Use of Fast Gas Chromatographic and Chemometric Technologies for Hydrocarbon Characterizations from Exploration Activities to the Refinery Floor and Beyond

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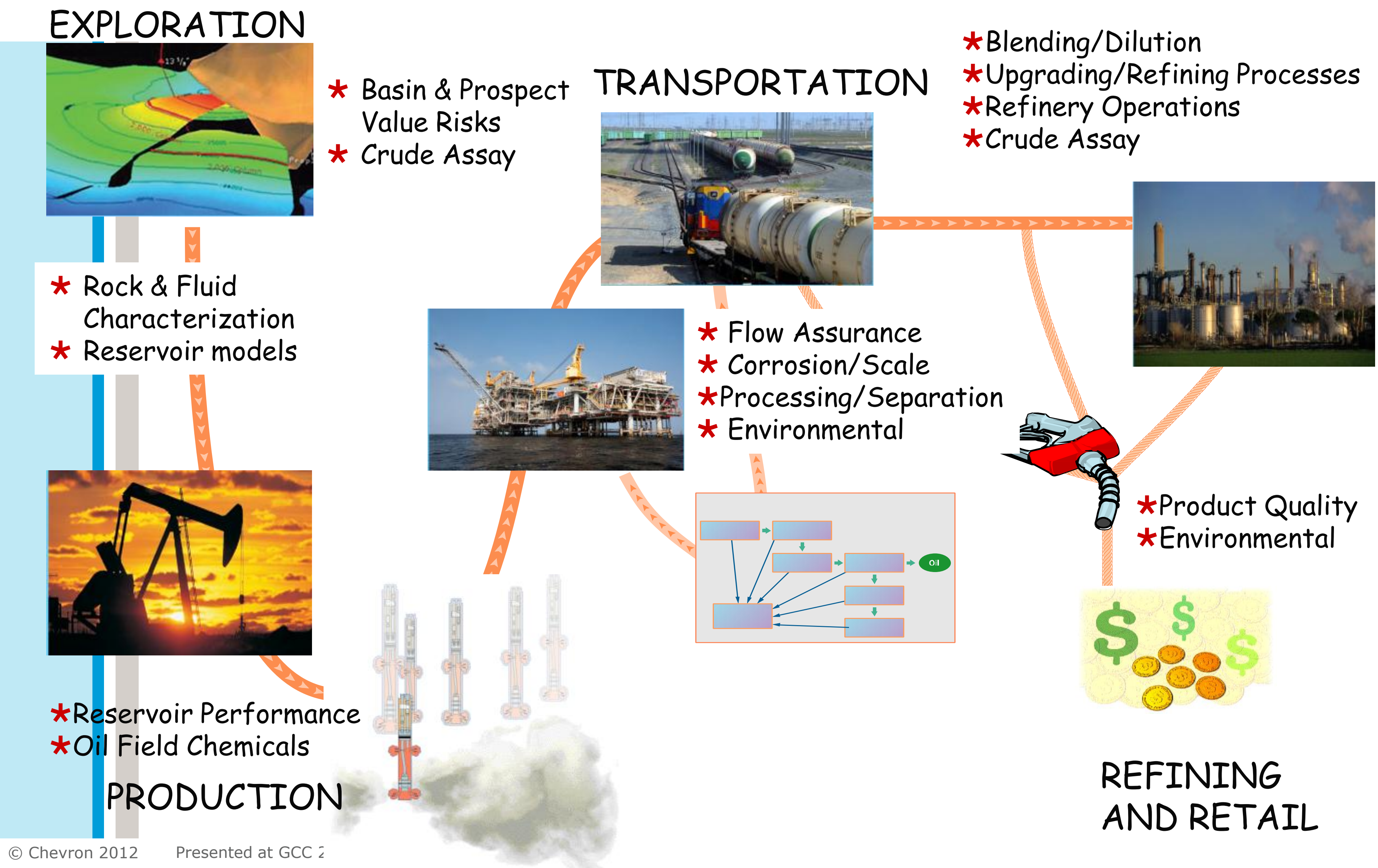
Presented at GCC 2012, Galveston, TX Oct. 16-17, 2012

Petroleum Value Chain

From Discovery to Customer Use



Petroleum Industry Application Coverage

From discovery to abandonment, from ingredient to finished product, - gas chromatography plays a prominent role in hydrocarbon evaluation

Upstream

Exploration | **Production**

Hydrocarbon System	Play Evaluation	Prospect Evaluation	Reservoir Delineation	Production Optimization	Field Development	Reservoir Management	Field Abandonment

Downstream

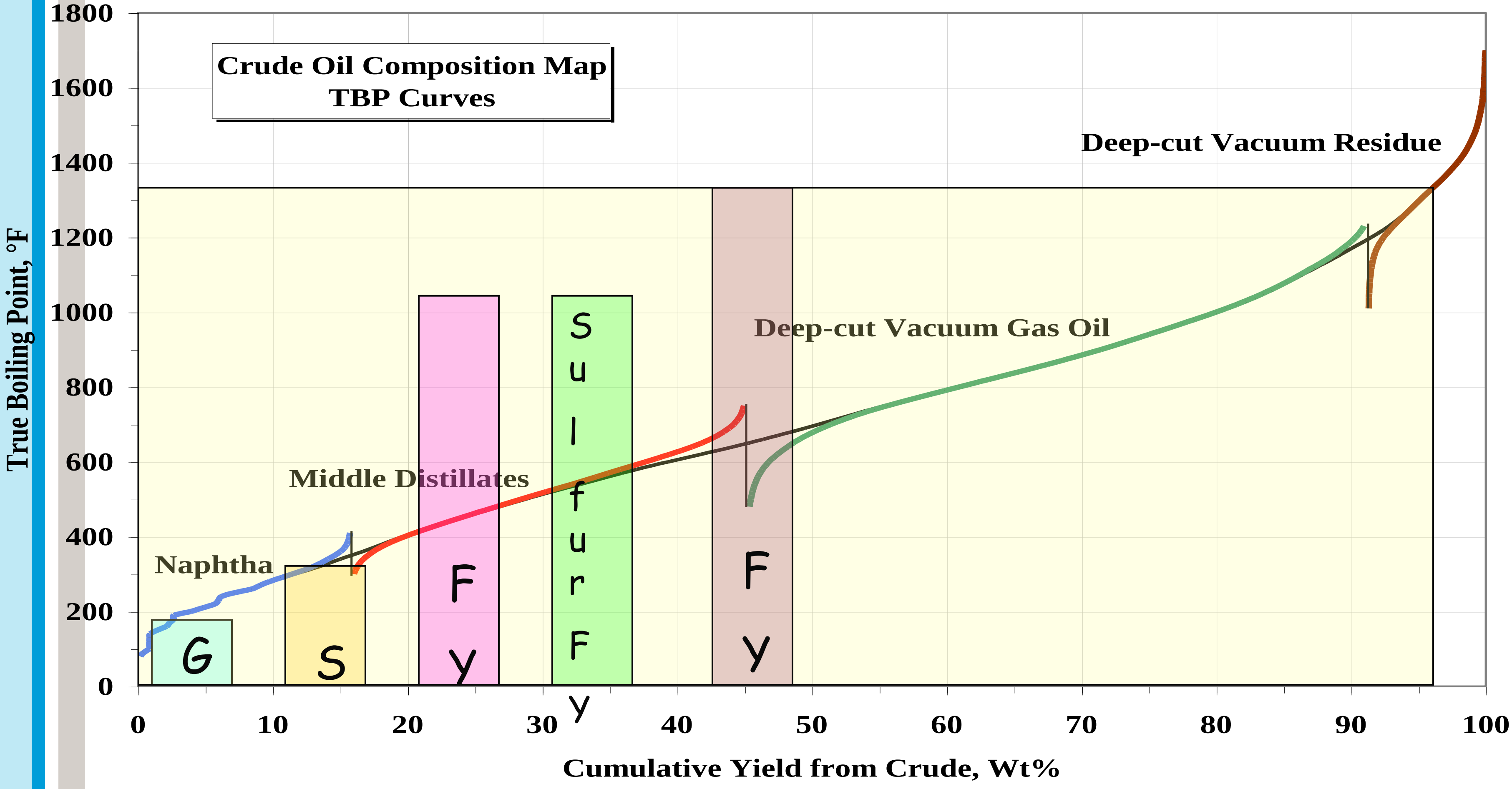
Transport & Storage	Processing QC	Product QC	Distribution & Retail

Refining and Distribution

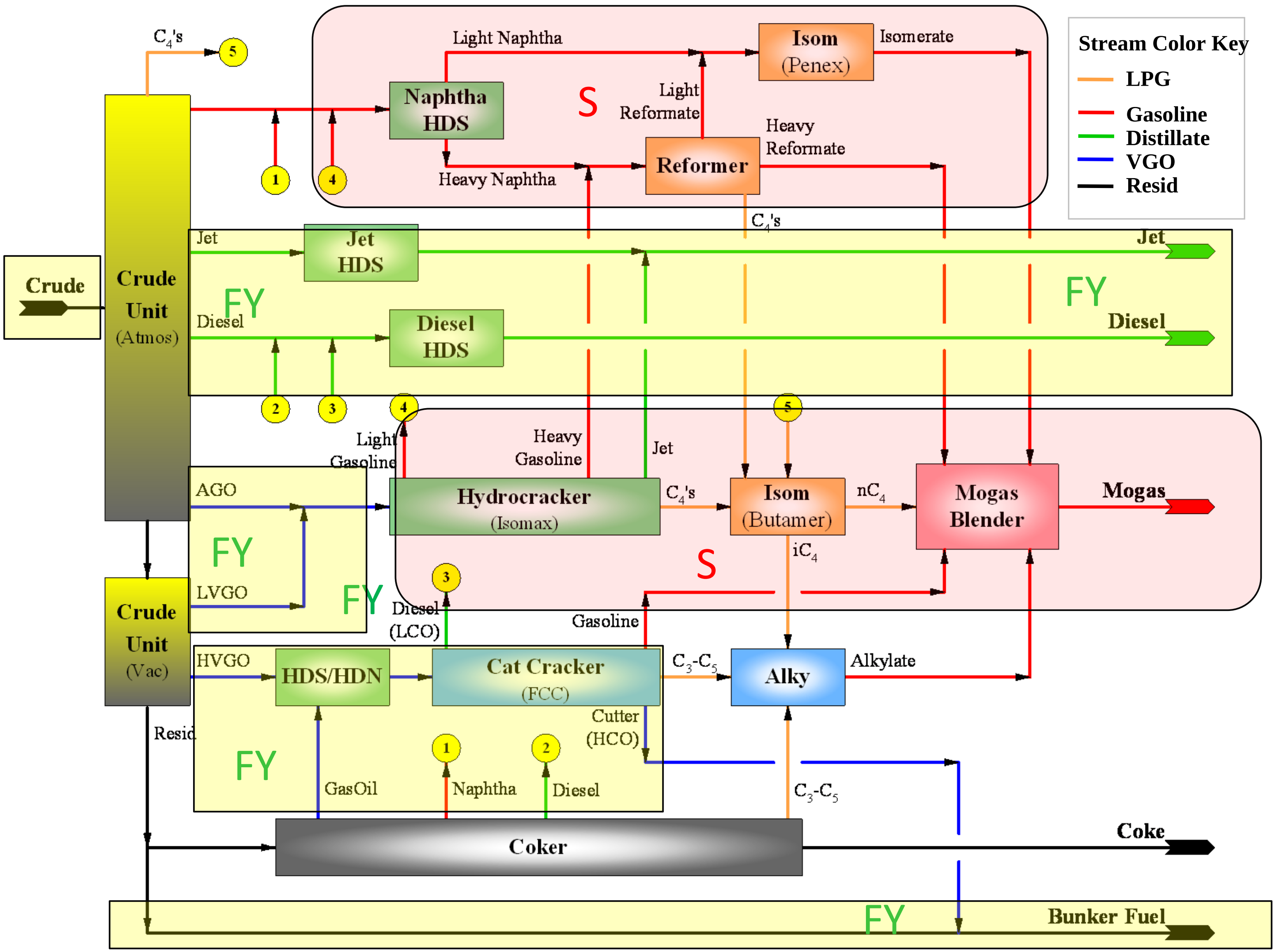
Areas where GC is critical

Downstream Playgrounds
(3 Refineries)

Attainable Yield Roadmap



GC Applicable to Most Refinery Streams



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Unfortunate Trend

(Reduced Skill Sets and Manpower)

UBS newsletter, ***Investment Intelligence:*** As baby boom US workers retire, we create a shortage that follow-on generations have neither the numbers nor the skills to fill.

And from the Gulf Coast Conference (ca. 2005) –

Randy Shearer, Rentek: We are graduating fewer scientists and engineers in the US. We need to apply the continuing improvements in computer technology.

- Chromatography is a key area
- In GC, that means faster analysis

Bill Winniford, DOW: We have to make do with a lot fewer people and they will have more to do. We are entering a time we have never seen before.

- Chief frustration is in data processing
- Not good at capturing knowledge from the experienced workforce

Comparison of Spectroscopy and Chromatography
(conventional wisdom)

Spectroscopy is faster (~ 1 minute per run)

Plumbing is slightly simpler

Maintenance is slightly easier

Speed favors spectroscopy

Information content favors chromatography

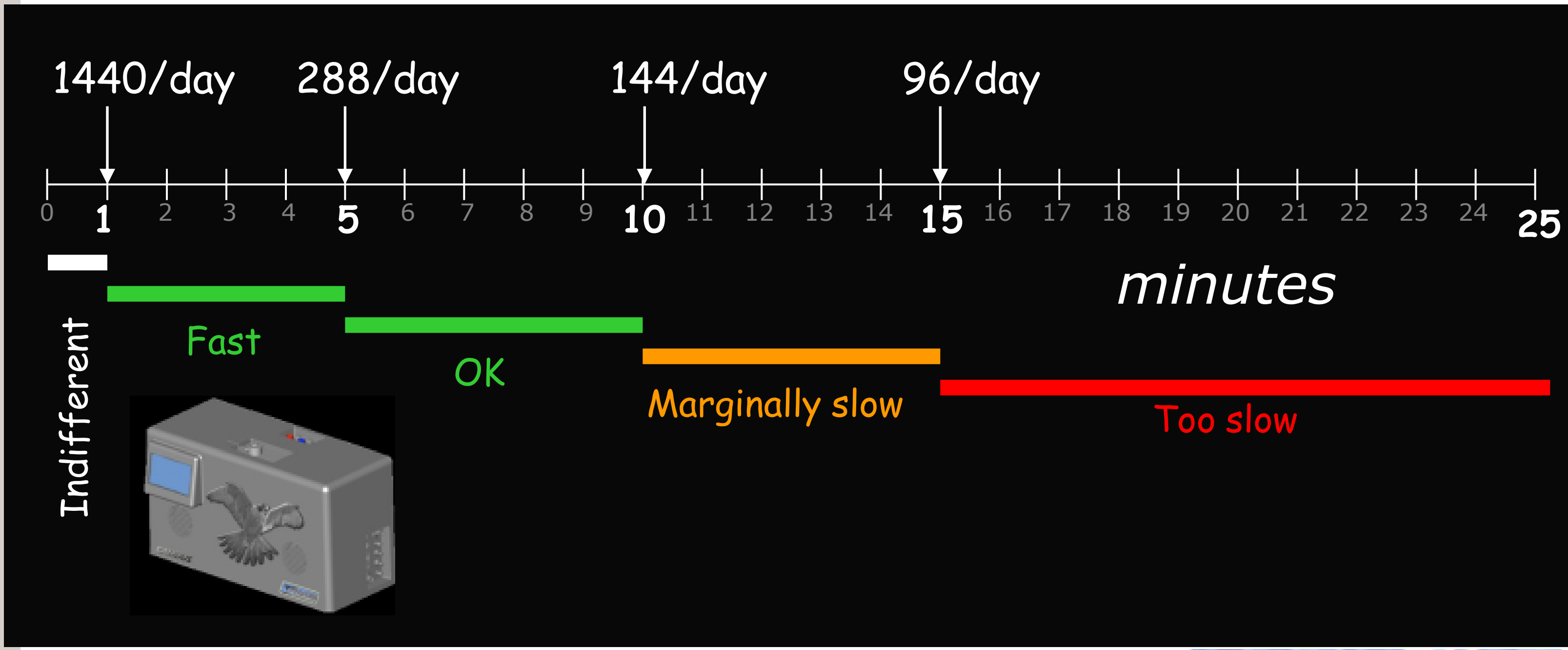
Overall cost of ownership is about the same

Chromatography is slower (~ 30 minutes per run)

System response is largely linear over a wide concentration range

Concentration of individual components is measured more directly

Speed of Analysis



If we are really going to use GC for **control**, speed means under 10 minutes for most applications.

Poll of Process Users

Routine use of fast GC means:

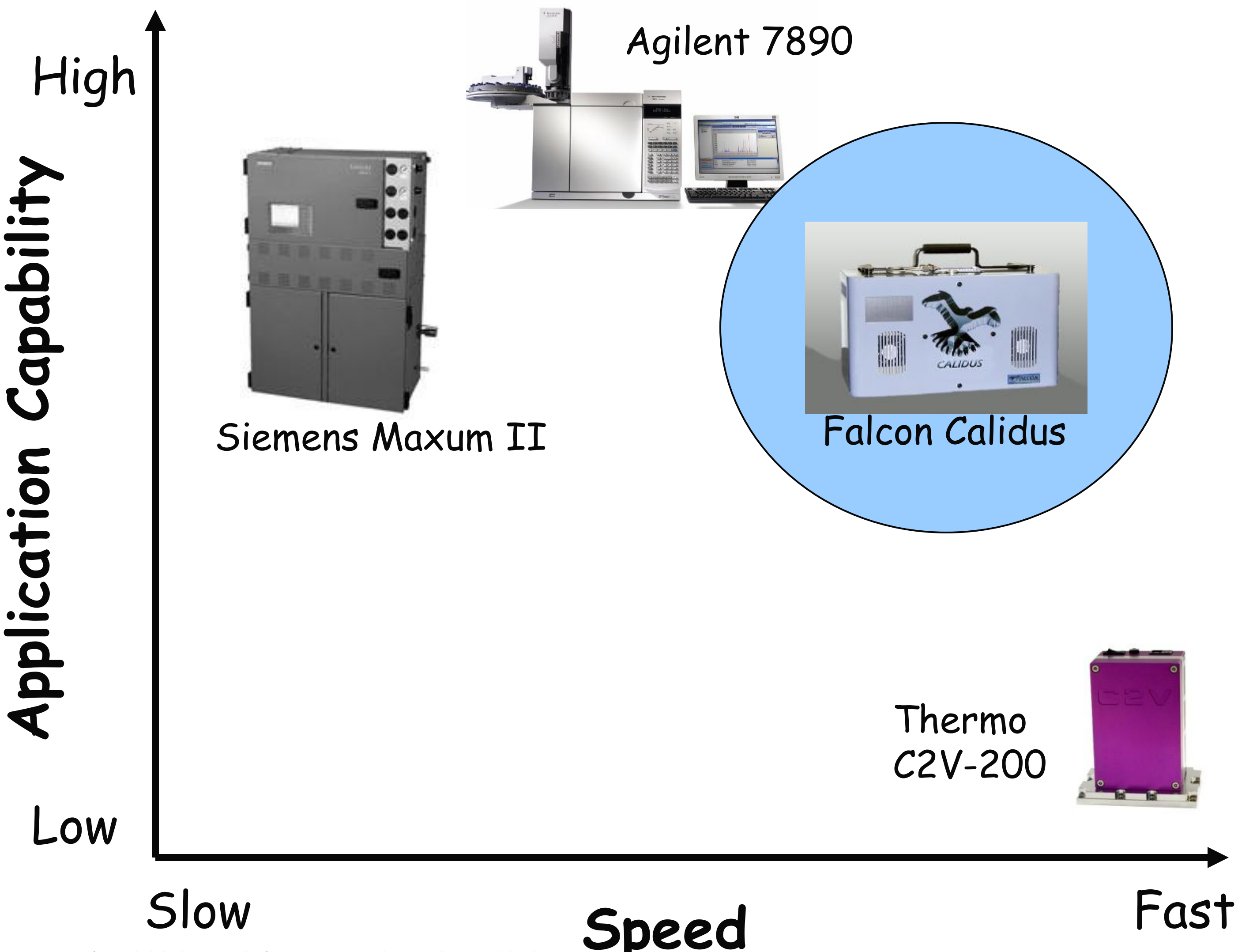
- Lots of data: 20 results per hour (~500 per day)
- Lots of interpretation (are the results correct?)
- Lots of opportunity for errors
- Drives the need for automation
  - analysis
  - data collection
  - preprocessing
  - interpretation
  - system suitability assessment
  - results
  - result validity
  - fault identification
  - pass/fail

Therefore …

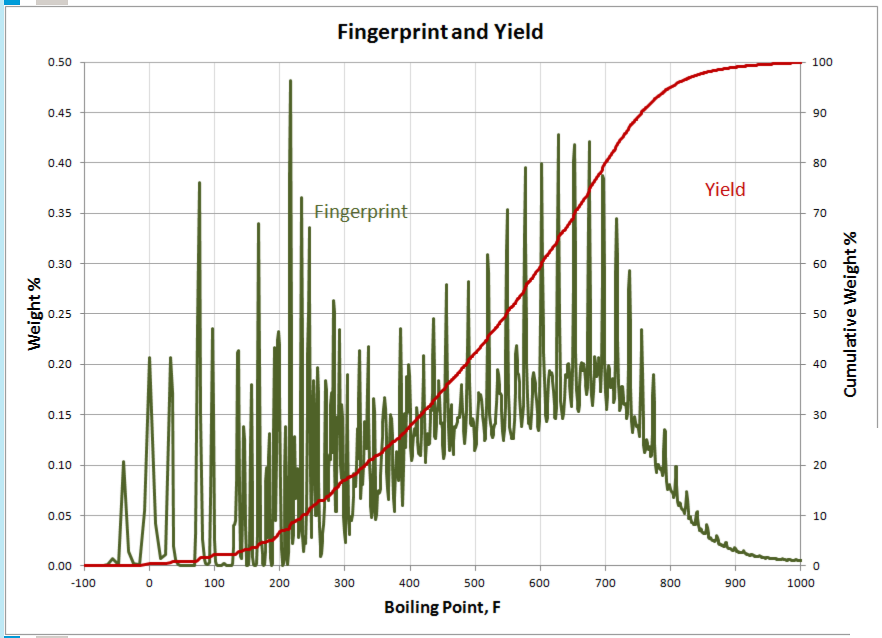
Chemometrics!

Sweet Spot in GC Technology

(Moving to smaller, faster yet capable systems)

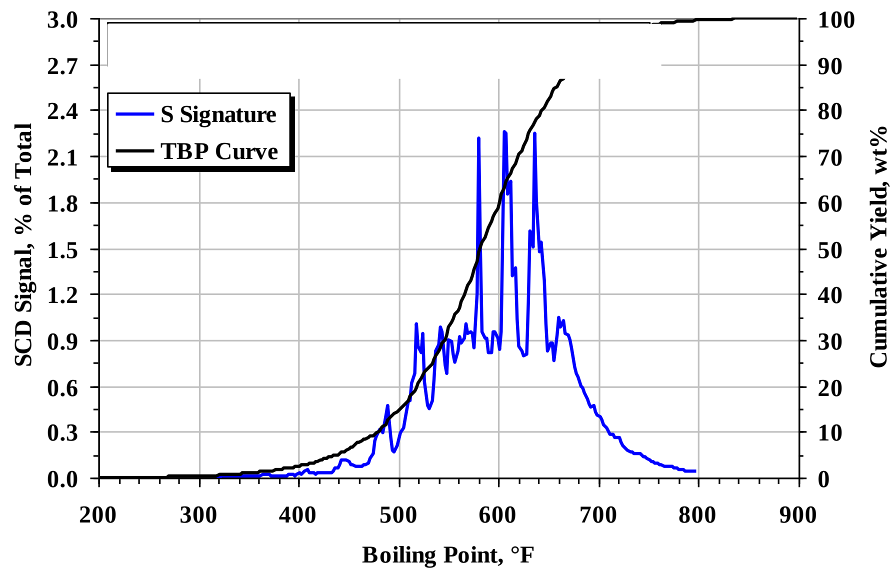


Downstream Fingerprint/Yield Applications



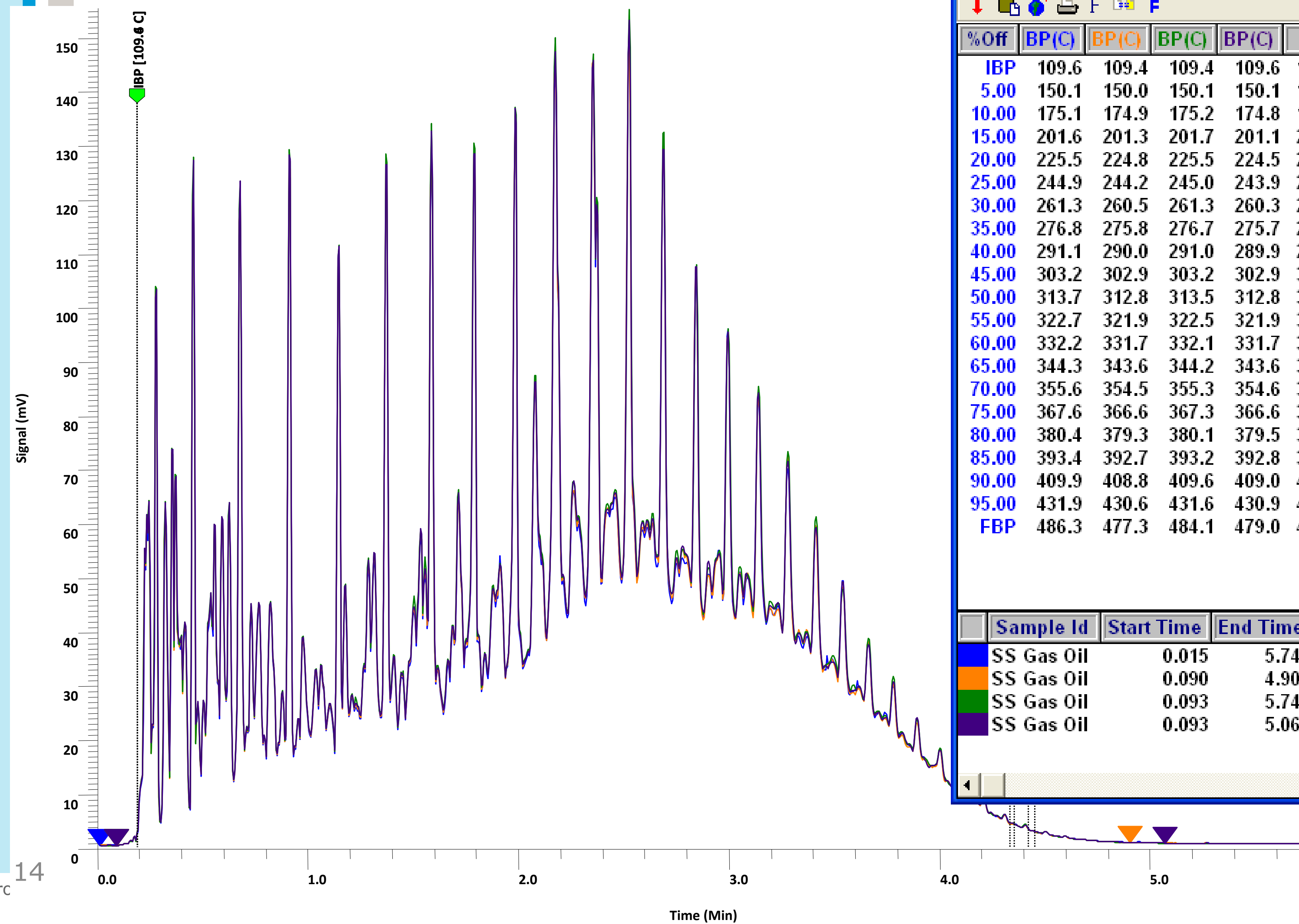
Example: FCC Feed

Example: Sulfur in Crude Fraction (Diesel Range)



ASTM D 2887 Reproducibility

(6 min run for Gas Oil)



Boiling Point Table (%Off)

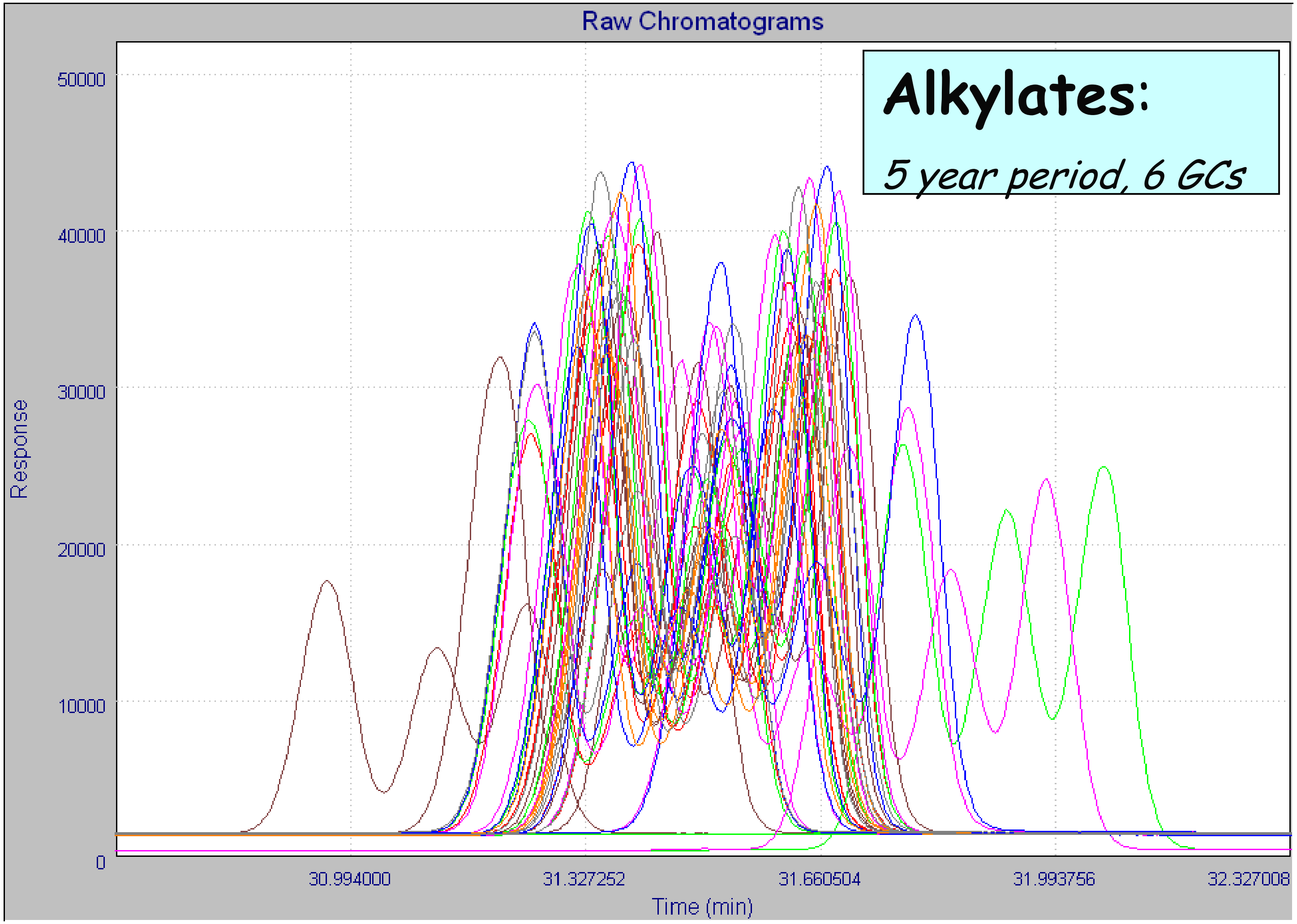
%Off	BP(C)	BP(C)	BP(C)	BP(C)	Avg	%SDV
IBP	109.6	109.4	109.4	109.6	109.49	0.12
5.00	150.1	150.0	150.1	150.1	150.08	0.03
10.00	175.1	174.9	175.2	174.8	174.97	0.10
15.00	201.6	201.3	201.7	201.1	201.43	0.13
20.00	225.5	224.8	225.5	224.5	225.08	0.23
25.00	244.9	244.2	245.0	243.9	244.50	0.23
30.00	261.3	260.5	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
(blue)	SS Gas Oil	0.015	5.746	100.00
(orange)	SS Gas Oil	0.090	4.904	100.00
(green)	SS Gas Oil	0.093	5.745	100.00
(purple)	SS Gas Oil	0.093	5.068	100.00

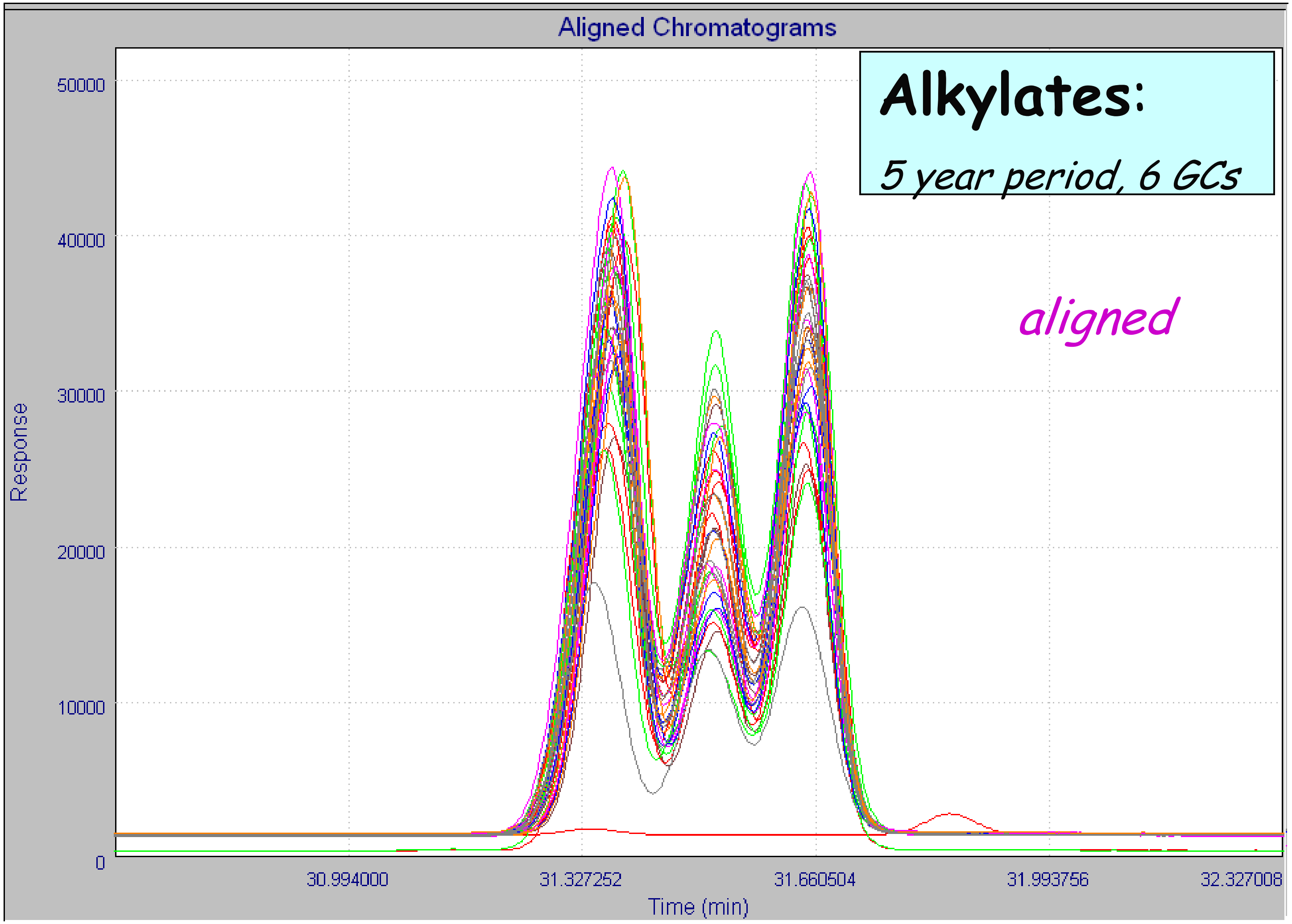
Implications of fast GC use

- GC provides for more information content than spectroscopy, but deployment of the more complex chromatographic systems on-line lags due to our need to do some handholding of each run – human review.
- The problem (unless there is a plug) is not in the intensity axis, the problem is that the peaks can move in the time domain.
- We need another tool in our kit to reduce the time domain variability, and thus reduce the level of skill and manpower needed to ensure we meet our data quality objectives.

Automated alignment works - 1

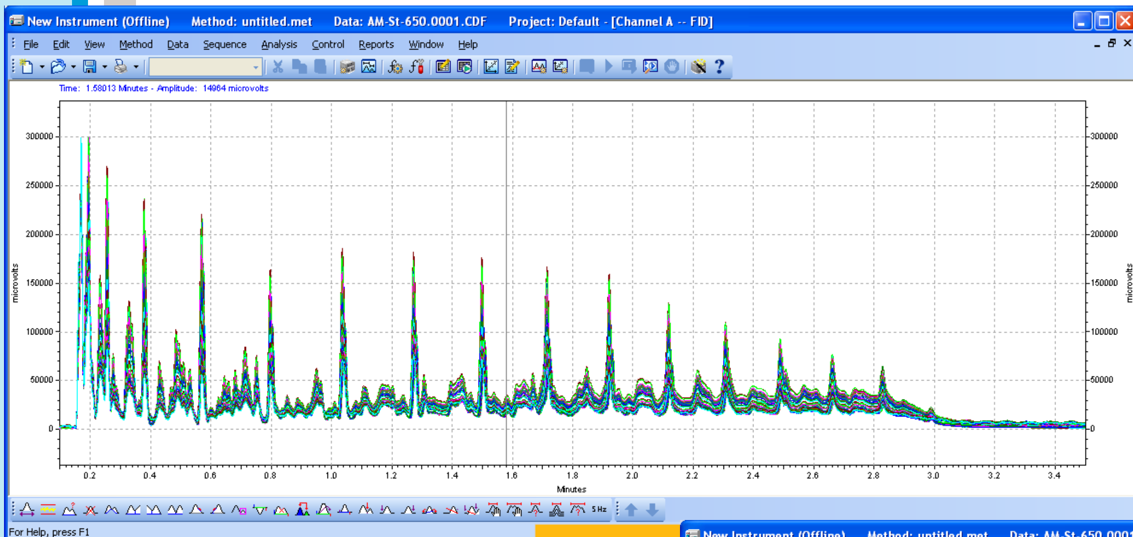


Automated alignment works - 2



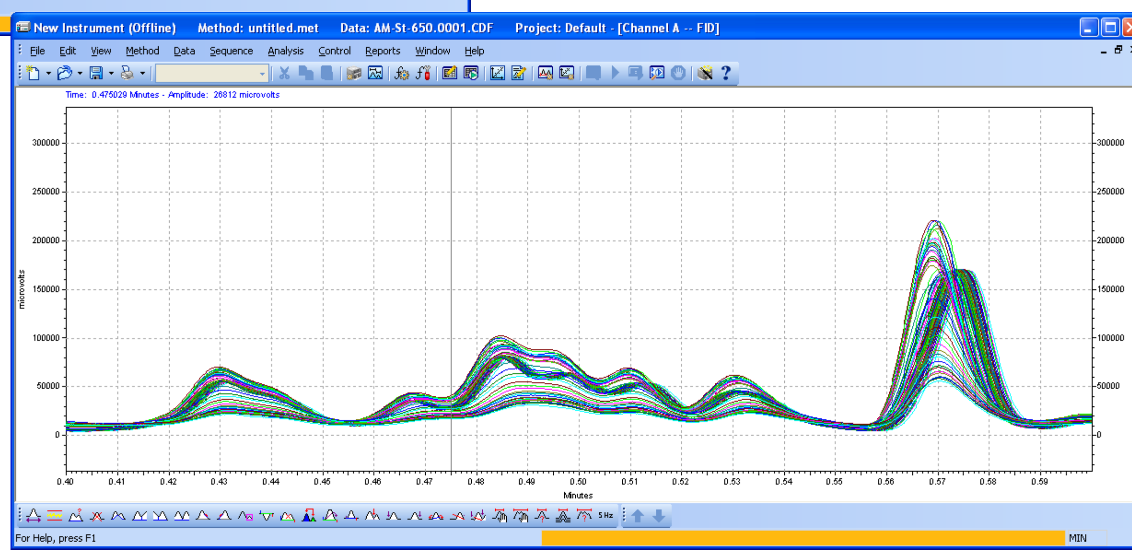
Repeatability for a Process Based MicroGC

(Native Repeatability – 2 weeks 6 minute cycle time)



Start to 650°F Sample of a Conventional Crude Oil

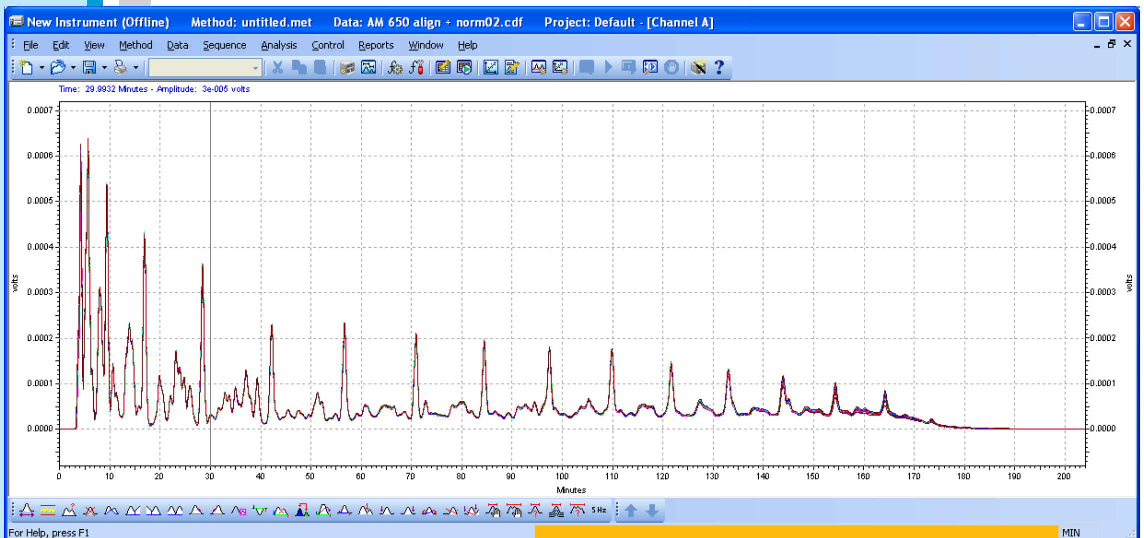
Above: 3.5 min run



Right: expansion from 0.4 to 0.6 min.

Repeatability for a Process Based MicroGC

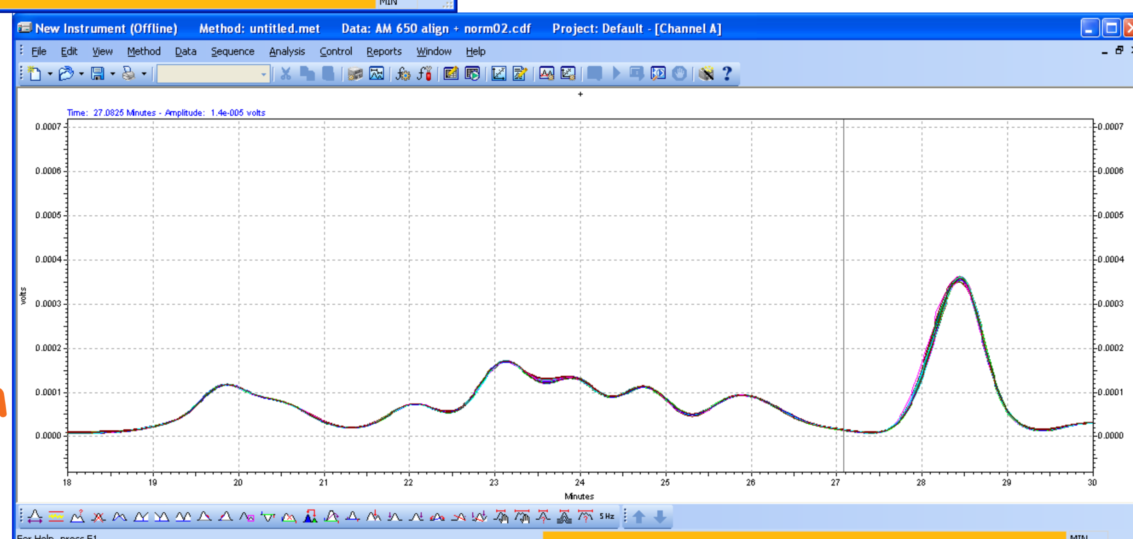
(Following Alignment and Normalization)



Substantial Reduction in Sample to Sample Variability

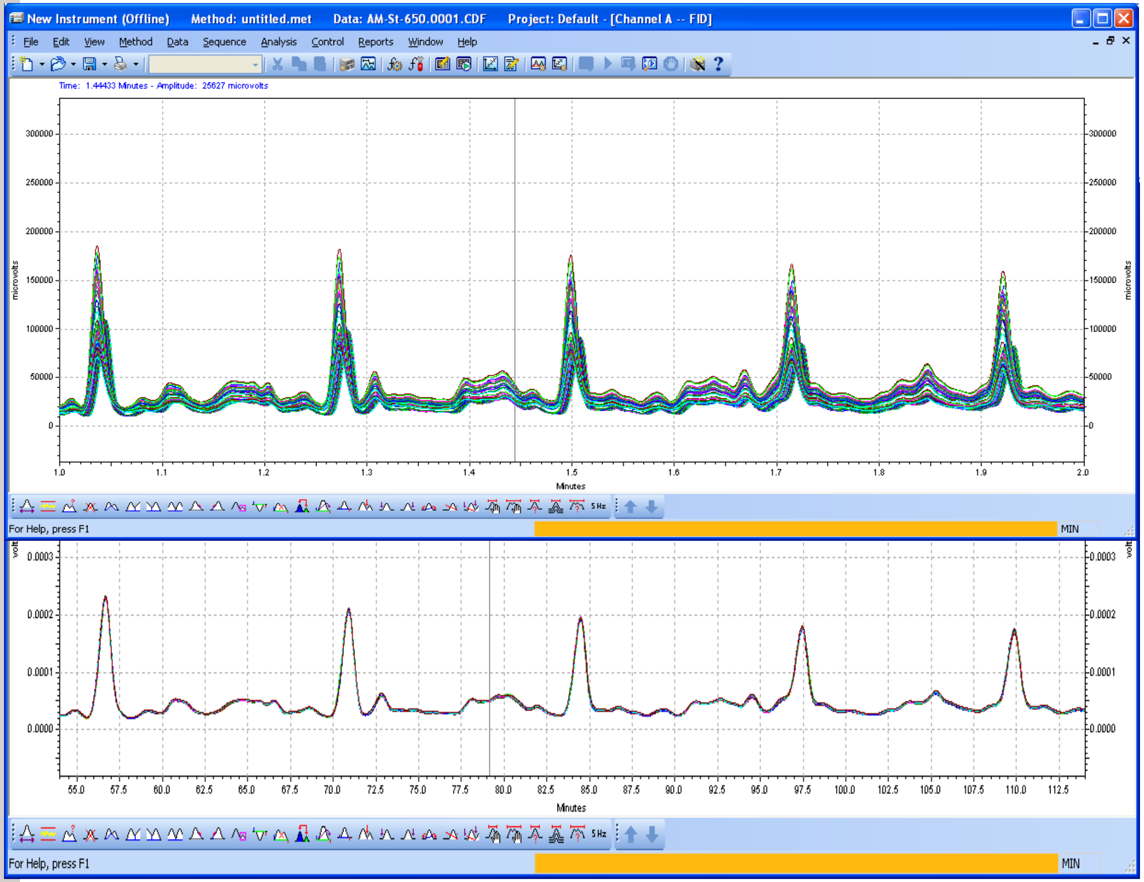
Above: 3.5 min run

Right: expansion from 0.4 to 0.6 min.



Direct Comparison of Native versus Align/Normalized Chromatograms

Region from 1 to 2 min displayed



Variation reduced by a factor > 20 with alignment

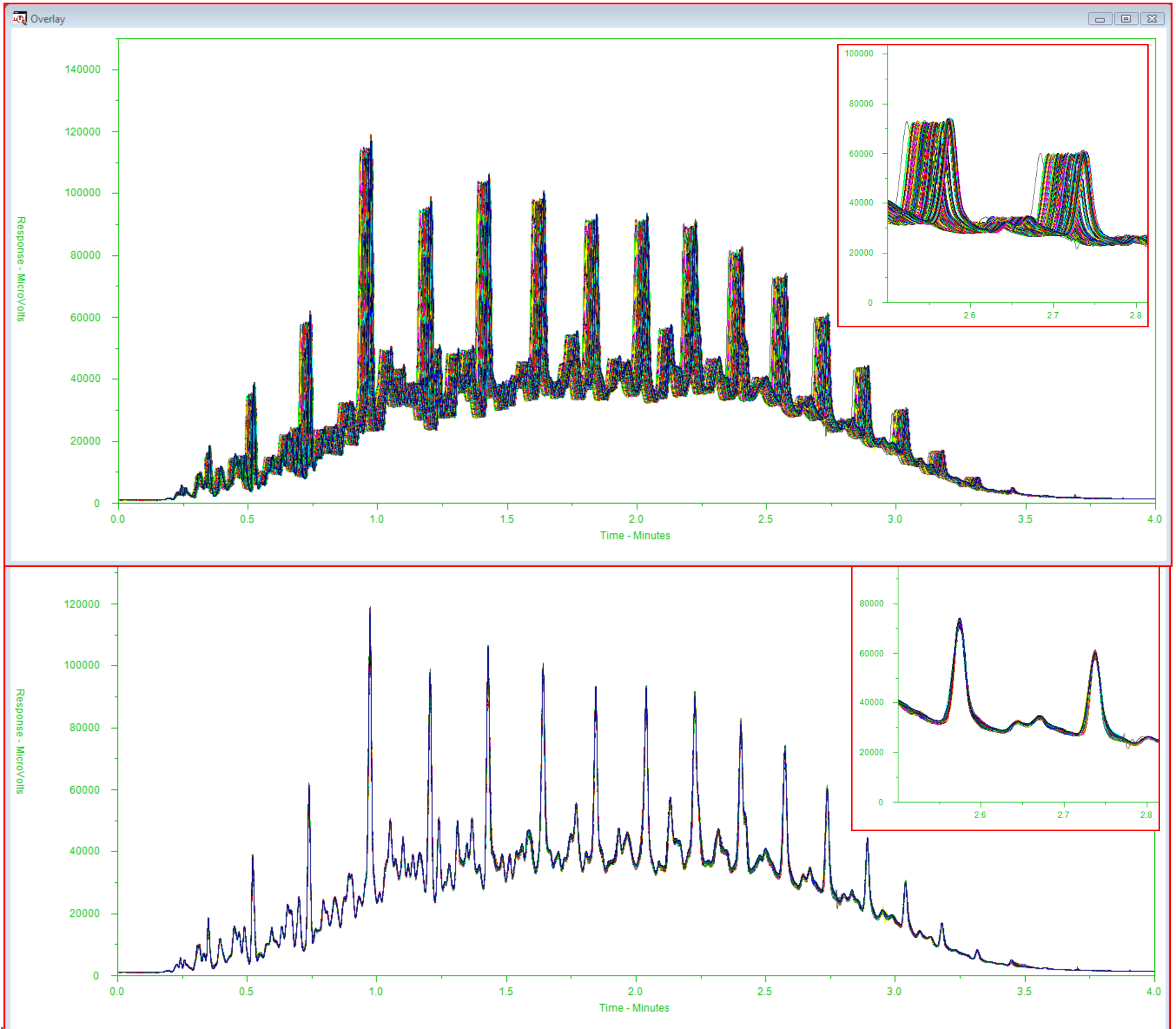
SimDis Statistics

Average 1.7°F

Minimum 0.3°F

Maximum 4.9°F

Comparison of Native to Aligned Chromatograms
(Extended Test)

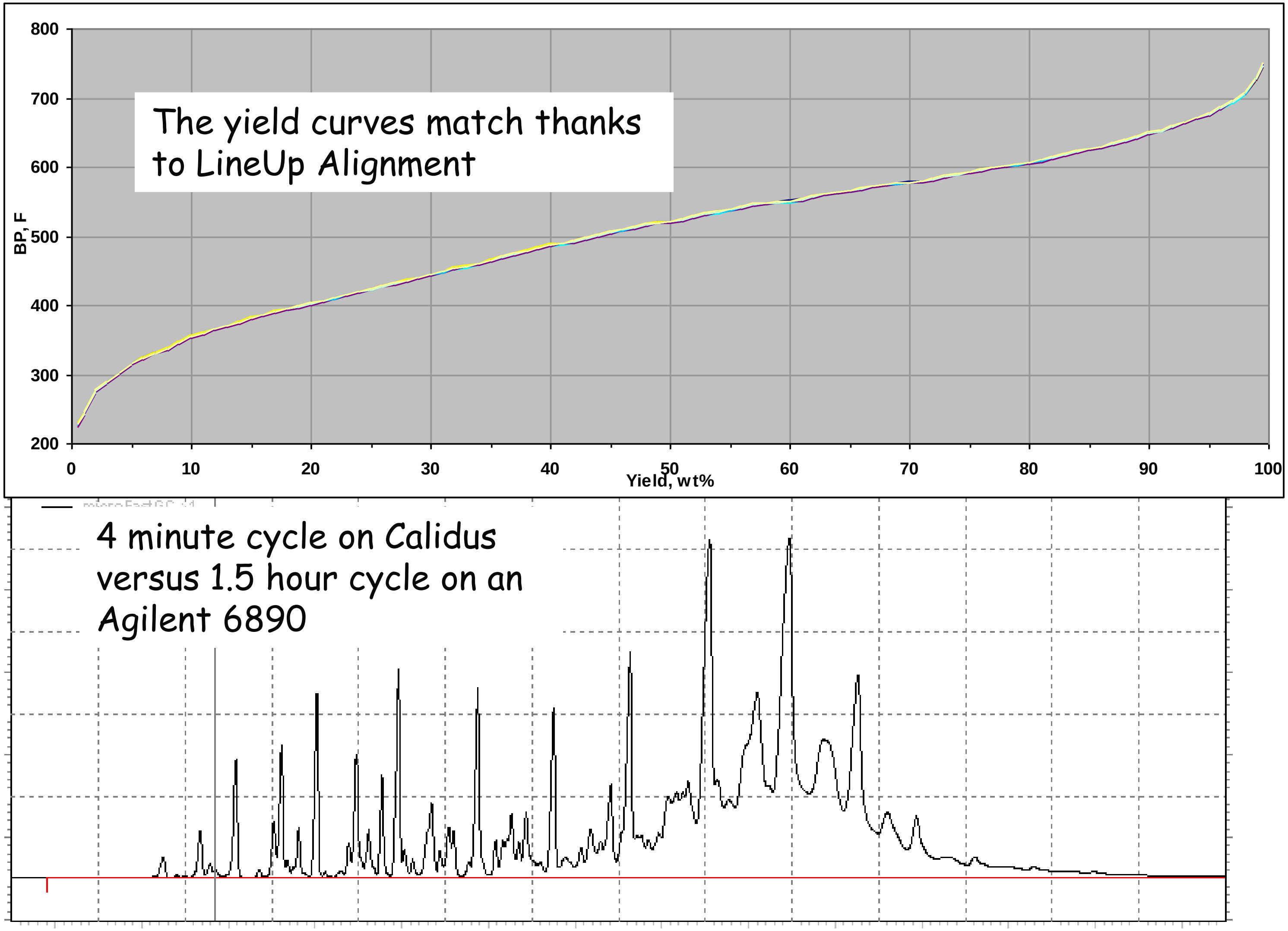


Increasing Automation

- With alignment automated into the system, the next step is to build confidence that any degradation in chromatographic separation won't cause problems or flag that there is a problem that needs human intervention.
- For many applications there is retention time to spare and research grade GCs are overkill.
- The goal is matching the resolution and speed requirements for any measurement with minimal overhead..

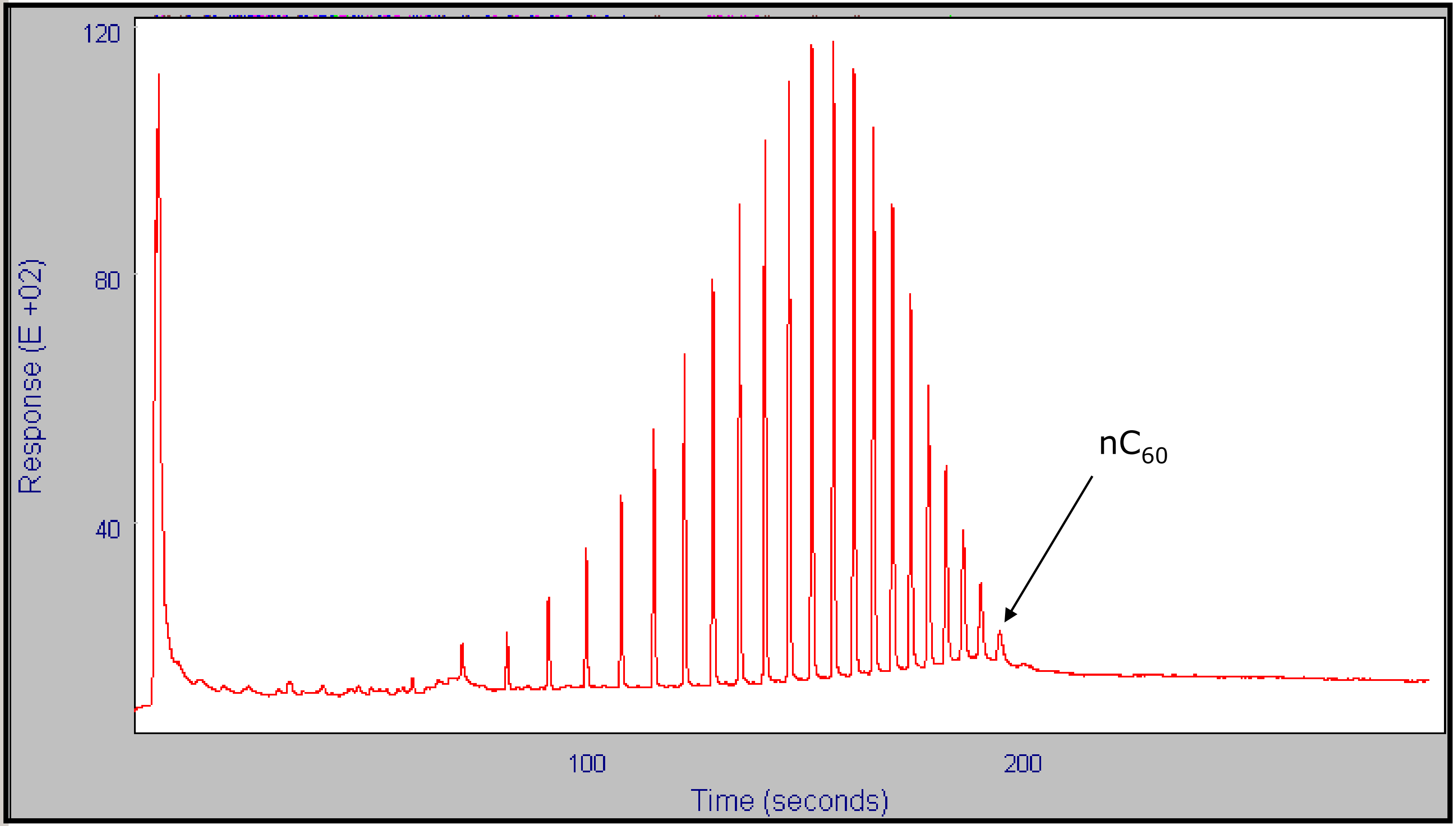
Information content maintained at faster speeds:

Data from μGC, lab GC, and process GC

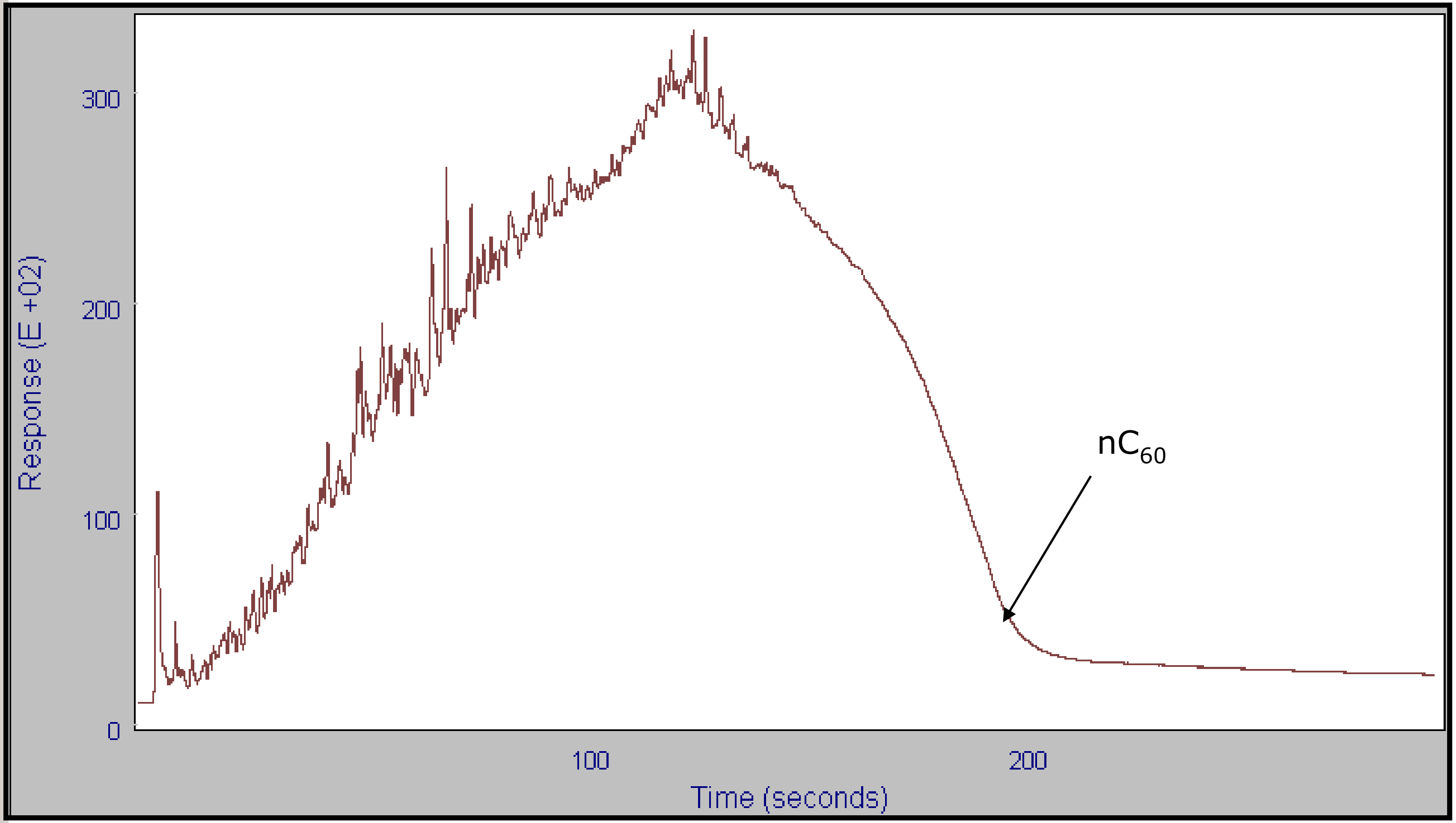


Polywax Standard

Allows transformation of retention time to a different basis
(e.g.carbon number or boiling point)



Representative Chromatogram for a Drill-stem test
(Heavy Oil)



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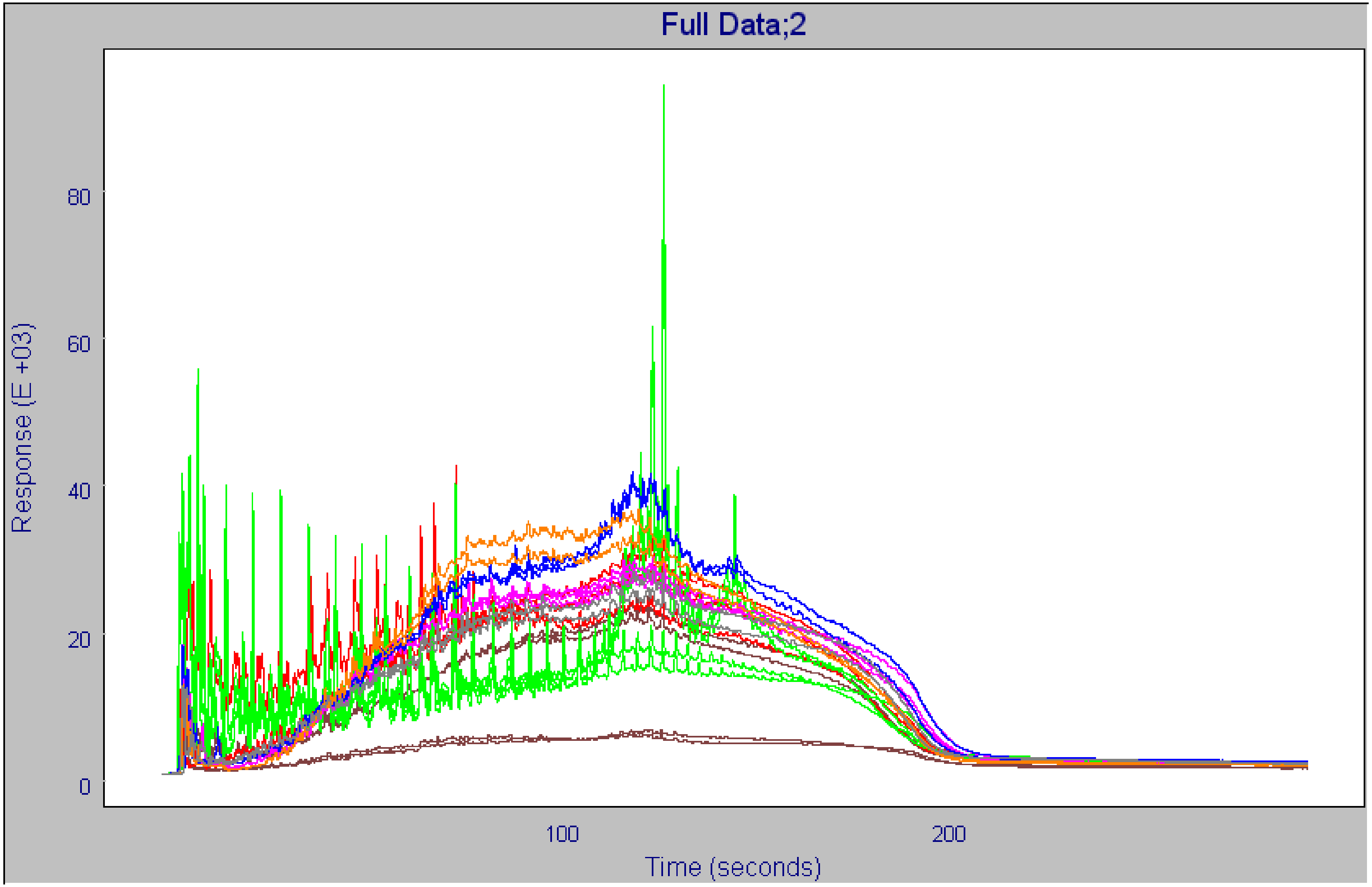
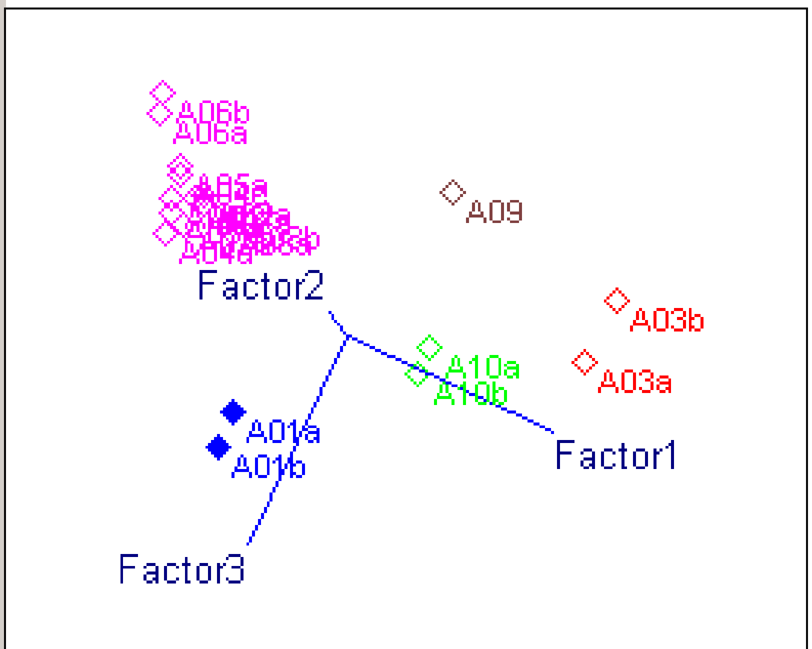
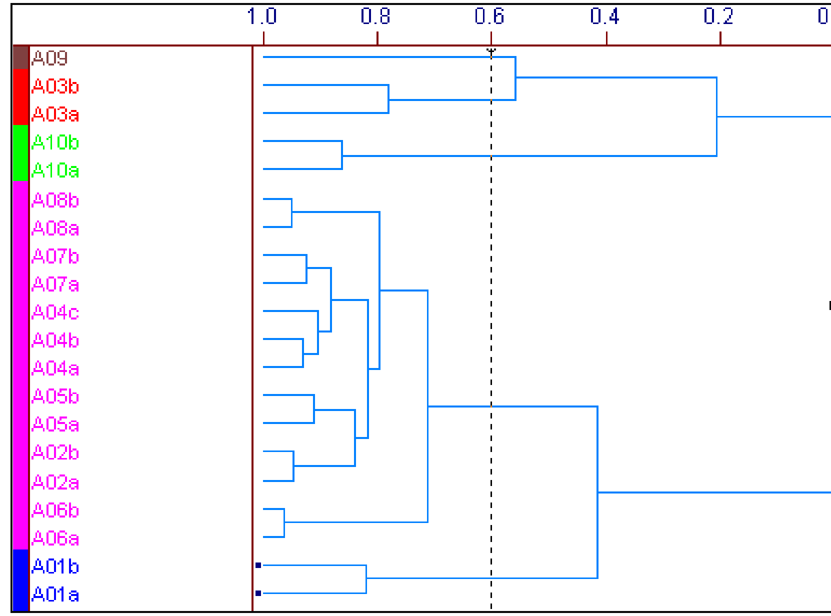
Overlay of a series of heavy oils
(Various fields)



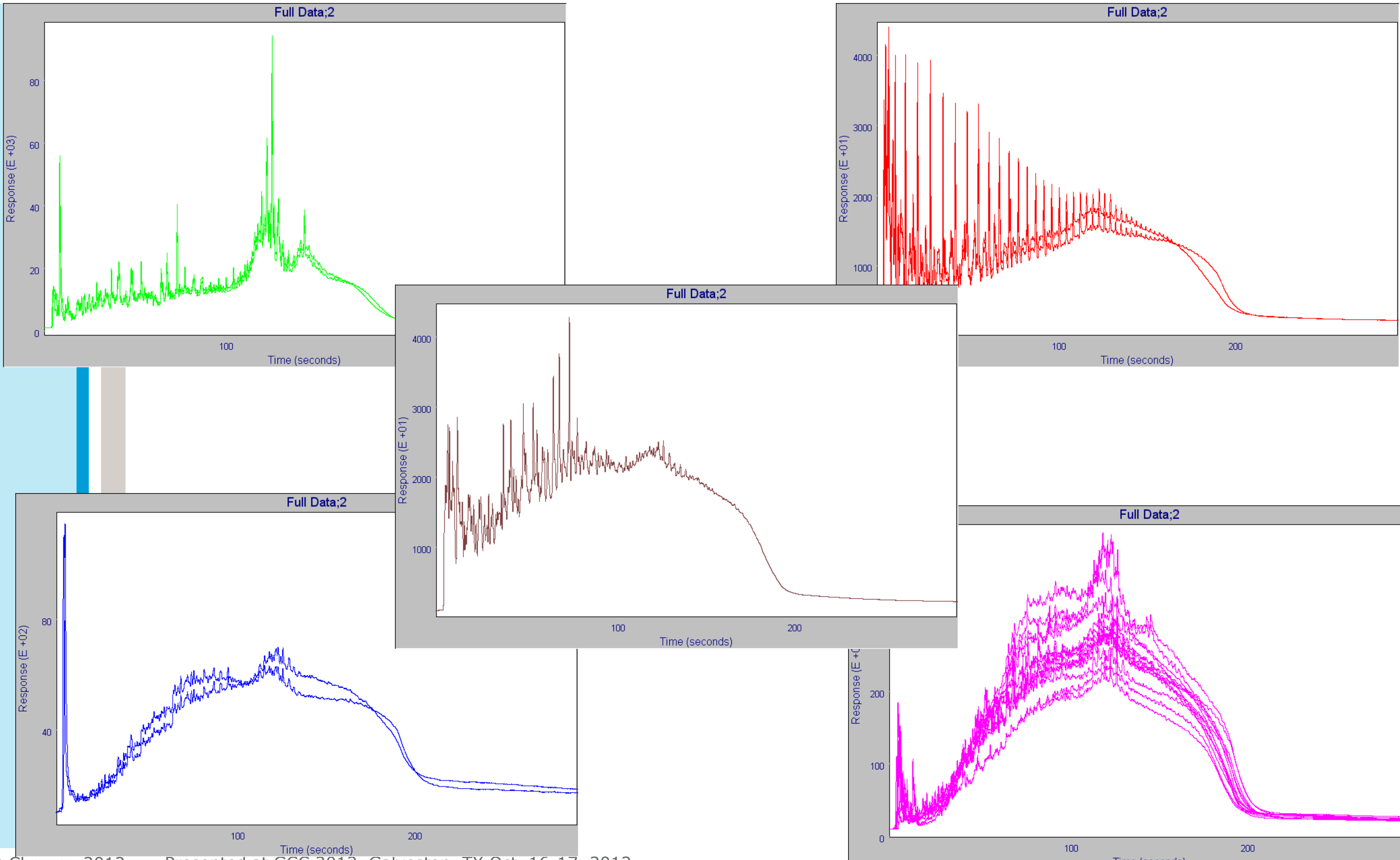
PCA Scores and HCA Dendrogram of Oil Types

Automated assessment of field similarity and/or continuity.





Establishing Oil Classes



Chemometrics enables plug-and-play GC

- We can correct retention times to match an application-specific relevant sample
- This eliminates the transfer of calibration problem
- Common regression and classification algorithms can be applied automatically to infer physical properties or characteristics
- This allows us to bring more complex analyses into on-line use
- With the current line of instrumentation, GC fast enough to allow true control even in complex analyses

Summary

- We are never going to displace spectroscopy's *analysis at the speed of light*, nor do we want to.
- But, as the GC cycle time changes from hours to minutes, the information content inherent in the chromatogram makes it extremely valuable for complex mixtures – *a little bit of separation goes a long way*.
- For petroleum composition understanding, slice and dice, is the only way.

Questions?