Resolving the Conflict between Lab and Process Data

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Abstract

Resolving the Conflict between Lab and Process Data 1:00-1:20

Dr. Carl Rechsteiner
CRechsteiner Consulting (Chevron retired)

The conflict between lab and process data has always existed because the process data doesn't always match the lab data. The lab's primary function is to validate and certify products and it is therefore the adjudicator should discrepancies in data arise. Consequently, if the two sources of information do not conform, the process side is required to make the necessary changes, corrections, and adjustments; hence the conflict.

This paper explores data results for petroleum fraction samples ranging up to C44 or 535 ºC end boiling point on a lab and a process gas chromatograph (GC) wherein the same hardware and methods were used. The two GC's differ only in their sample introduction, sample volume and start time. The paper will discuss the operational parameters and the differences in results from liquid syringe autosampler based inlets used in laboratories to rotary valve based inlets required in the process.

Reasons for “Conflicts”

Objectives, Requirements, Tools (ORT)

	Laboratory	Process
Objectives	Product Release Process Troubleshooting Methods Development/Improvement	Stable Operations Performance Indicators Corrective Actions
Requirements	Meet Product Specifications Meet Data Quality Objectives Auditable Data	Speed to make control decisions Repeatability Data Consistency
Tools	Laboratory grade instruments Adherence to standard protocols (ASTM) Statistical quality control Discrete samples	Mixture of instruments and sensors Inferential spectroscopic common Locally developed assessments Continuous flow

To resolve “conflicts” need systems that can meet both the lab and process (ORT) in a safe, sustainable way.

Practical Solution

A Single Instrumental Core for Both Lab and Process

The initial Calidus strategy was to design a system that would span applications in both realms. A natural extension is to make it mobile.

LAB

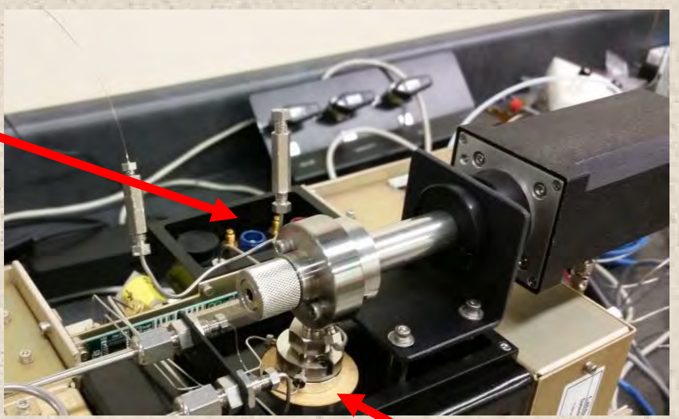
PROCESS

TRANSPORTABLE

Sample Delivery System

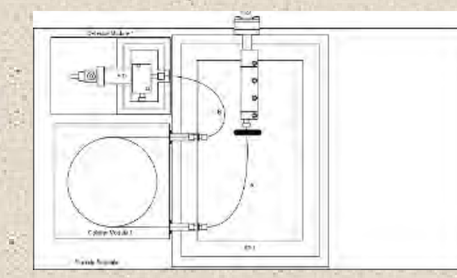
The core difference between lab and process versions is how the sample is introduced (discrete or continuous). The separation components, detectors, etc. are the same. The exterior casing is appropriate to the local environment.

Sample Loop (Process)



Injection Port (Lab)

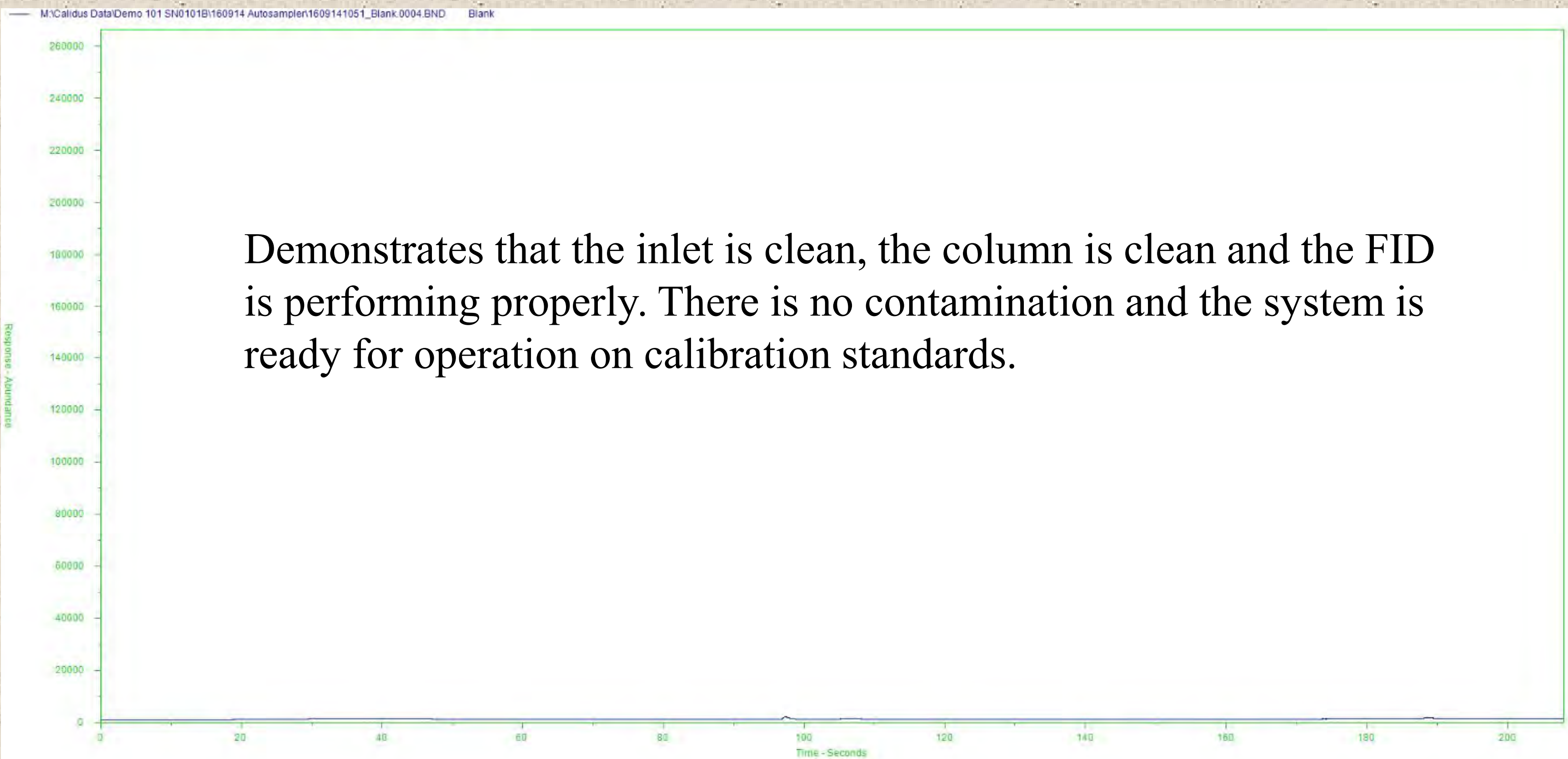
Lab Application – Simulated Distillation (SimDis)
Calidus 101-HT with Liquid Syringe Autosampler



- ASTM D7798 was followed
  - Split injection
    - 350^{o}C
    - 70 nanoliter sample injected
    - Split ratio ~ 50:1
  - FID at 350^{o}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^{o}C
    - Programmed temperature rate 2^{o}C per second
    - Final temperature 385^{o}C
  - **Injection to injection cycle time <5 minutes**

Blank Chromatogram

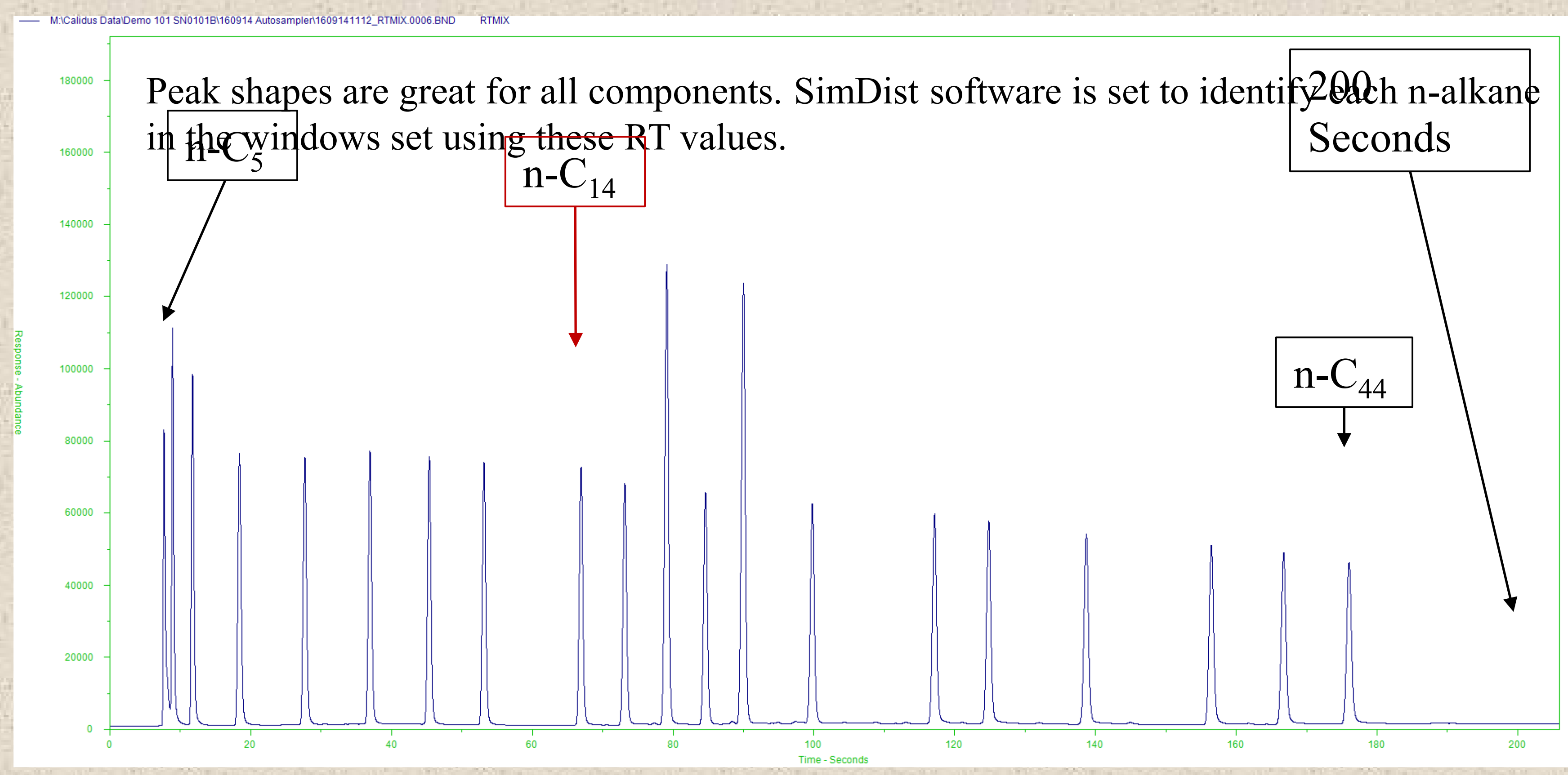
Injection of an empty, clean syringe



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.

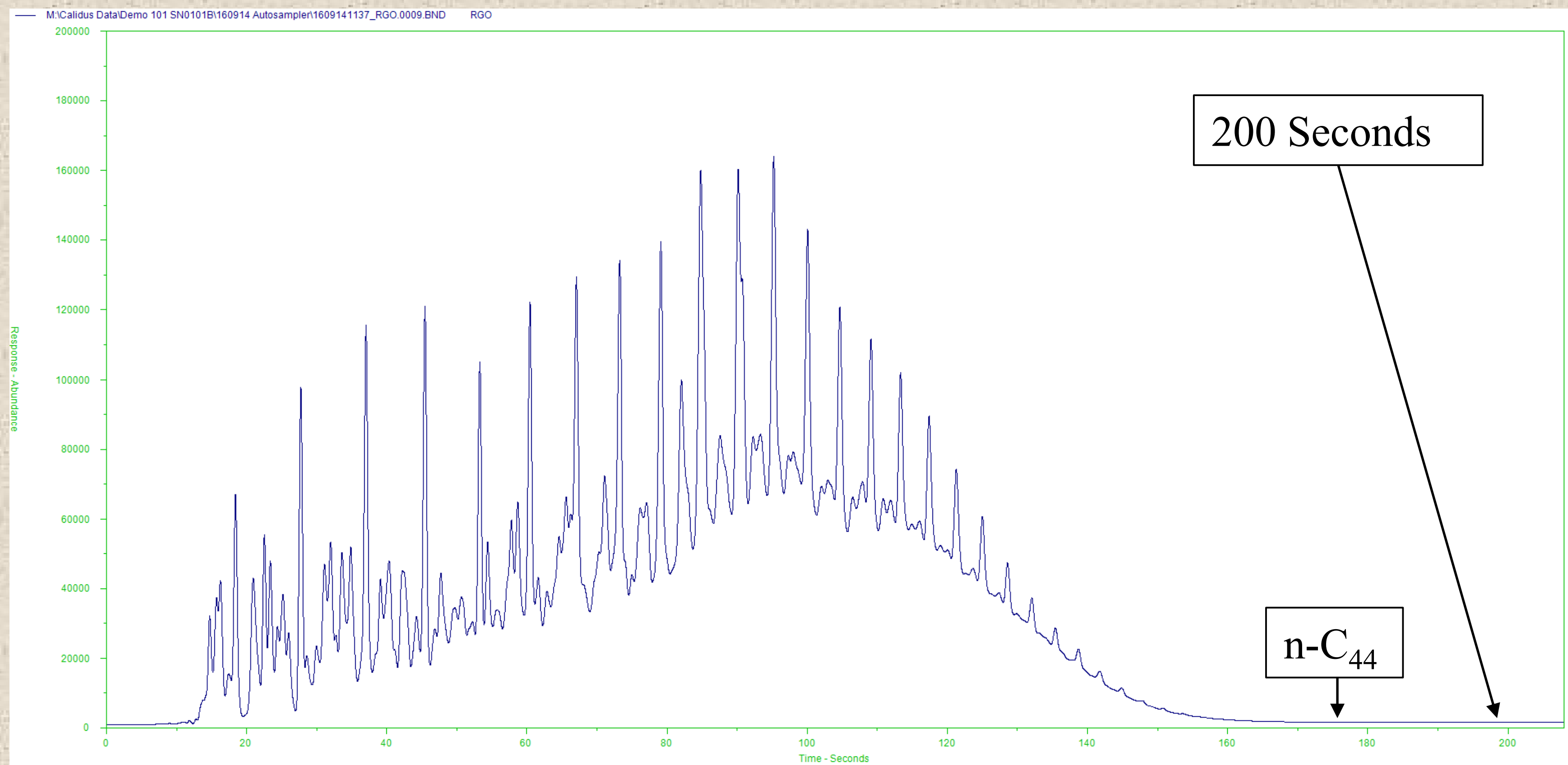
Retention Time Standard Mix

Standard mix, n-C_5 to n-C_{44} in CS_2 solvent injected



Reference Gas Oil Example

Run completed in 200 seconds,
100 second cool-down until ready to inject new sample



RGO SimDis Results (Lab)

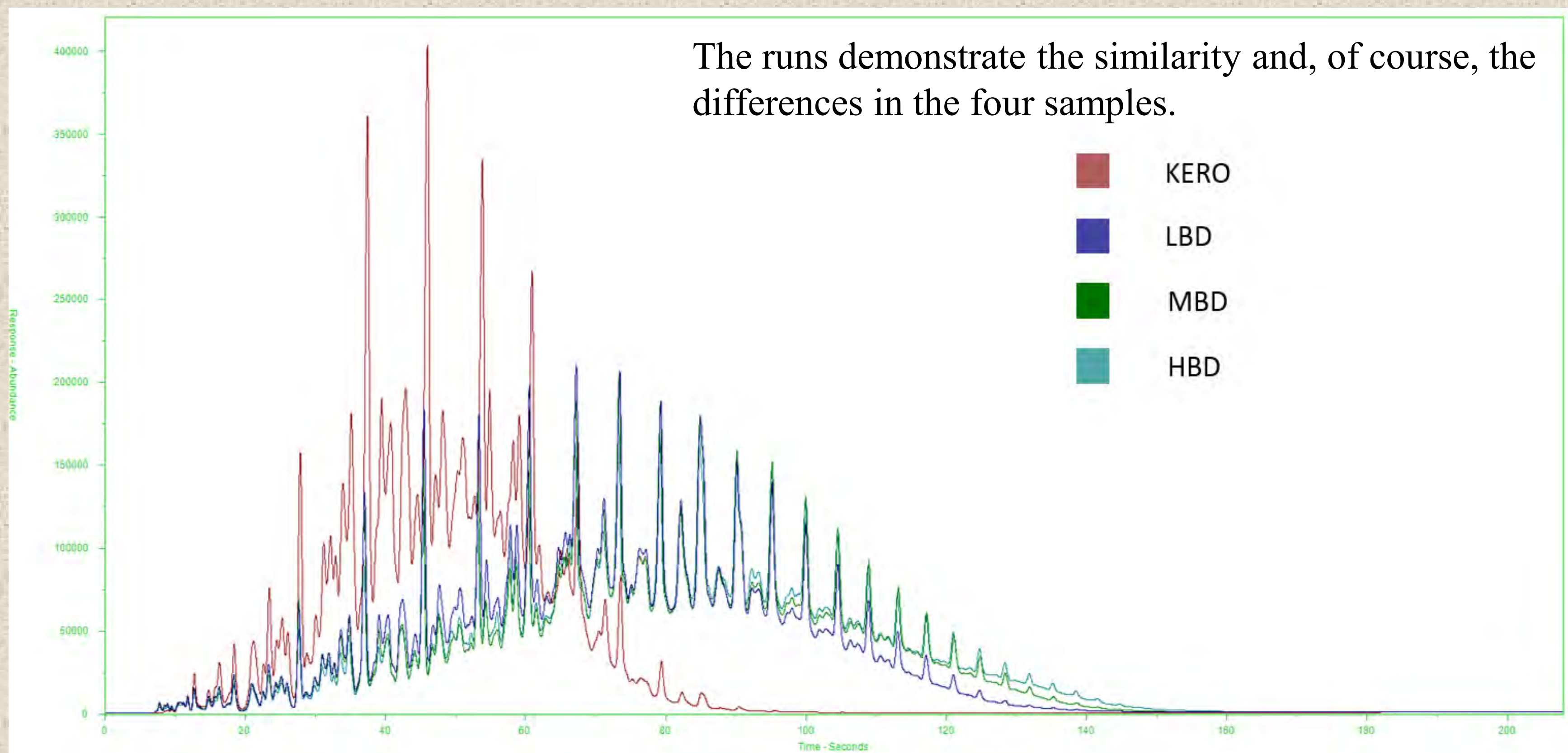
All boiling points are within the tolerance of ASTM D-7798 method.

RGO (ºF)

% OFF	Accepted	Measured	**Difference**	D-7798 Specification
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

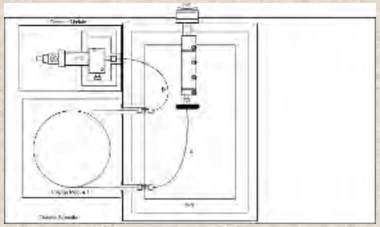
Test Samples Run (Lab)
LBD, MBD, HBD, Kerosene

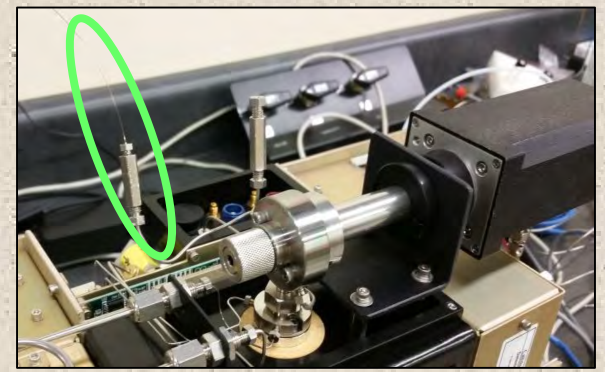
The runs demonstrate the similarity and, of course, the differences in the four samples.



Process Application – Simulated Distillation (SimDis)

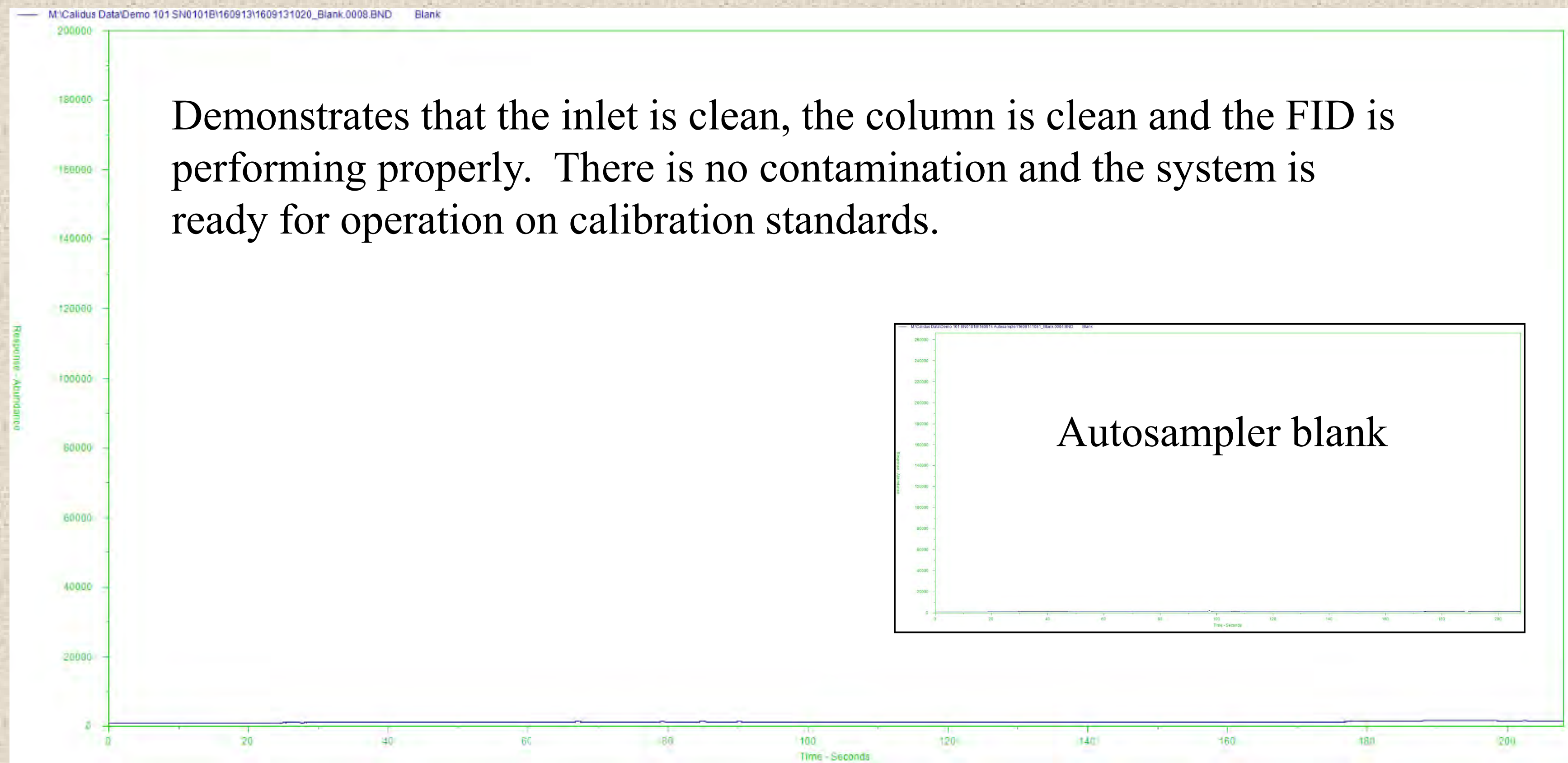
- ASTM D7798 was followed
  - Sample inlet via heated Valco rotary valve
    - Maintained at 225°C
    - Syringe loaded with capillary outlet to maintain pressure in the loop
    - 3 second delay was employed for pressure balance reasons (now proven unnecessary)
  - Split injection
    - 350°C
    - 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 during process GC cycle)



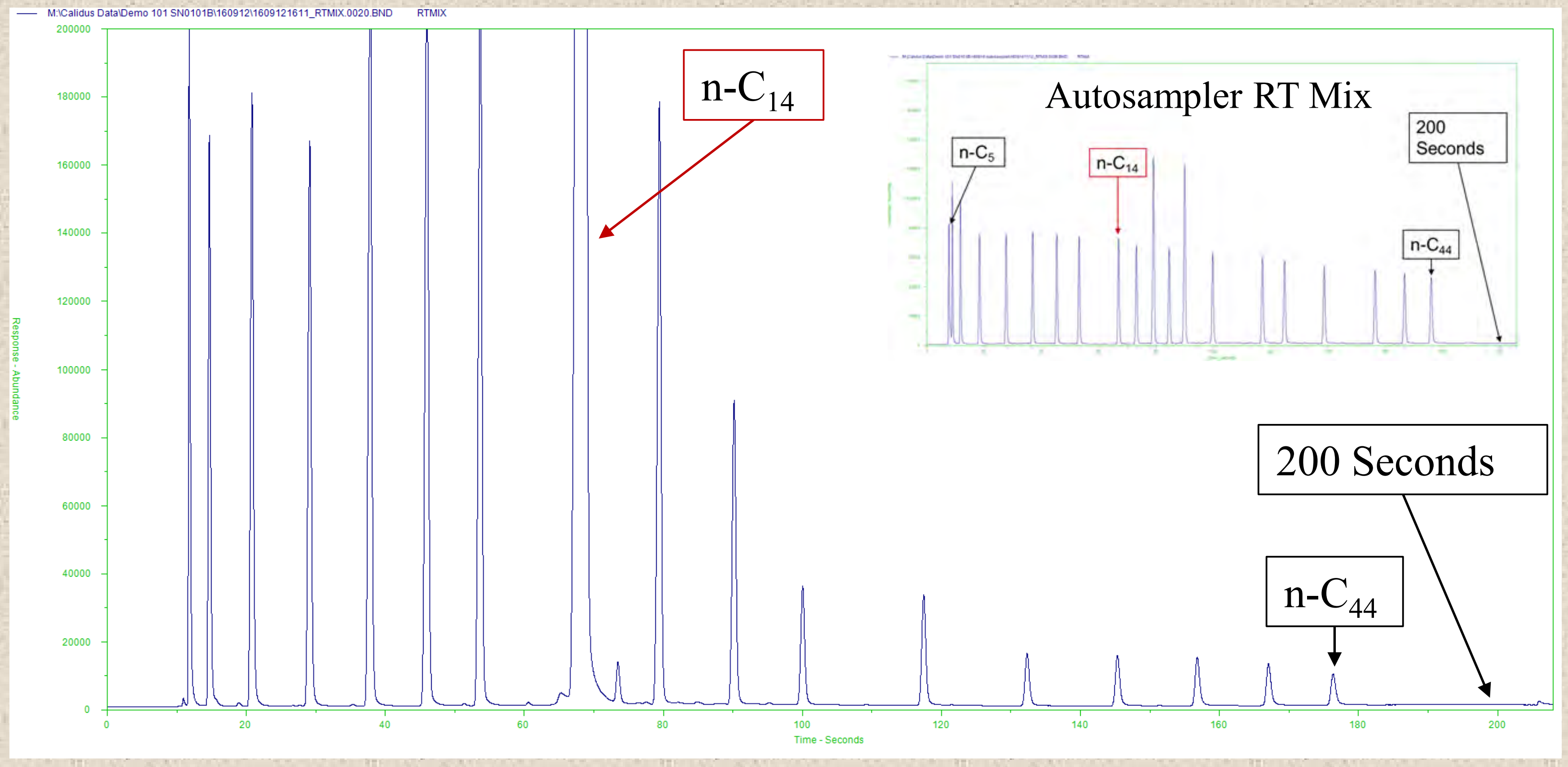
Demonstrates that the inlet is clean, the column is clean and the FID is performing properly. There is no contamination and the system is ready for operation on calibration standards.

Autosampler blank

Note similarity between process and lab GC performance

Retention Time Standard Mix

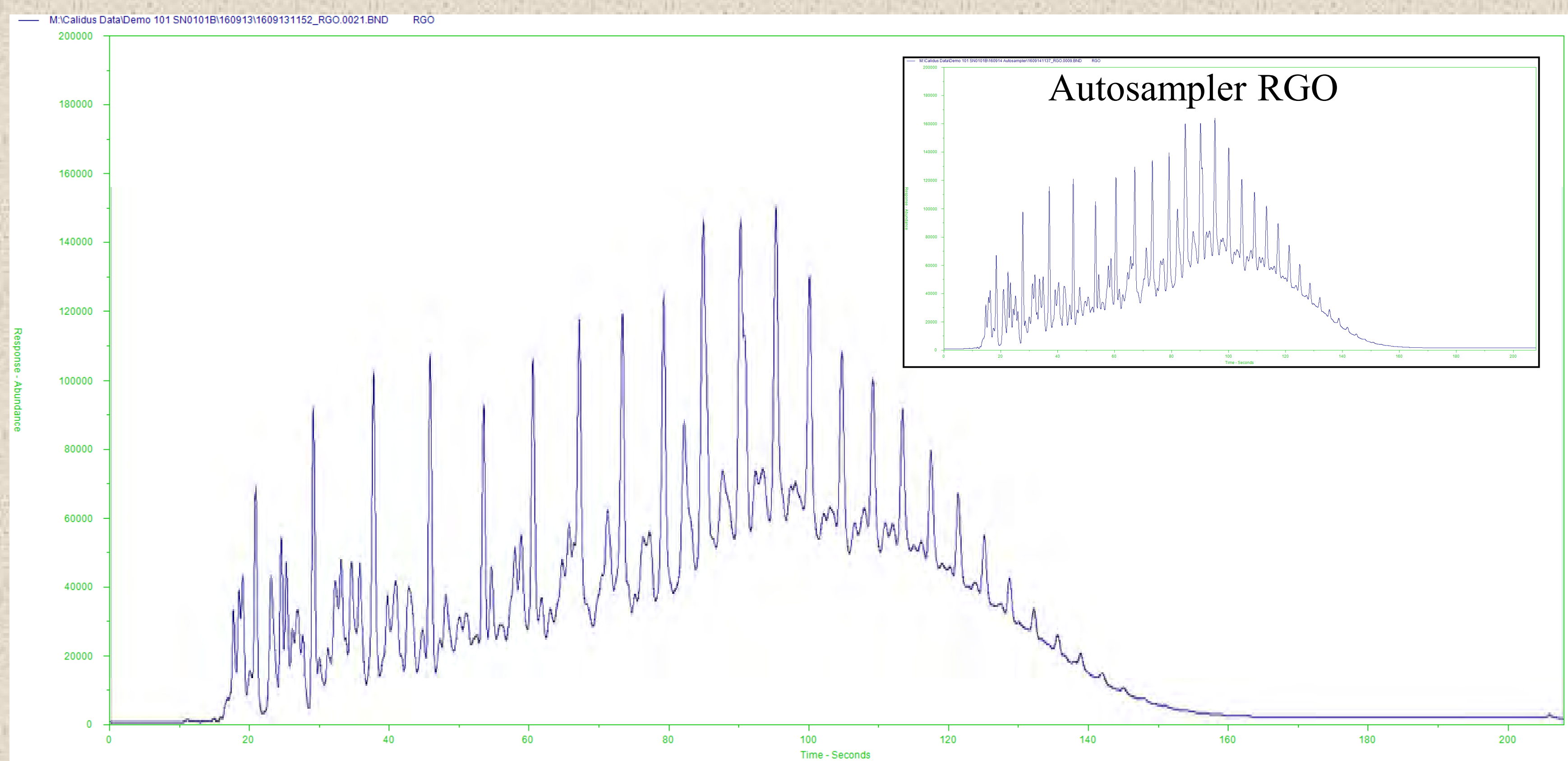
Specially prepared neat n-alkane mix with n-C_{14} instead of CS_2 solvent i(used in the lab system)



Note similarity between process and lab GC performance

Reference Gas Oil – Process System

(Loop valve injection of the Reference Gas Oil sample)



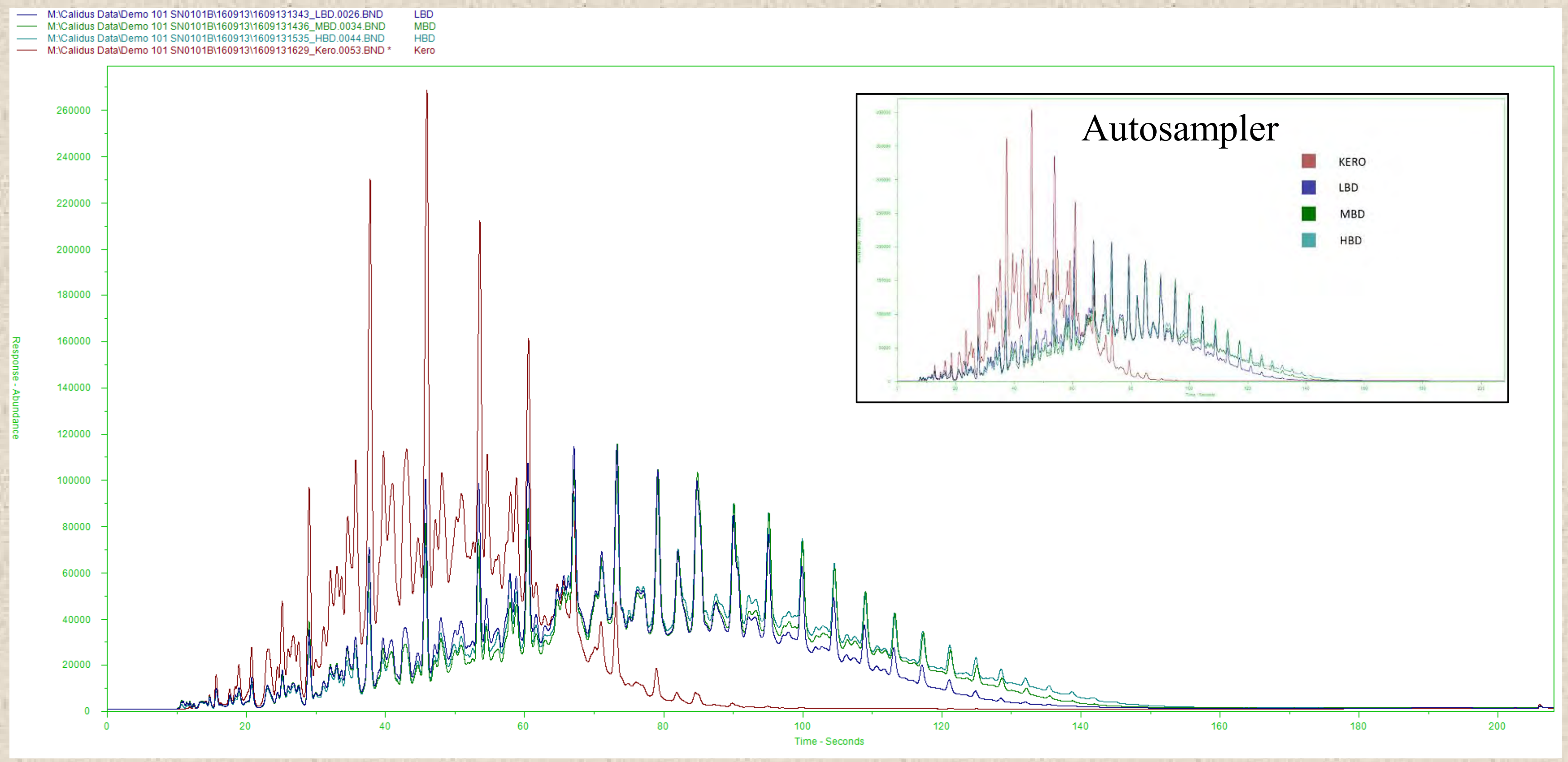
RGO SimDis Results (Process)

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

RGO (ºF)

% 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

Test Samples Run (Process)
LBD, MBD, HBD, Kerosene



RGO (Autosampler Minus Valve Results)

RGO Lab		RGO Process		
% 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**

Diferrence at 40% off likely due to variation in C_{16} peak position in calibrant (BP 548°F)

4 Samples, 8 Replicate Statistics
(Lab and Process)

	Autsoampler °F								Valve °F							
	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 Pooled Statistics

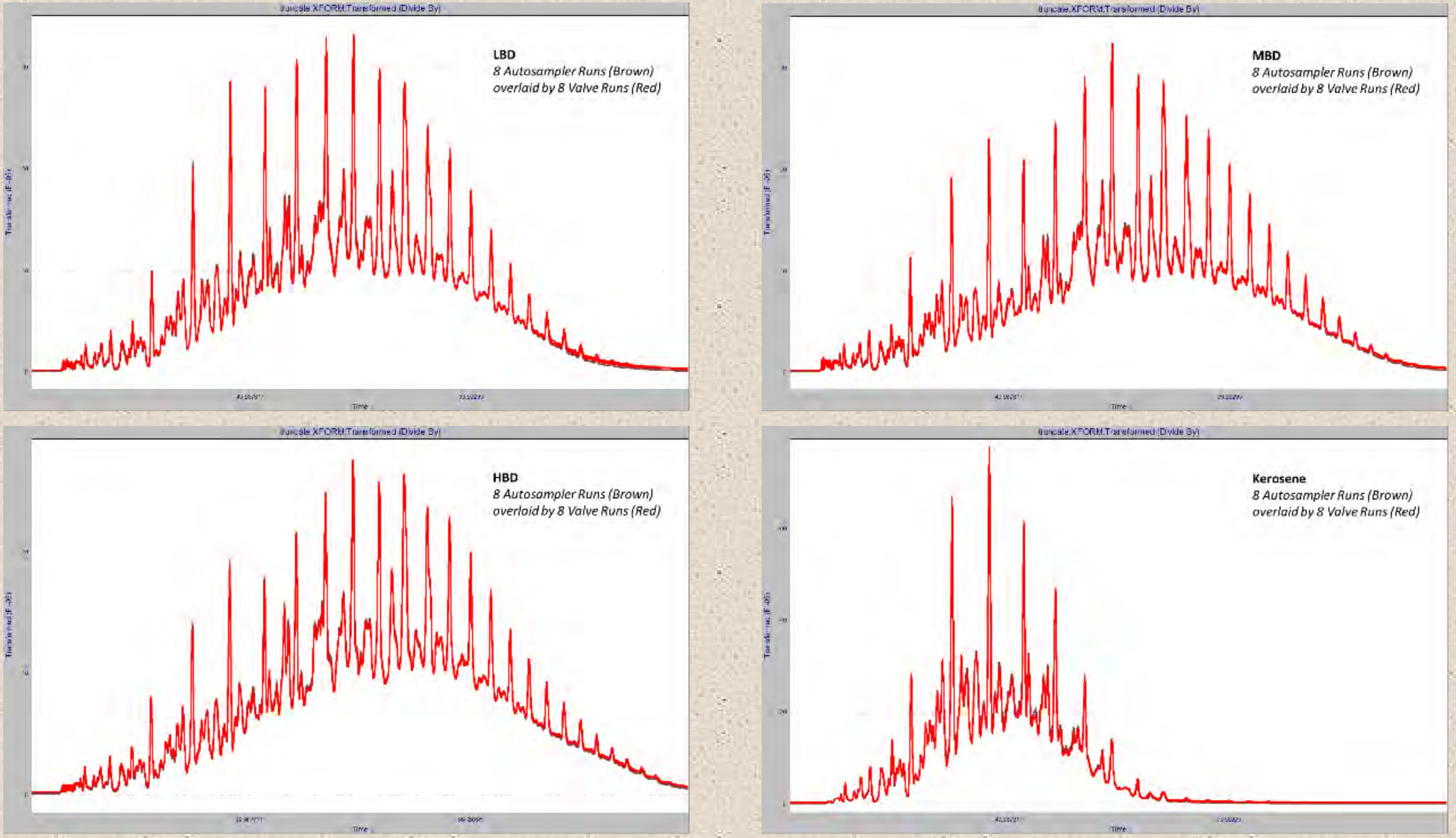
(Lab and Process)

Combined °F

	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**

Pooled Lab and Process Results Overlaid

(Aligned and Normalized)



Next Steps

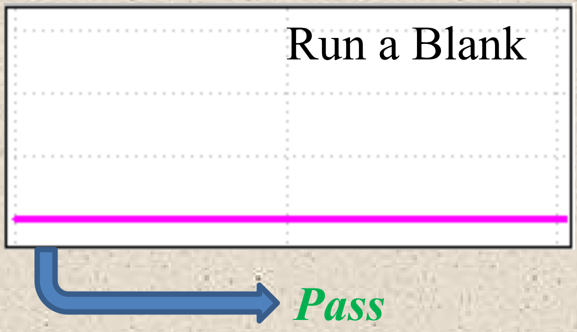
With lab and process instruments giving equivalent results, significant total cycle time improvements can be made for product release, and process troubleshooting and improvement.

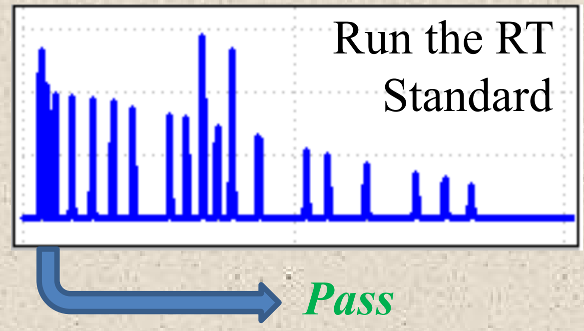
With measurement cycle times consistent with process control needs, the use of primary measurements with sensors, improves upon the control done with inferential devices.

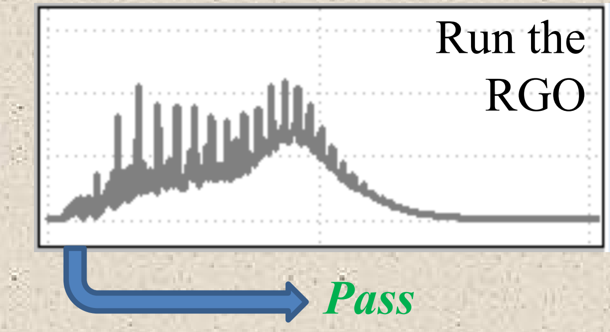
Advanced statistical approaches can improve the robustness of these measurements. The 11:40 and 1:20 papers by Dr. Brian Rohrbach will discuss some of these points.

SimDis D7798: lab versus process

Laboratory – examples are 7 lab ILS samples overlaid







1. Run a Blank
to ensure a clean system

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

3. Run the Reference
to check results with a known

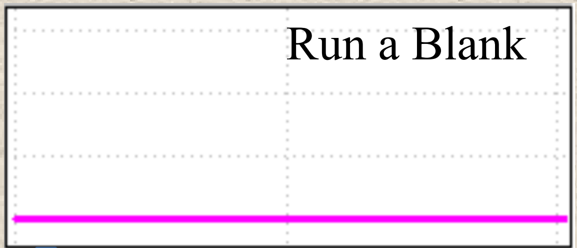
4. Run Samples

Presented 2017 Gulf Coast Conference
Houston, TX January 17 – 18 2018

Slide courtesy Infometrix
Dr. Brian Rohrback

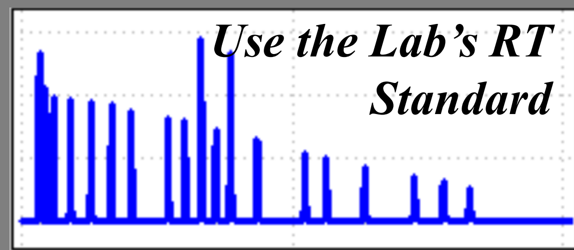
SimDis D7798: lab versus process

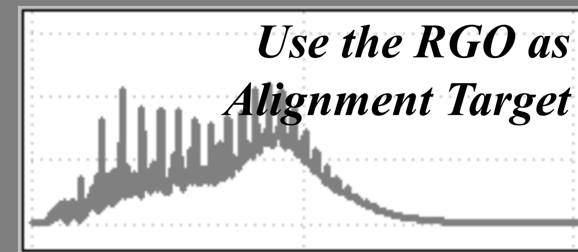
On-Line



Pass

Chromatographic files from the laboratory





1. Run a Blank
to ensure a clean system

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

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

4. Run Samples

Slide courtesy Infometrix
Dr. Brian Rohrback

Process and Lab GC's: Working Together

- The exact same GC core instrumentation 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
  - Can be used for on-line product release
  - 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.** That is, one can calibrate in one place and use that calibration in many places.

Acknowledgements

The presenter would like to thank all those who helped make this presentation possible:

Staff at Falcon Analytical, especially John Crandall and Ned Roques.

The happy customers using the Calidus GC for sharing their data while making a difference at their companies.