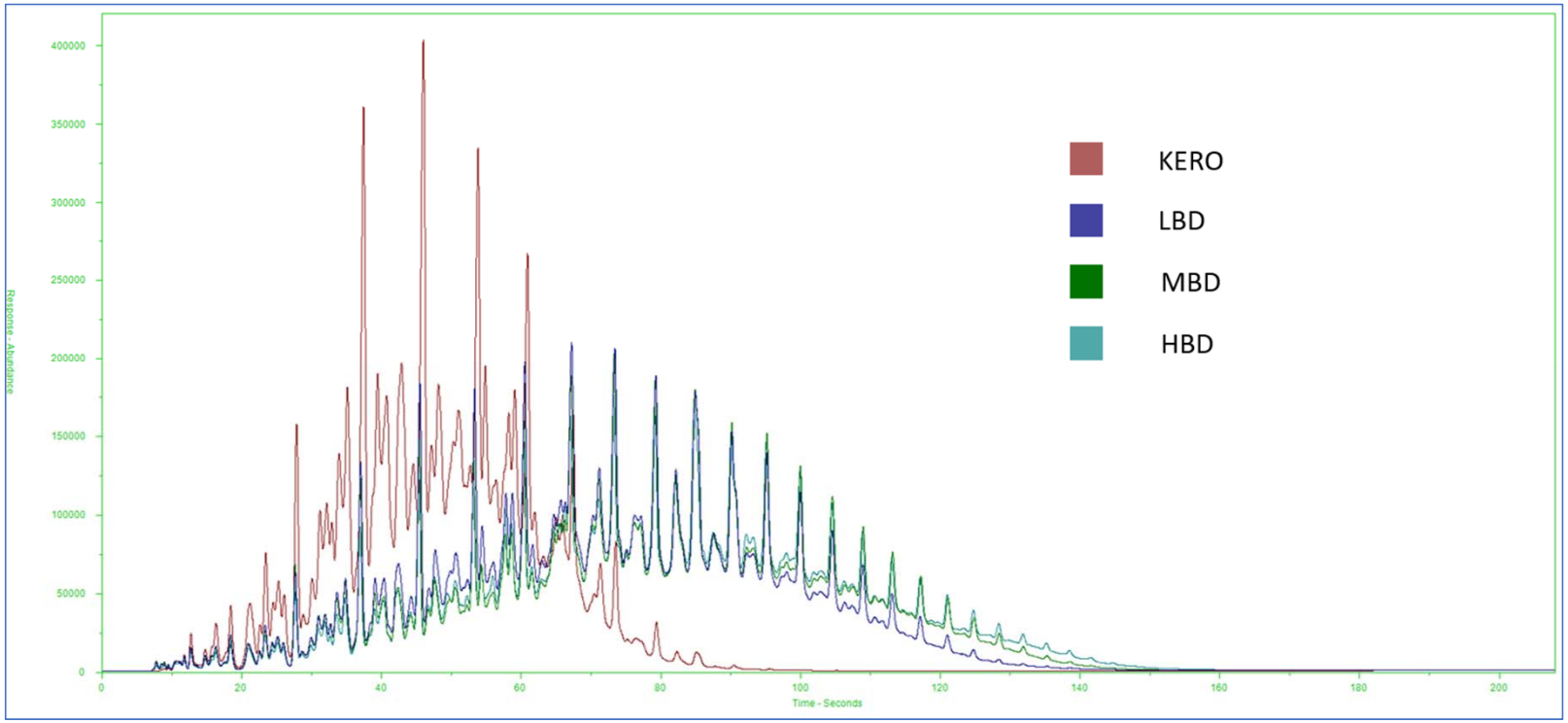
RGO SimDist Result using the Autosampler

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

RGO (deg. F)				
% OFF	Accepted	Measured	**Difference**	D-7798 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

Samples Run with Autosampler - LBD, MBD, HBD, Kerosene

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



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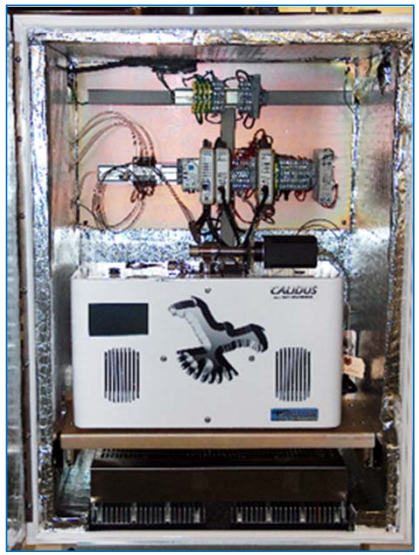
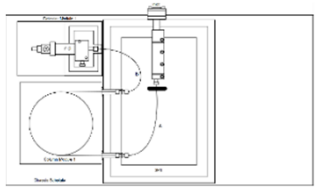
Process Use

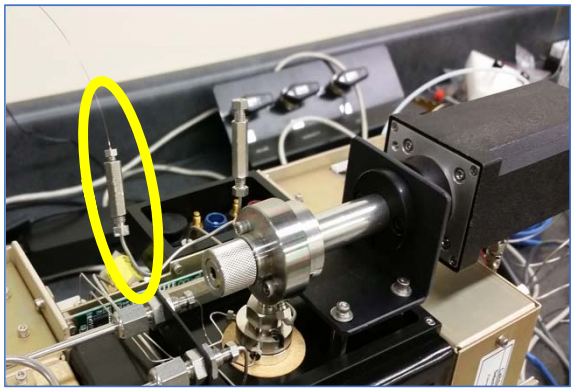
- Injections Using a Valco™ Liquid Injection Sample Valve
- Boiling Point Analysis using Simulated Distillation



Fast GC with Rotary Liquid Injection Valve

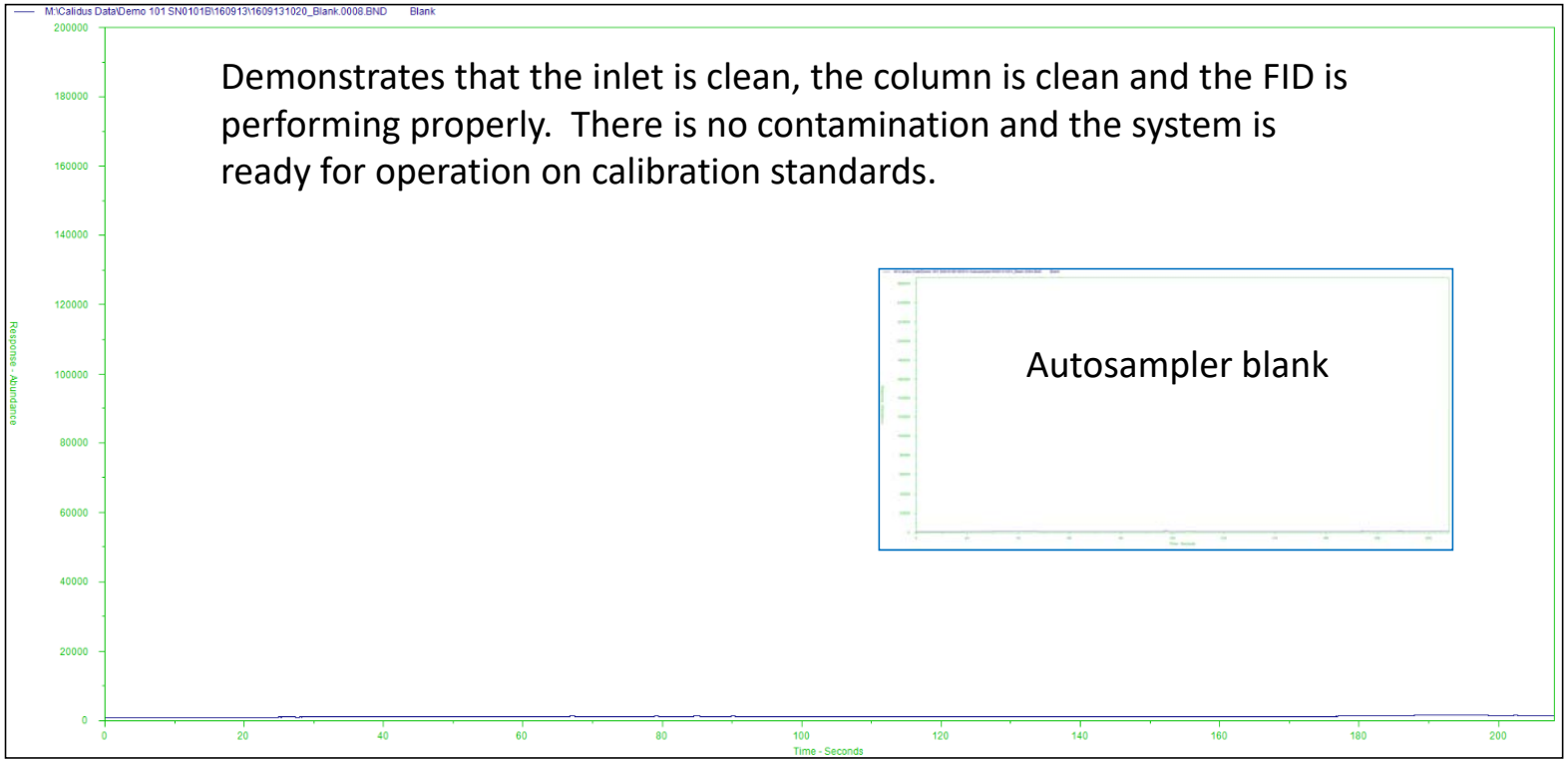
- ASTM D7798 was followed
  - Sample inlet via heated Valco rotary valve
    - Maintained at 225°C
    - Syringe loaded with capillary outlet to maintain pressure in the loop
    - 3 second delay was employed for pressure balance reasons (now proven unnecessary)
  - Split injection
    - 350°C
    - 60 nanoliter sample injected
    - Split ratio ~ 50:1
  - FID at 350°C
  - MXT-1 HT resistively heated capillary stainless steel column module
    - 320 micron ID x 0.2 micron film x 2 meter length
    - Initial temperature 40°C
    - Programmed temperature rate 2°C per second
    - Final temperature 385°C
  - Injection to injection cycle time <5 minutes



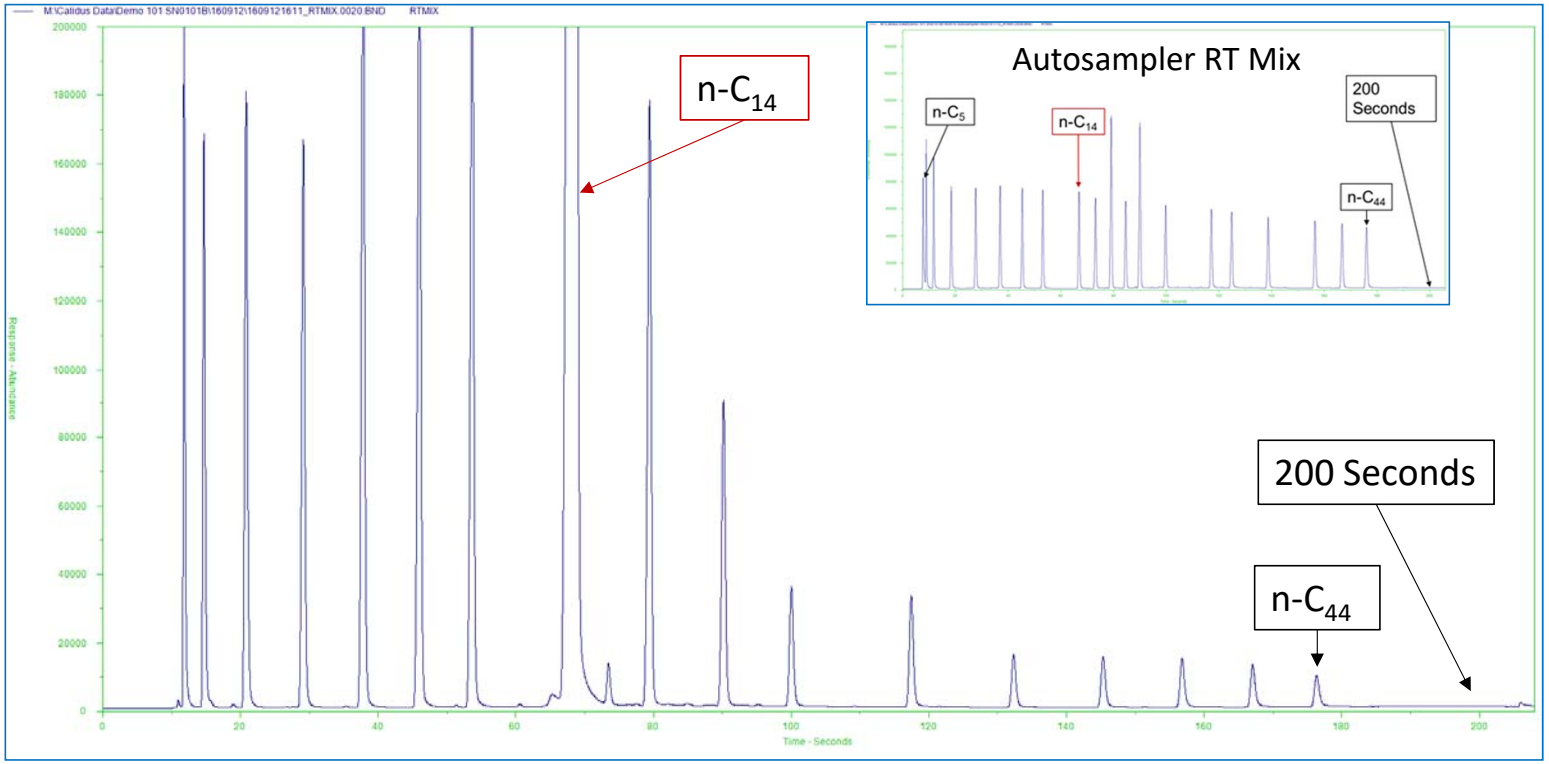


Non-injection Blank

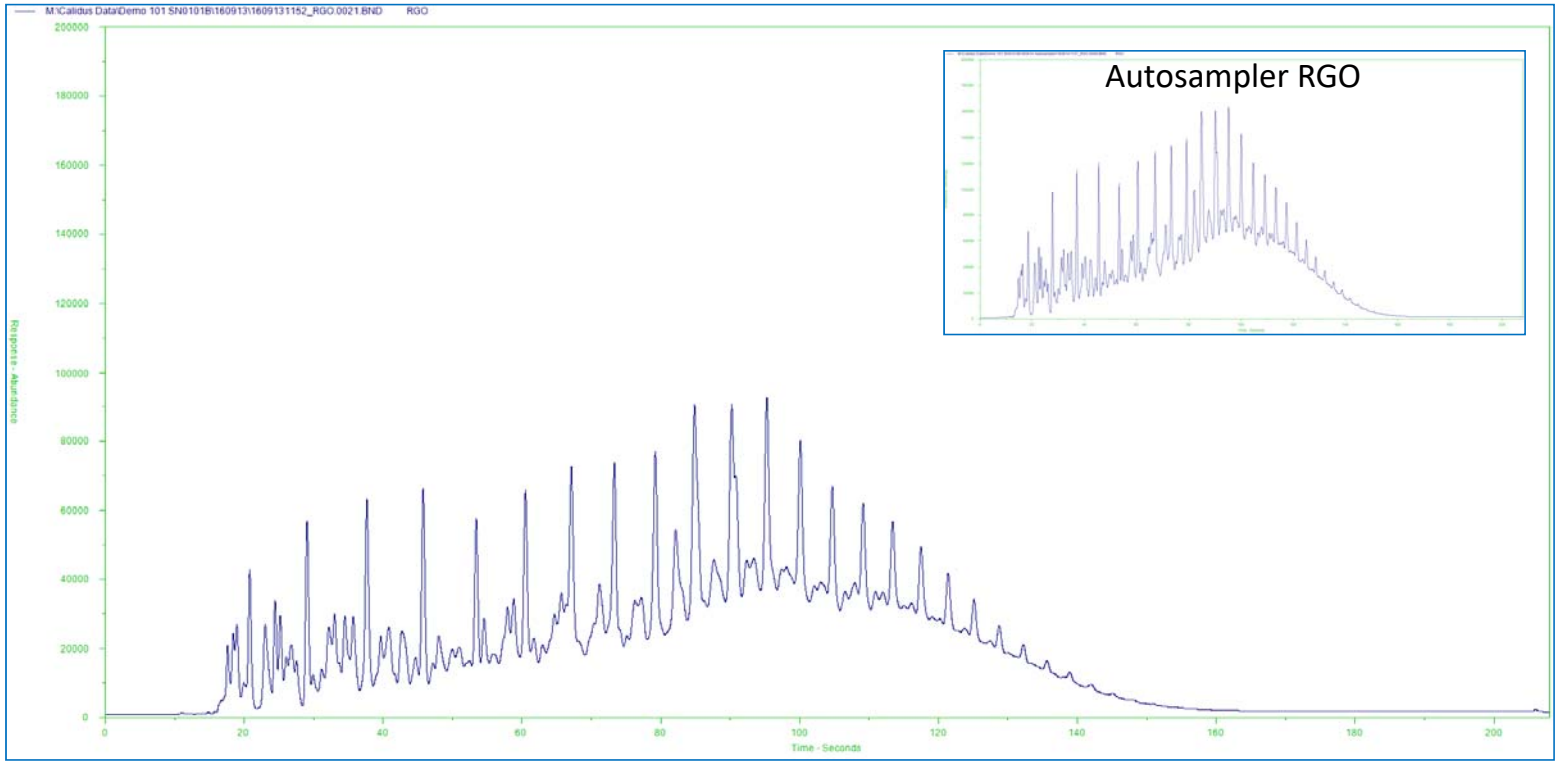
(Valve - actuator is turned off and the PTGC cycle is started)



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



RGO (Valve- injects the Reference Gas Oil sample)

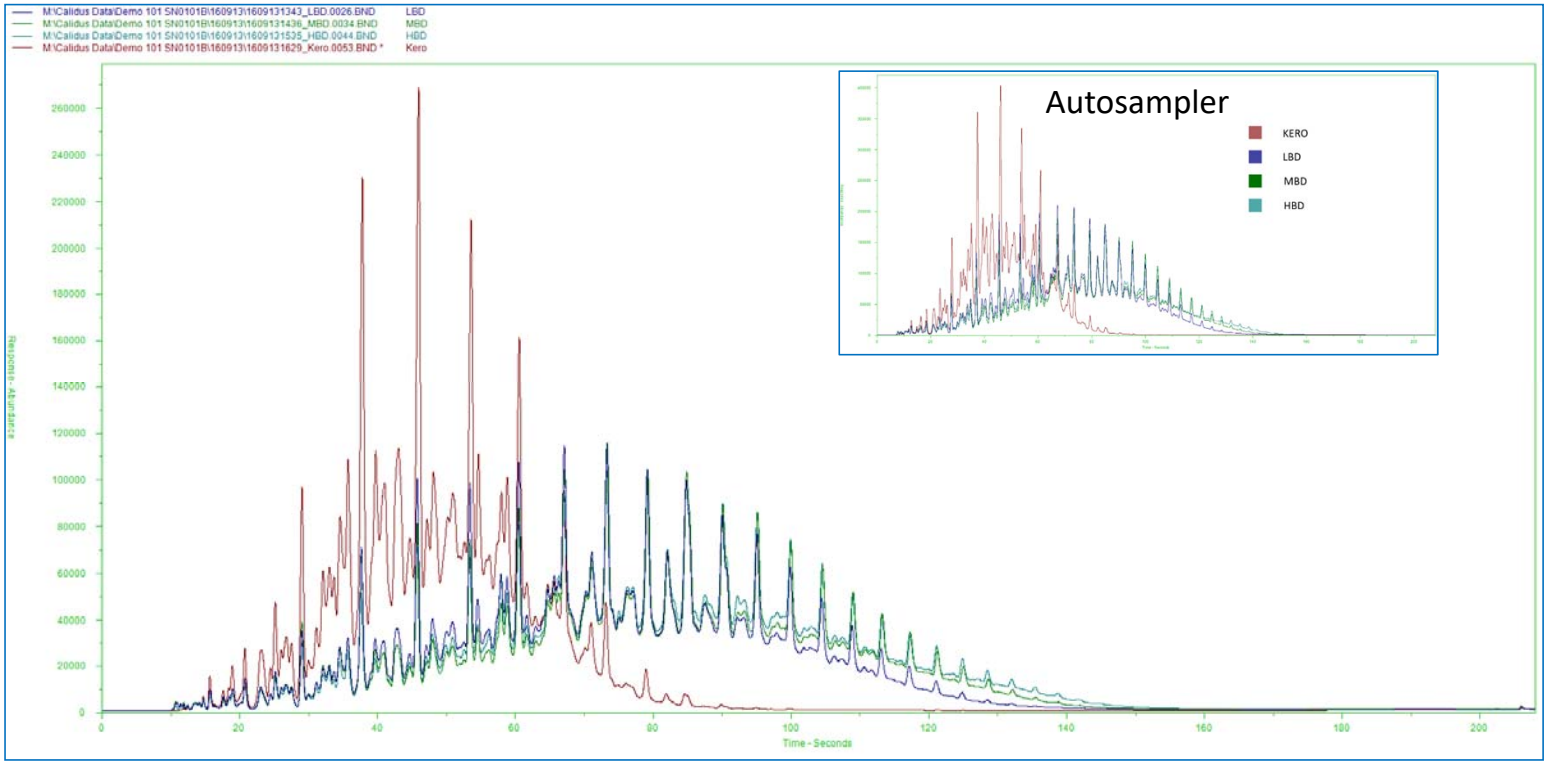


RGO SimDist Results (Valve)

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

RGO (deg. F)				
% OFF	Accepted Value	Measured Value	**Difference**	D-7798 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

Samples Run with Valve - LBD, MBD, HBD, Kerosene



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Lab and Process Comparison

Autosampler Inlet

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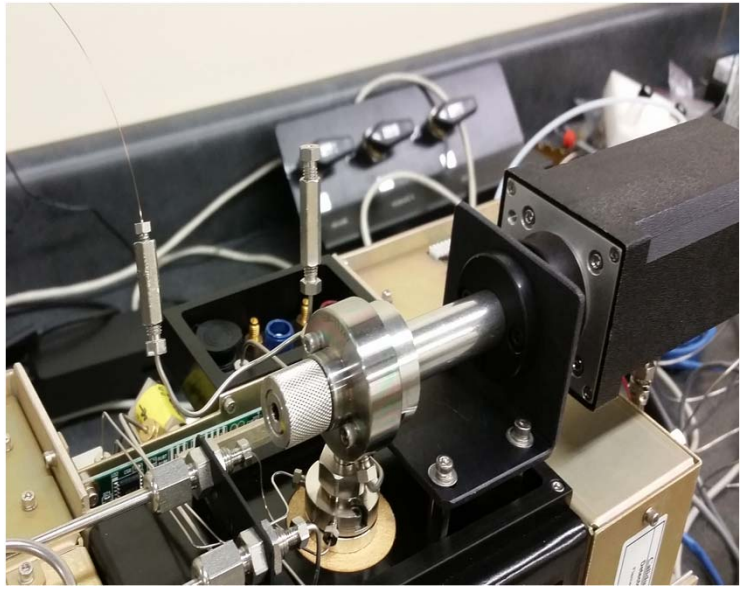
Rotary Valve Inlet



RGO (Autosampler Minus Valve Results)

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**

RGO Autosampler Minus Valve (°F)

	LBD		MBD		HBD		Kero	
		Allowable		Allowable		Allowable		Allowable
% OFF	AVG	Delta	AVG	Delta	AVG	Delta	AVG	Delta
IBP	-0.4	11.8	0.6	11.8	-2.0	11.8	-2.3	11.8
5	0.2	7.2	0.2	7.2	-1.4	7.2	-0.2	7.2
10	-1.5	7.7	0.0	7.7	0.8	7.7	0.8	7.7
20	-1.2	8.5	-0.4	8.5	1.9	8.5	1.9	8.5
30	3.9	7.8	4.8	7.8	5.4	7.8	2.2	7.8
40	7.3	7.7	2.6	7.7	4.1	7.7	2.1	7.7
50	4.9	7.7	-0.5	7.7	-3.2	7.7	2.8	7.7
60	-3.0	7.7	-1.7	7.7	-2.2	7.7	2.6	7.7
70	-2.3	7.7	-3.4	7.7	-0.9	7.7	4.4	7.7
80	-1.3	7.7	-3.7	7.7	-2.5	7.7	6.9	7.7
90	-1.9	7.7	-2.9	7.7	-3.7	7.7	9.1	7.7
95	-3.9	9.0	-3.1	9.0	-2.5	9.0	7.1	9.0
FBP	-13.8	21.2	-12.5	21.2	-13.1	21.2	-16.5	21.2

Note:
8 replicates of each sample type were run with each injection method. These results were averaged to obtain the data in this table. Allowable delta is determined according to ASTM D2887 reproducibility rules

4 Samples, 8 Replicate Statistics (°F)
(Autosampler and Valve)

	Autsoampler								Valve							
	LBD		MBD		HBD		Kero		LBD		MBD		HBD		Kero	
% OFF	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	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	228.3	2.4	225.1	3.5	239.9	0.3	227.1	0.5
5	329.1	0.1	329.5	0.1	339.9	0.3	292.5	0.1	329.0	0.2	329.3	0.7	341.4	0.4	292.7	0.3
10	363.3	0.2	370.1	0.1	384.3	0.2	319.4	0.1	364.8	0.6	370.1	1.0	383.6	0.1	318.6	0.2
15	391.1	0.2	404.0	0.1	415.6	0.4	333.0	0.1	391.9	0.3	404.9	1.4	416.9	0.5	331.8	0.3
20	416.3	0.2	432.5	0.1	442.4	0.4	345.5	0.0	417.5	0.2	432.9	1.5	440.6	0.3	343.6	0.2
25	435.7	0.2	456.6	0.1	462.8	0.5	353.6	0.1	435.9	0.2	453.2	0.7	461.0	0.6	351.8	0.4
30	455.4	0.2	480.2	0.1	485.0	0.6	362.8	0.1	451.4	0.1	475.5	0.8	479.7	0.3	360.6	0.3
35	473.5	0.2	495.1	0.1	503.3	0.7	373.3	0.1	469.7	0.1	490.5	1.5	498.6	0.5	370.9	0.3
40	489.1	0.2	514.2	0.1	520.5	0.7	384.4	0.1	481.9	0.1	511.6	1.1	516.4	0.5	382.2	0.5
45	505.4	0.2	529.8	0.1	538.1	0.8	389.3	0.1	500.4	0.3	529.6	1.0	538.8	0.7	386.4	0.4
50	520.7	0.2	548.2	0.0	555.7	1.0	398.8	0.1	515.8	0.3	548.6	0.5	559.0	0.6	396.0	0.5
55	536.7	0.2	565.0	0.1	575.0	1.0	409.2	0.1	536.6	0.4	567.0	0.9	575.1	0.4	406.5	0.5
60	551.9	0.2	579.7	0.1	589.7	1.1	419.0	0.1	554.9	0.7	581.4	0.9	591.8	0.6	416.4	0.6
65	571.1	0.3	598.9	0.1	605.7	1.3	425.7	0.1	573.2	0.4	600.7	0.3	608.6	0.7	422.2	0.5
70	585.4	0.3	616.0	0.2	626.3	1.3	436.2	0.1	587.7	0.6	619.4	0.9	627.2	0.5	431.8	0.7
75	603.0	0.2	636.1	0.2	647.2	1.4	447.6	0.1	604.3	0.7	639.8	0.9	649.4	0.5	442.1	0.6
80	624.4	0.3	658.0	0.2	669.2	1.5	458.4	0.1	625.8	0.5	661.7	1.0	671.7	0.6	451.5	0.4
85	647.5	0.3	682.7	0.2	694.7	1.6	471.2	0.1	649.6	0.7	686.2	1.2	696.1	0.7	463.9	1.3
90	673.9	0.2	712.3	0.2	726.4	1.7	488.9	0.1	675.8	1.7	715.2	1.0	730.1	1.2	479.8	0.7
95	711.0	0.3	751.9	0.3	773.3	1.9	511.3	0.1	714.9	1.9	755.0	1.9	775.9	2.0	504.2	3.2
FBP	793.1	1.3	828.6	1.1	856.2	2.3	576.7	0.2	806.9	8.9	841.1	12.7	869.3	12.3	593.2	26.8
Avg. St. Dev		**0.3**		**0.2**		**1.0**		**0.1**		**1.0**		**1.7**		**1.2**		**1.9**

4 Sample, All 16 Replicates Combined Statistics (°F)

(Autosampler and Valve)

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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	20.2
Avg. Std. Dev.		**1.8**		**1.9**		**1.9**		**2.7**

LineUp™

Retention Time Alignment

and

Pirouette®

Chemometrics

Autosampler and Valve Comparison

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

InfoMetrix®

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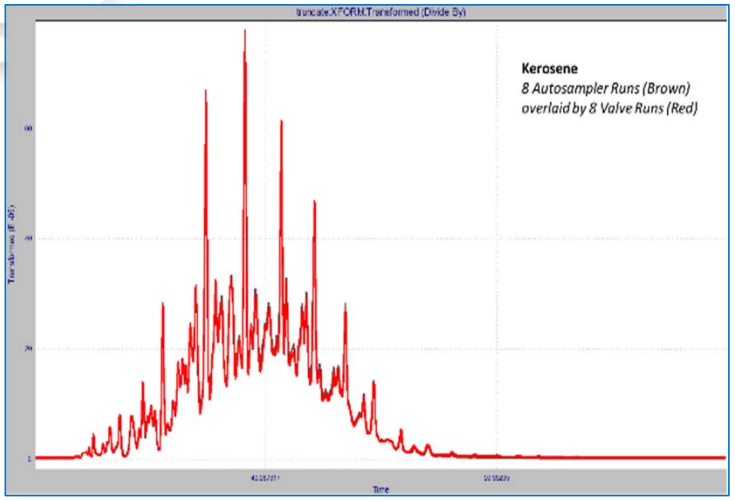
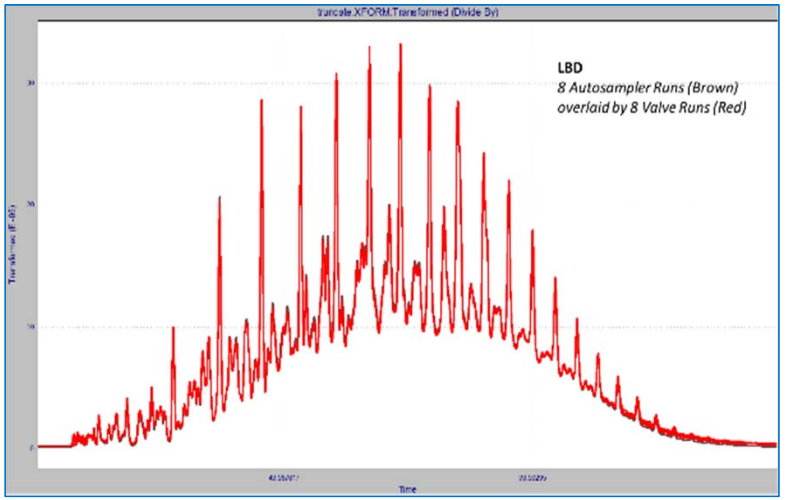
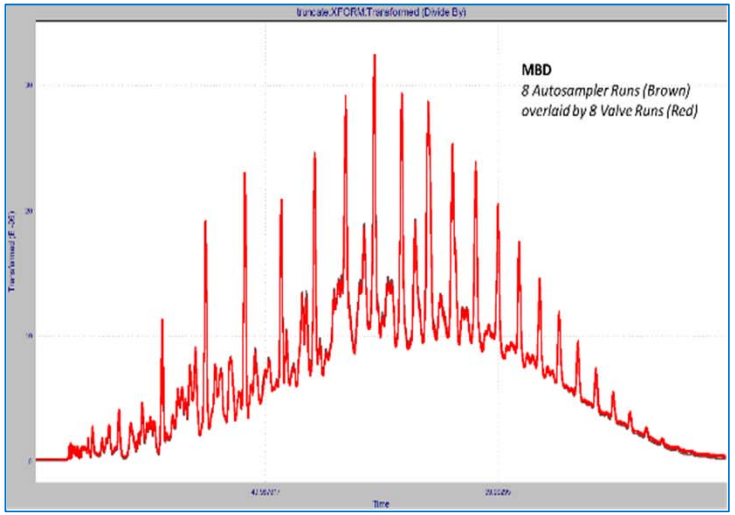
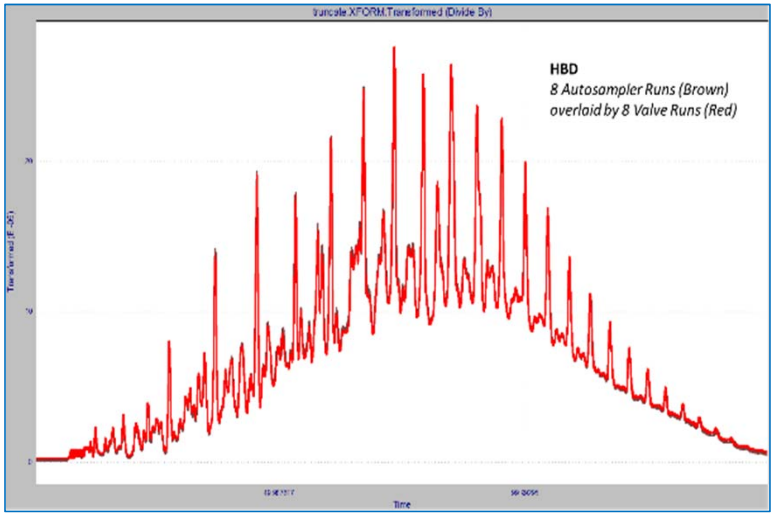
Data Equivalency

All 16 Autosampler and Valve Results Overlaid after Alignment and Normalization





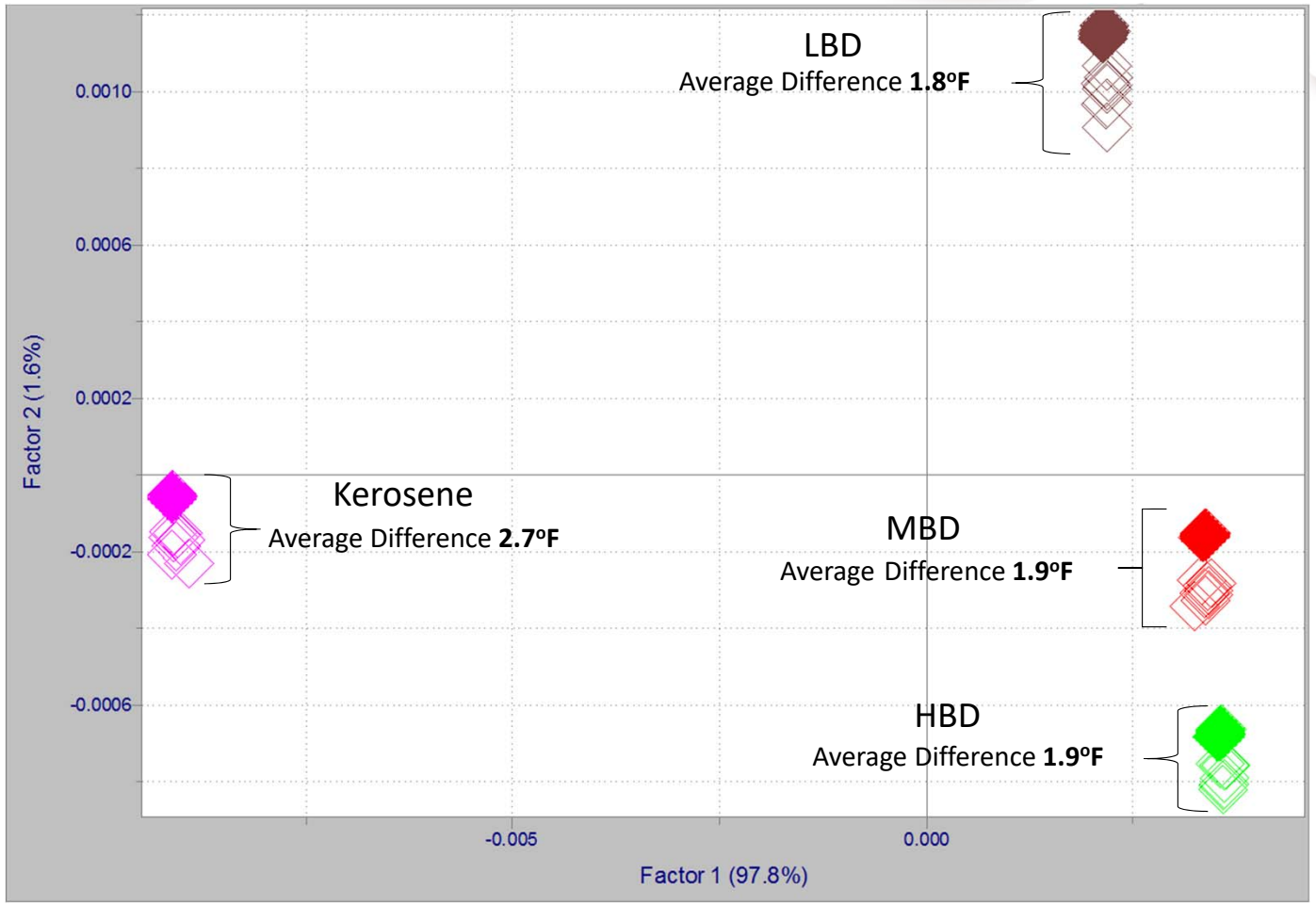




PCA Scores Plot – 16 Runs Per Sample Type

(8 Autosampler and 8 Valve, all results within ASTM D-7798 tolerances)

Y-axis amplified x50

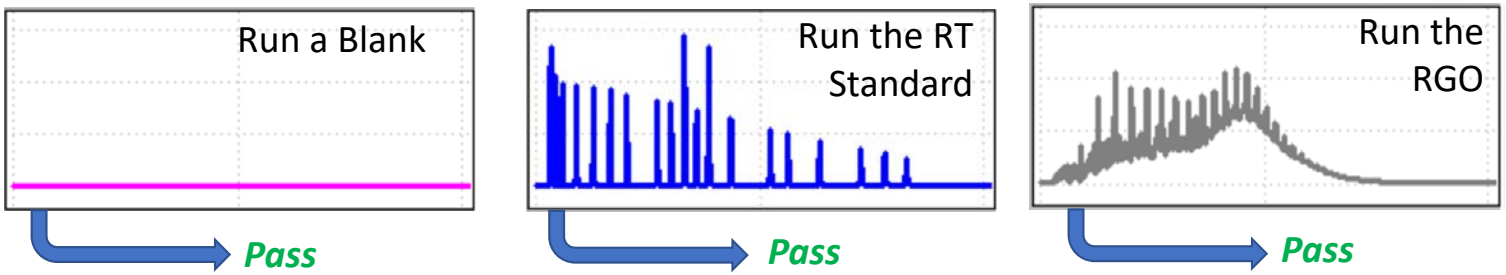


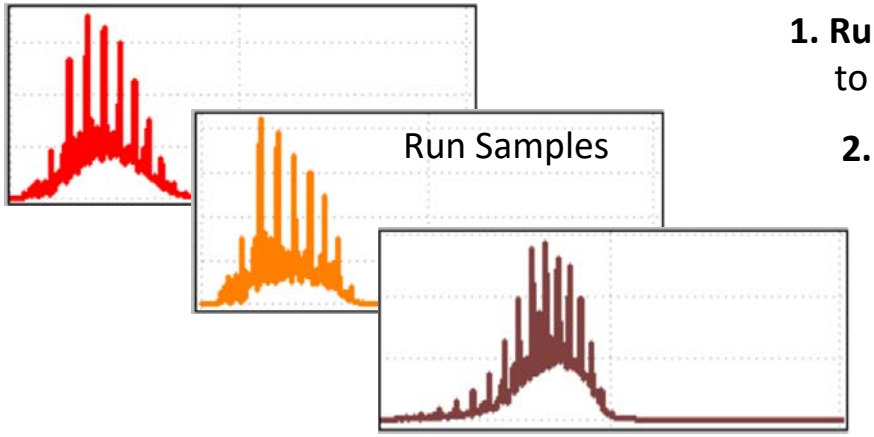
Autosampler

Sample Valve

SimDist D7798: lab versus on-line

Laboratory





1. Run a Blank
to insure a clean system

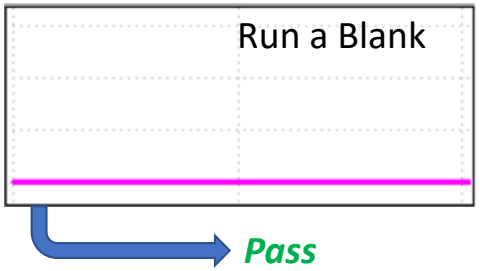
2. Run the n-Paraffin Standard
relates retention time to temperature

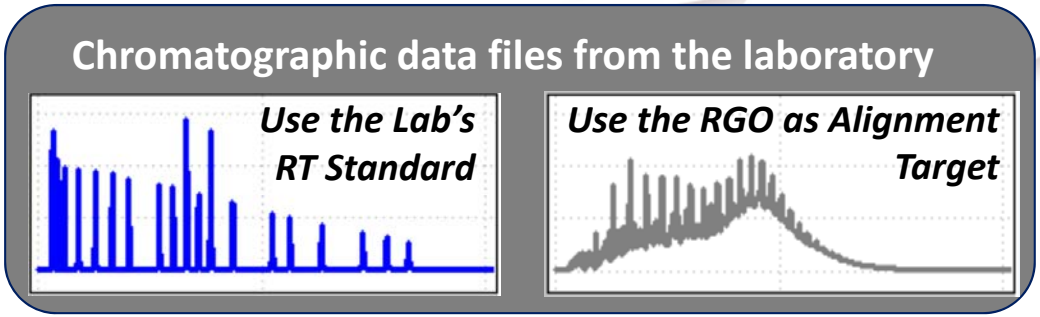
3. Run the Reference
to check results with a known

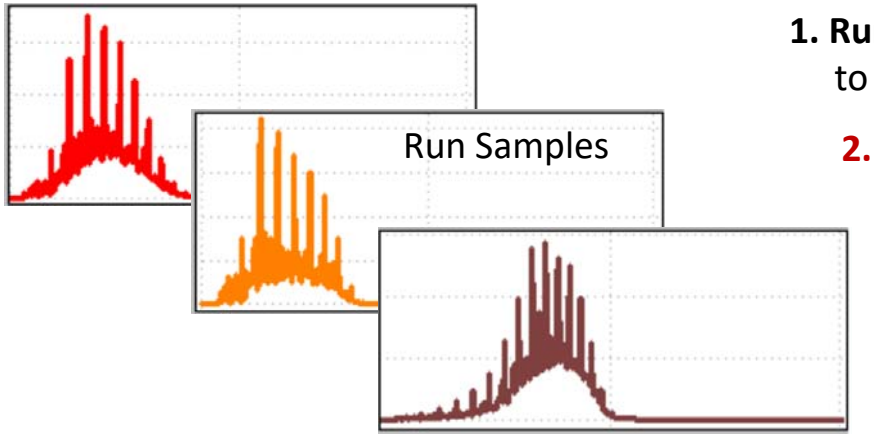
4. Run Samples

SimDist D7798: lab versus on-line

On-Line







1. Run a Blank
to insure a clean system

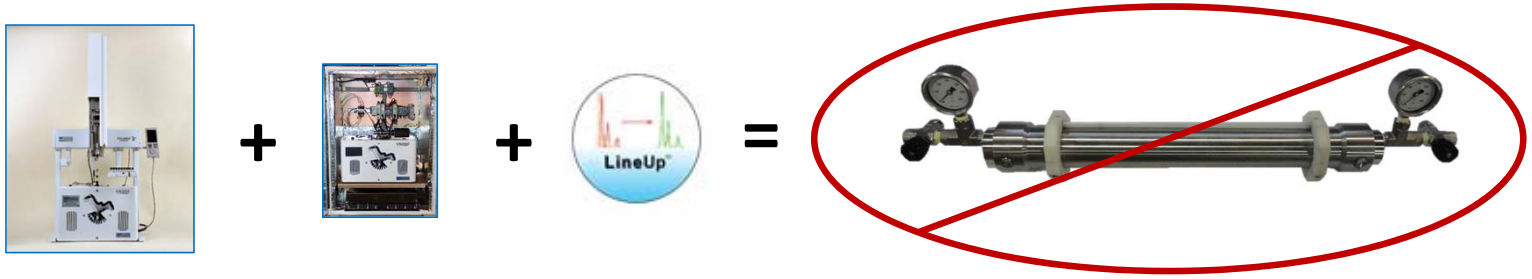
2. Use the *same* n-Paraffin Standard
from the run in the laboratory

3. Use the RGO or Process Sample
as an alignment target

4. Run Samples

Process and Lab GC's: Working Together

- The exact same GC model and methods can be used in the lab and the process
- What does this mean?
  - Lab GC data can completely ***eliminate*** the need for time consuming, complex work and ***costly calibration standards*** used on process GC's
  - The normal calibration process is: Blank→RTMIX→RGO
  - With chromatographic alignment, the process GC can be calibrated with ONLY ONE BLANK RUN using lab GC data files



Data Equivalency…

Regardless of Location the Result Are the Same

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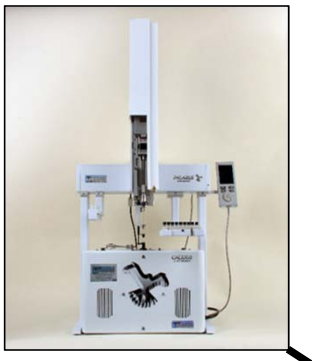
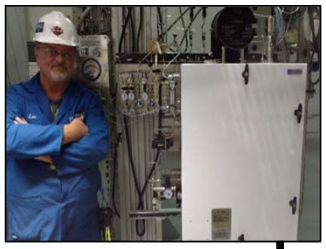
LAB



PROCESS



TRANSPORTABLE

Questions?

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Thank you for your interest & attention!