Making SimDist Faster and More Robust

Minimizing the impact of retention time drift

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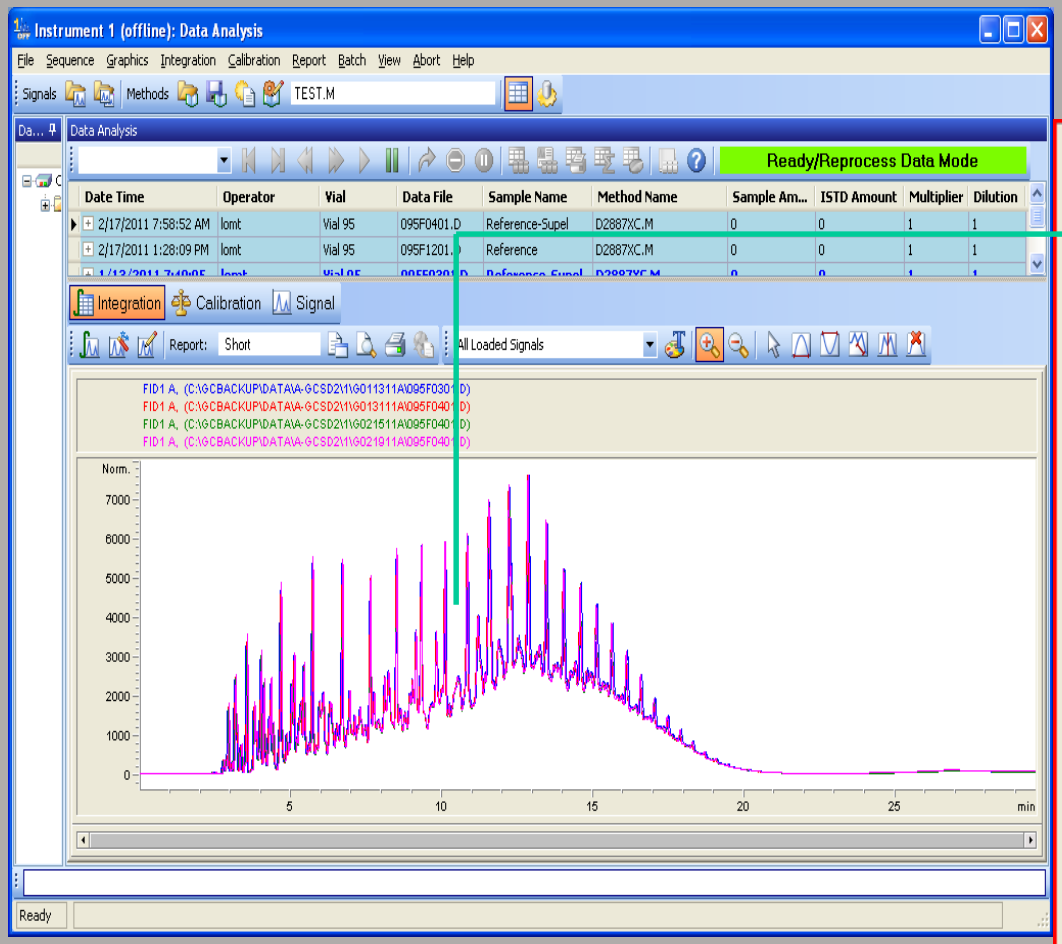
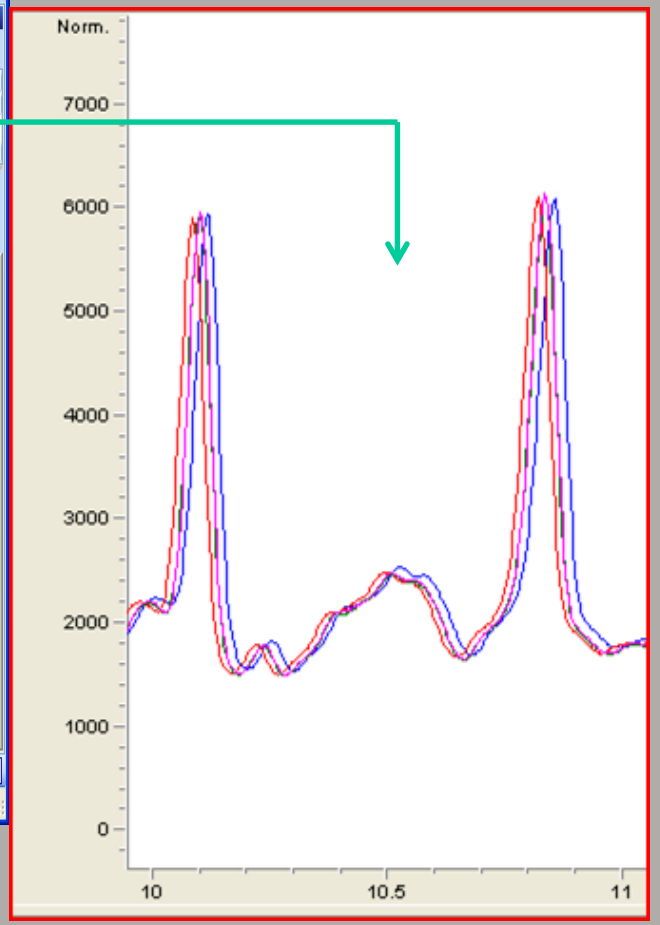
Processing Whole Chromatograms

- Chromatograms will show an x-axis (retention time) shift for a variety of reasons:
  - Changing columns
  - Aging columns
  - Different instruments
- We need to eliminate retention time variability to improve the precision of our assessments.
- Think about how alignment relates to simulated distillation…
  - We run an n-paraffin standard to correlate temperature to retention time.
  - We use this new axis to map the cumulative percent of total area as we progress along this set of temperatures.

Retention Time Misalignment is a General Chromatography Problem





You can spot small changes in retention time even in proximal runs.

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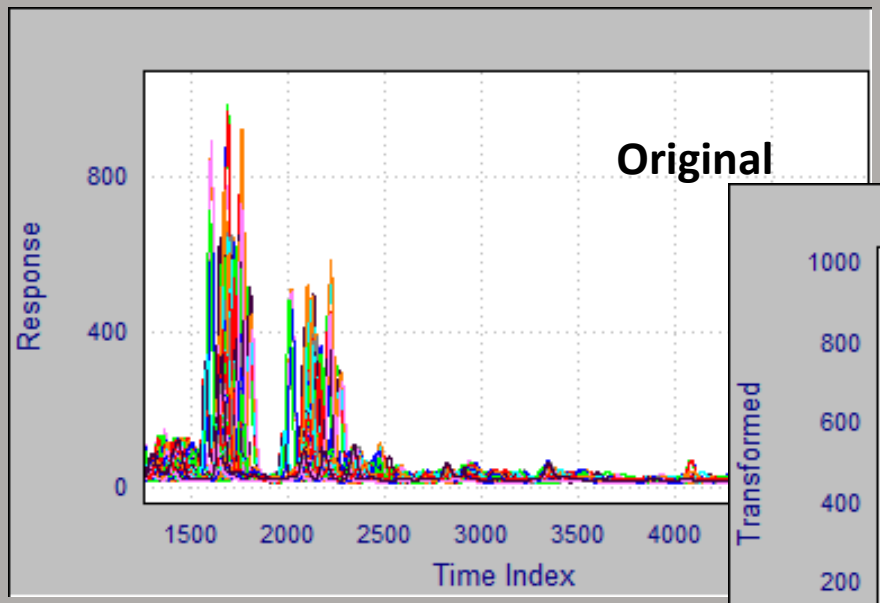
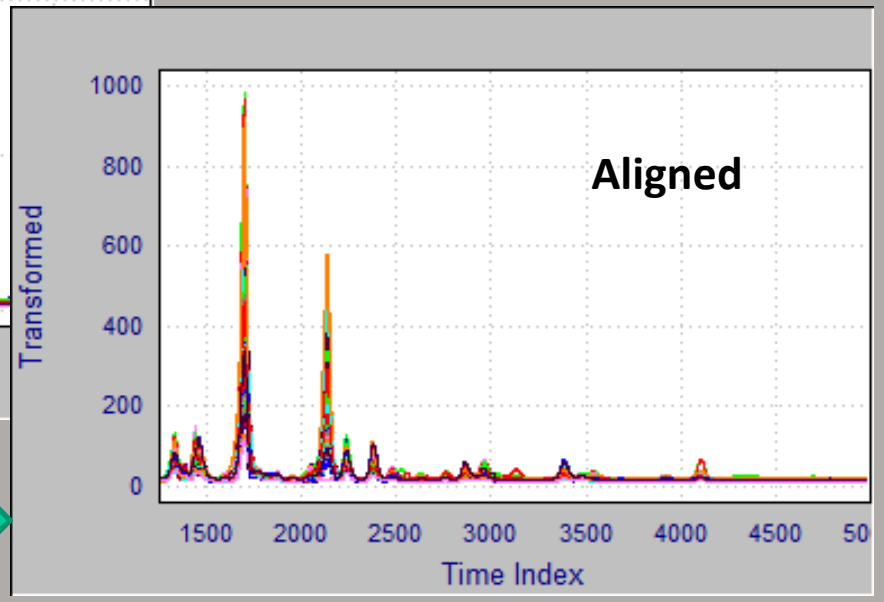
Alignment via Software

Over time, original chromatograms often show large variation in retention pattern; aligned chromatograms do not



6-year period



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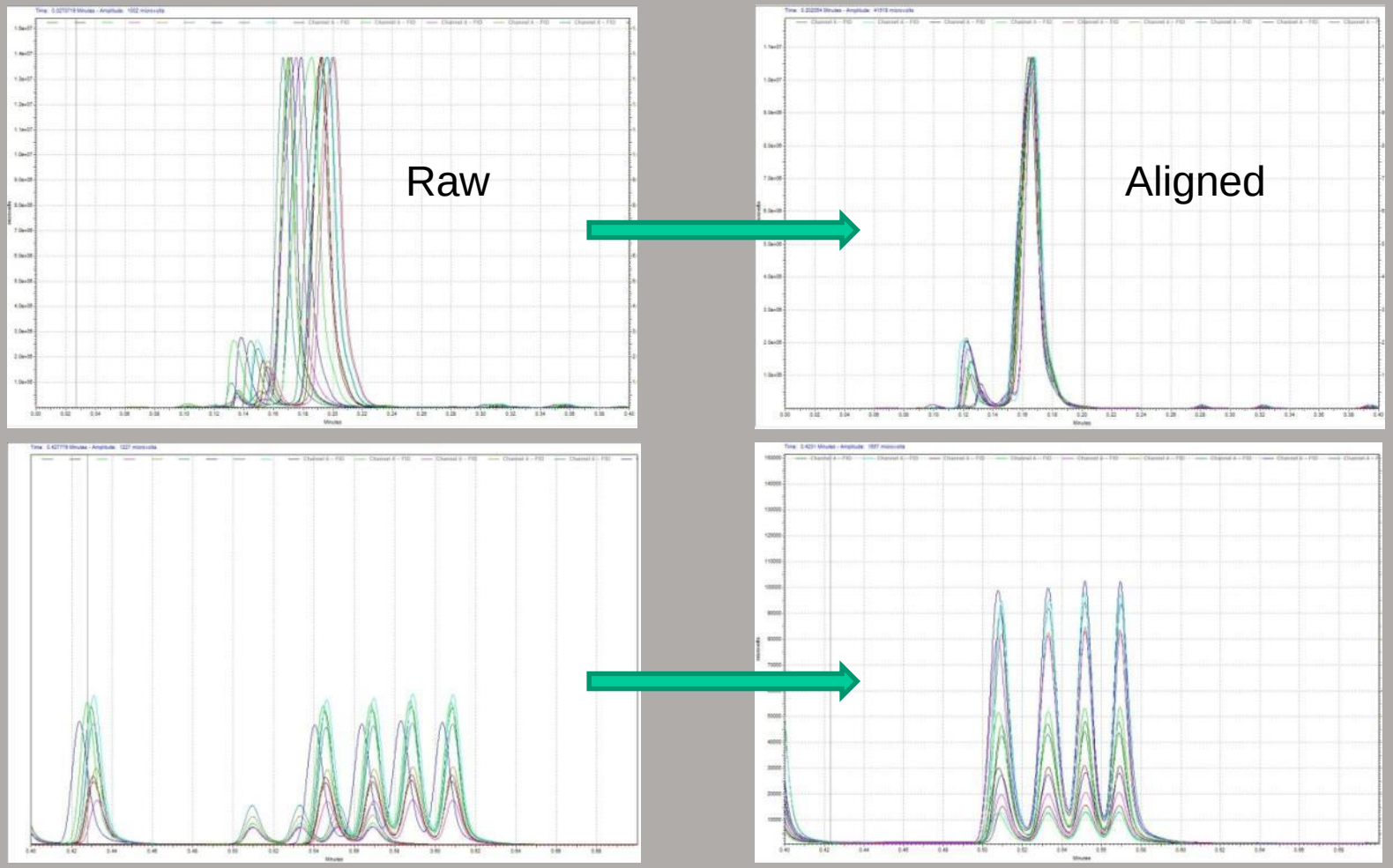
Alignment Across Instruments



Two instruments with nominally the same method and columns, manual injection

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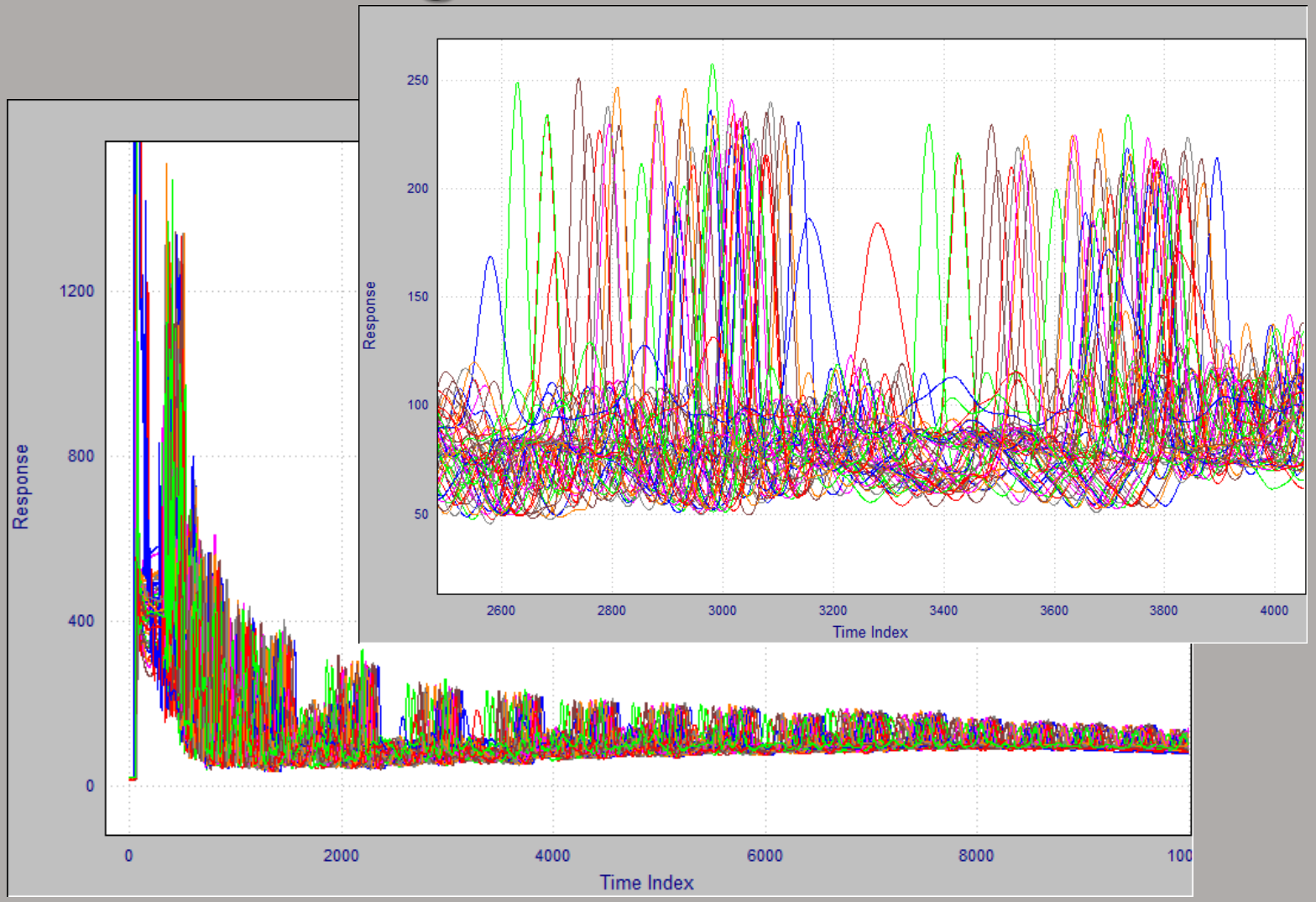
Alaska North Slope Crude Oil:
The quintessential column drift problem

- Same container of oil analyzed over 2 ½ years
- 1% crude in CS_2
- The chromatography is challenging
  - Column changes every 3-6 weeks
  - Inlet liner every week
  - Work burden: need to recalibrate every 8-12 hours
  - Some band focusing due to inlet at +30°C and column at -20°C

Chromatograms – RT Drift



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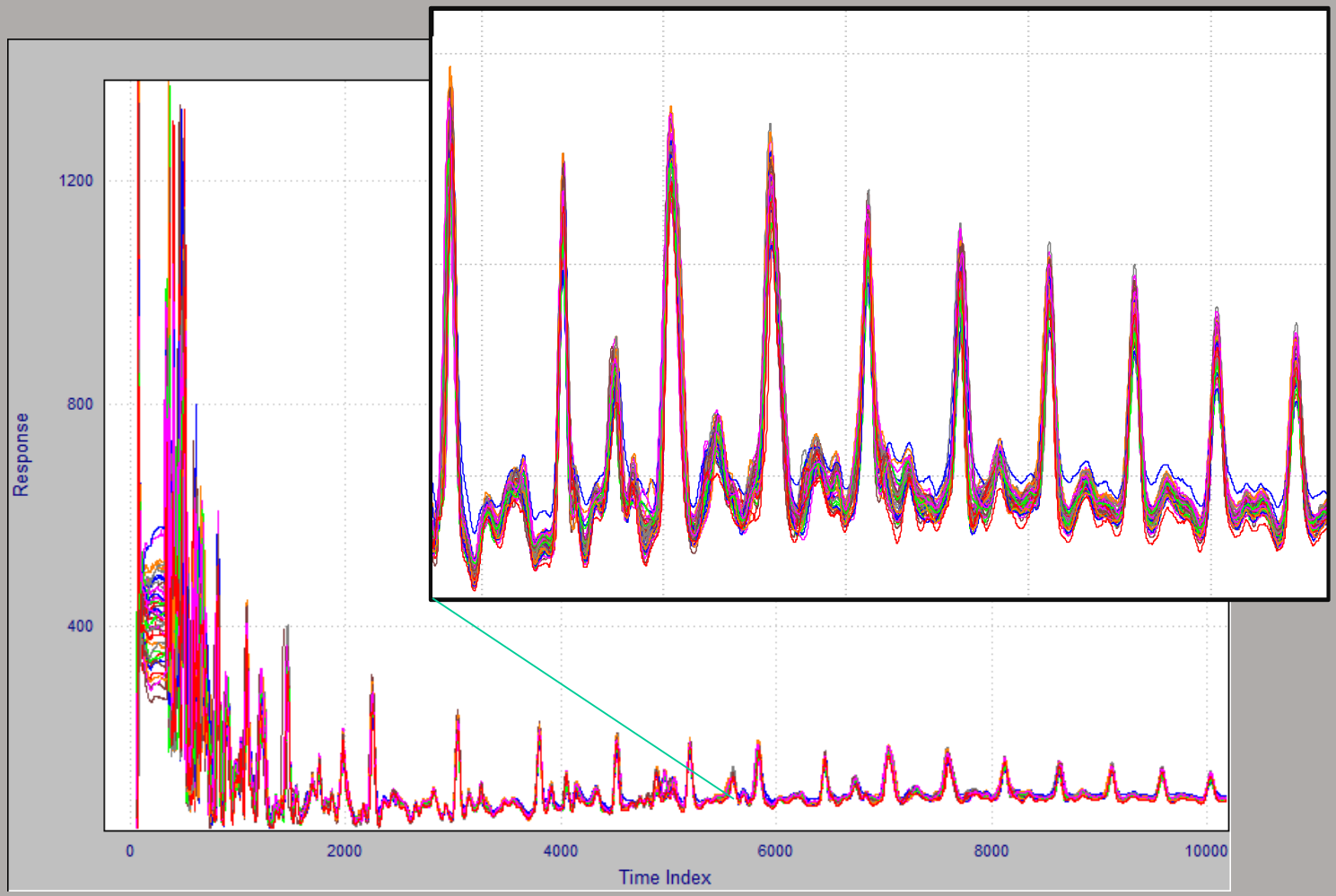
Alignment

- Alignment with COW algorithm is challenged because in these data early-eluting compounds are shifted considerably more than late-eluting compounds, for some samples; drift can be as much as the separation between n-paraffins
- After evaluating several combinations of alignment parameters, these were chosen:
  - Segment = 30; Warp = 6; Start = 201; Stop = 15000
  - Processing requires about 85 sec
- 70 of the 83 samples processed between 2014 and 6/2016 aligned well; the remaining 13 samples were much more challenging

Well Aligned Profiles – 2014



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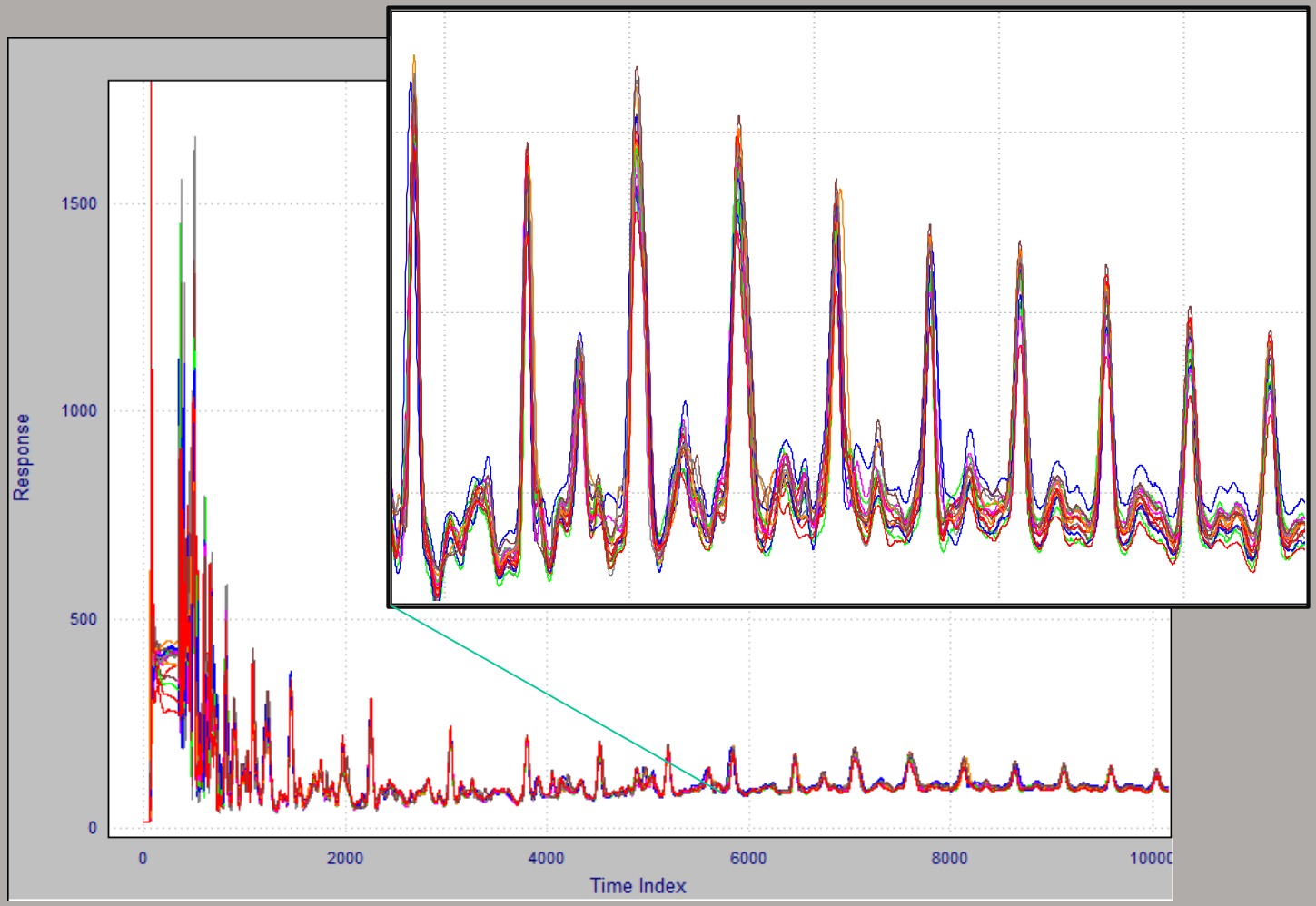
Well Aligned Profiles – 2015



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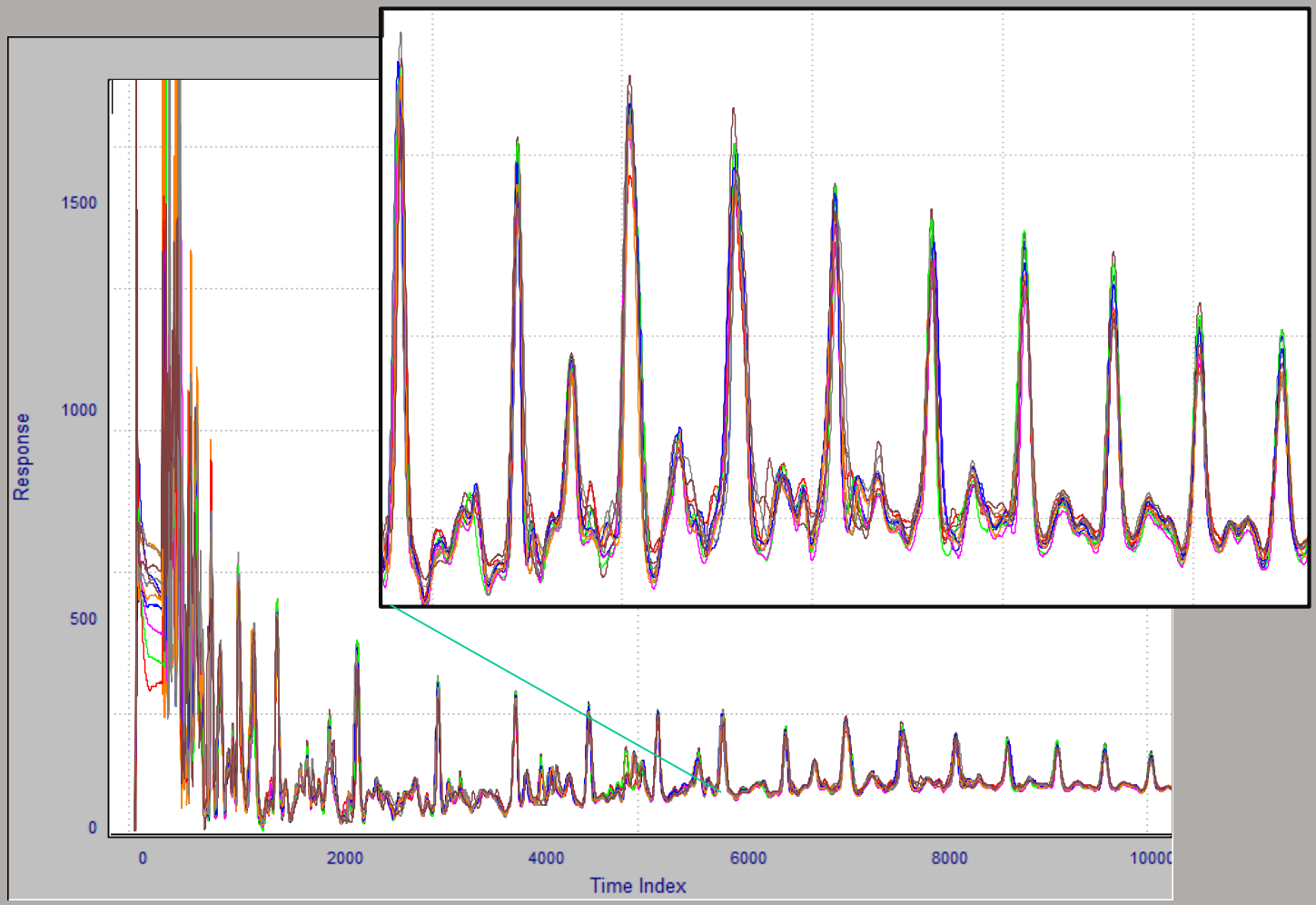
Well Aligned Profiles – 2016



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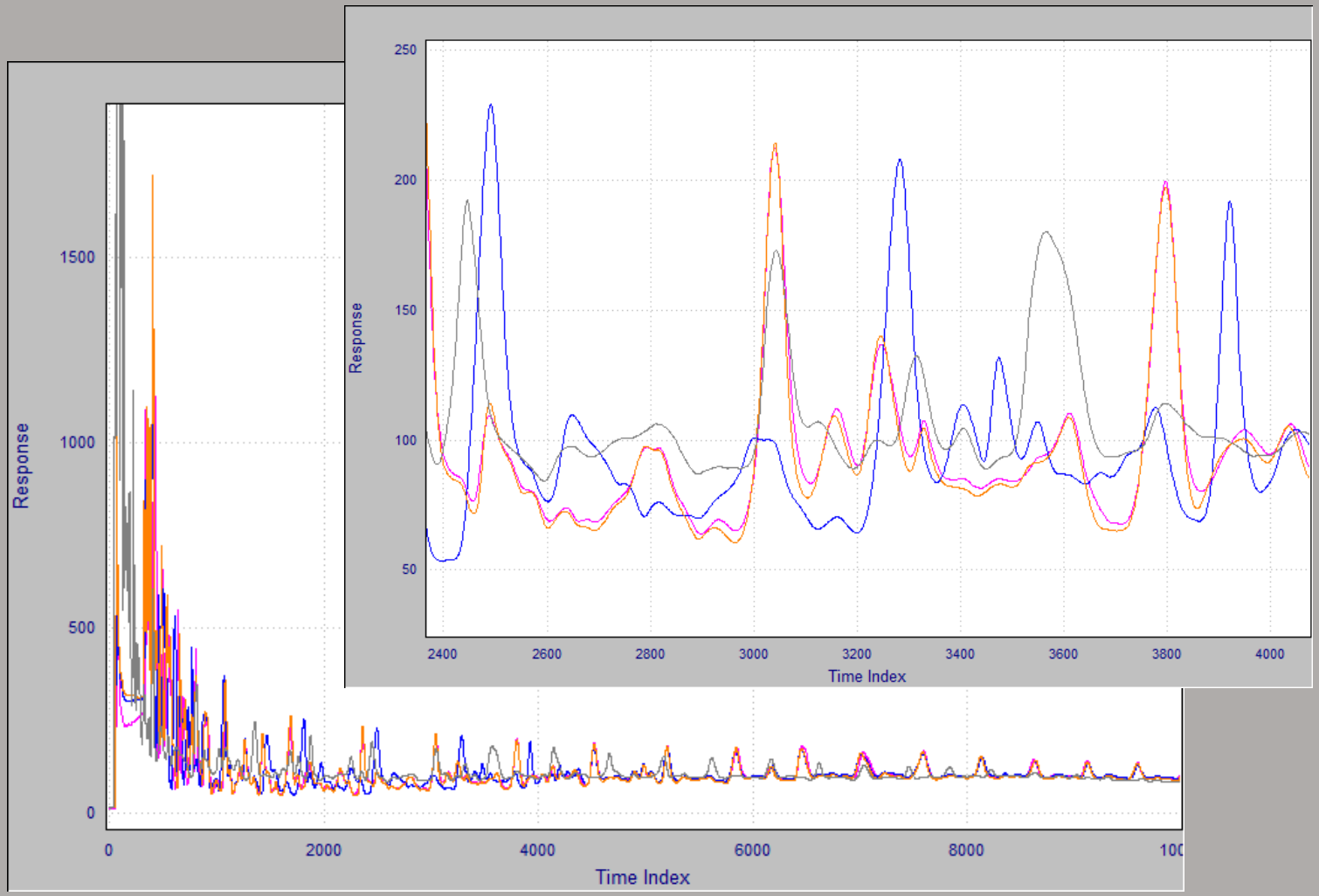
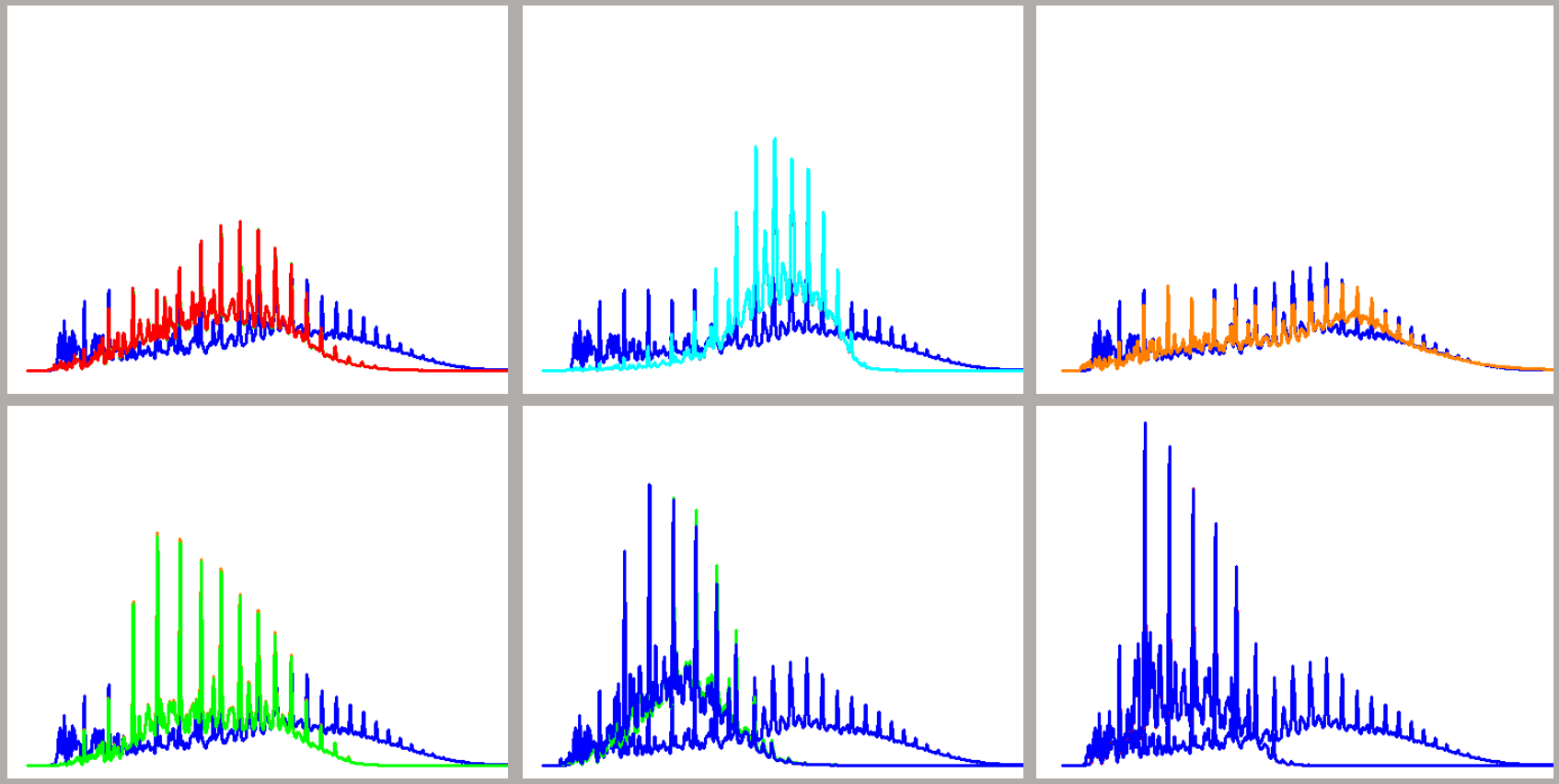
Poorly Aligned Profiles



Takeaway

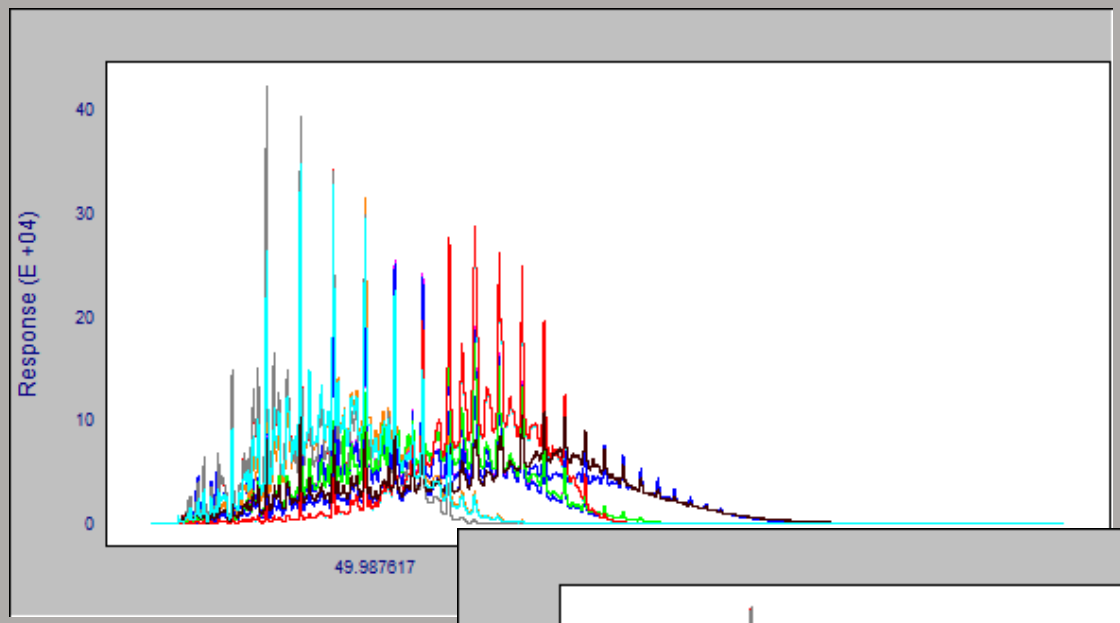
- Alignment (coupled with pattern recognition) provides a hard decision point on when to change the column or recalibrate
- 3-3½% change in Boiling Points was the experience prior to alignment
- 1-1½% variation is the experience for the aligned chromatograms

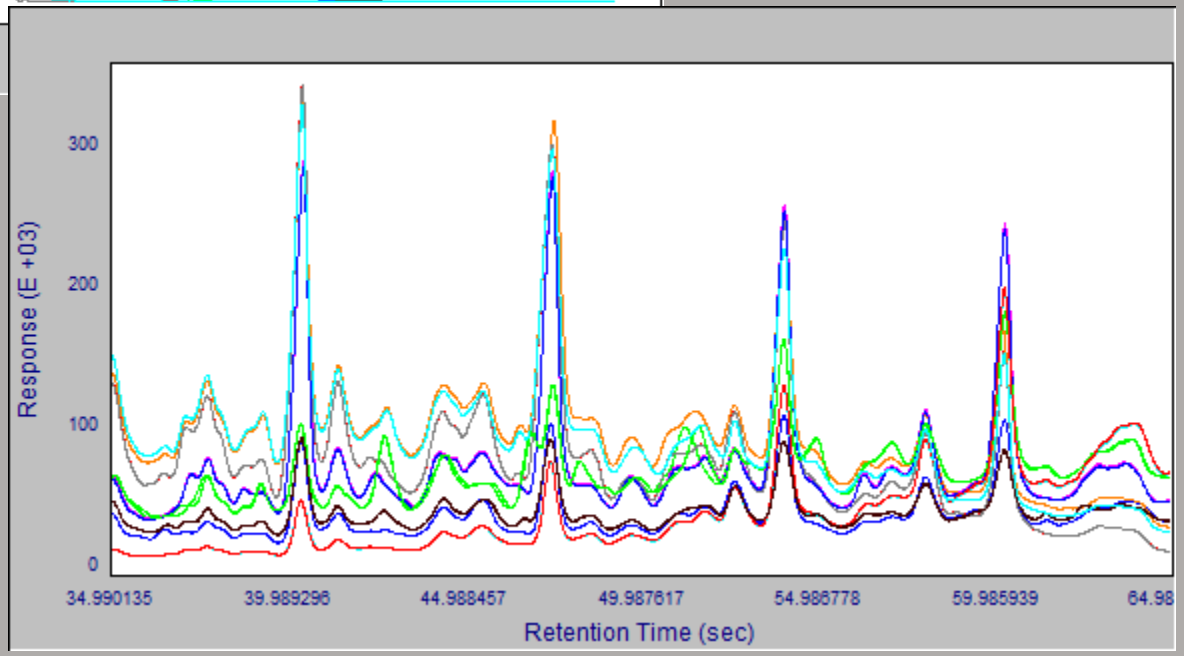
SimDist Test Samples vs. RGO



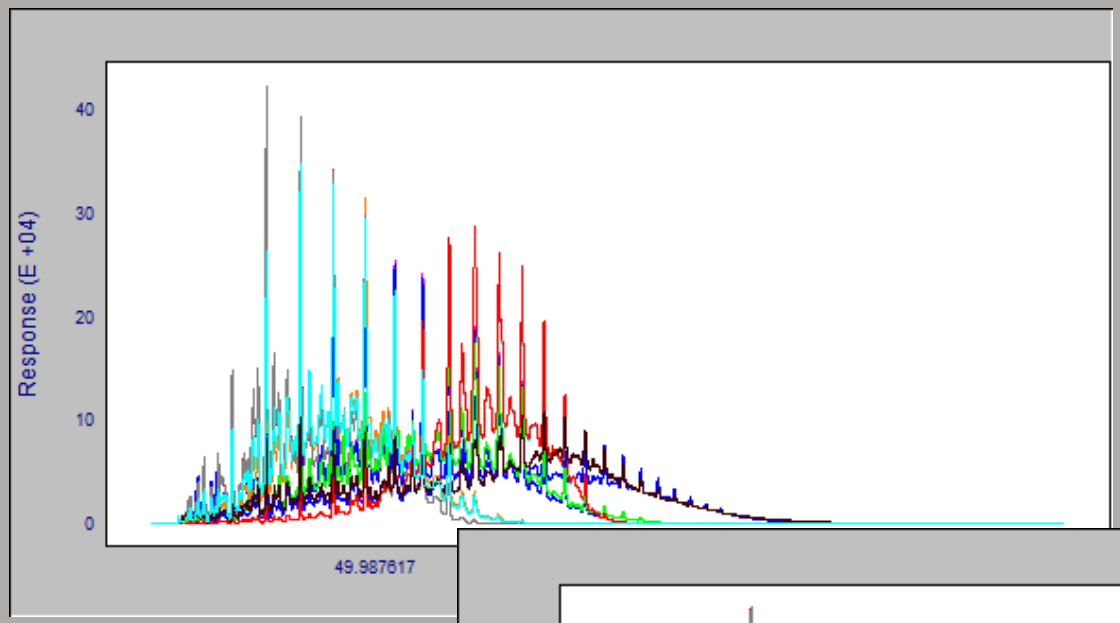
ASTM 7798 ILS

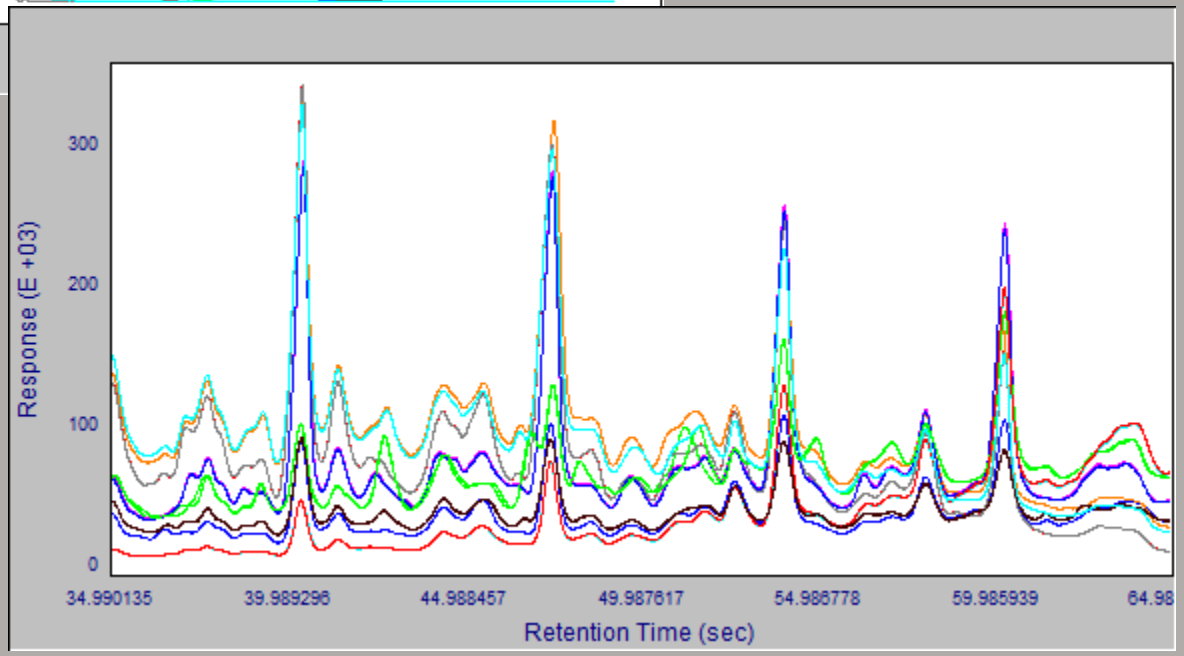
Location 1 – Aligned to the Location 1 Standard





Location 2 – Aligned to the Location 2 Standard





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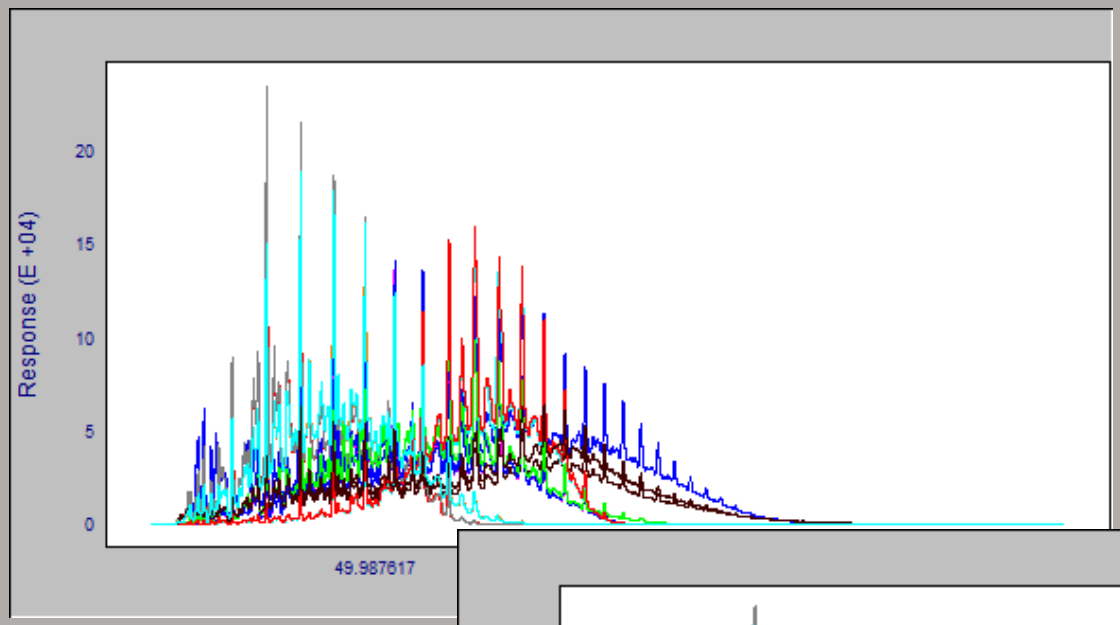
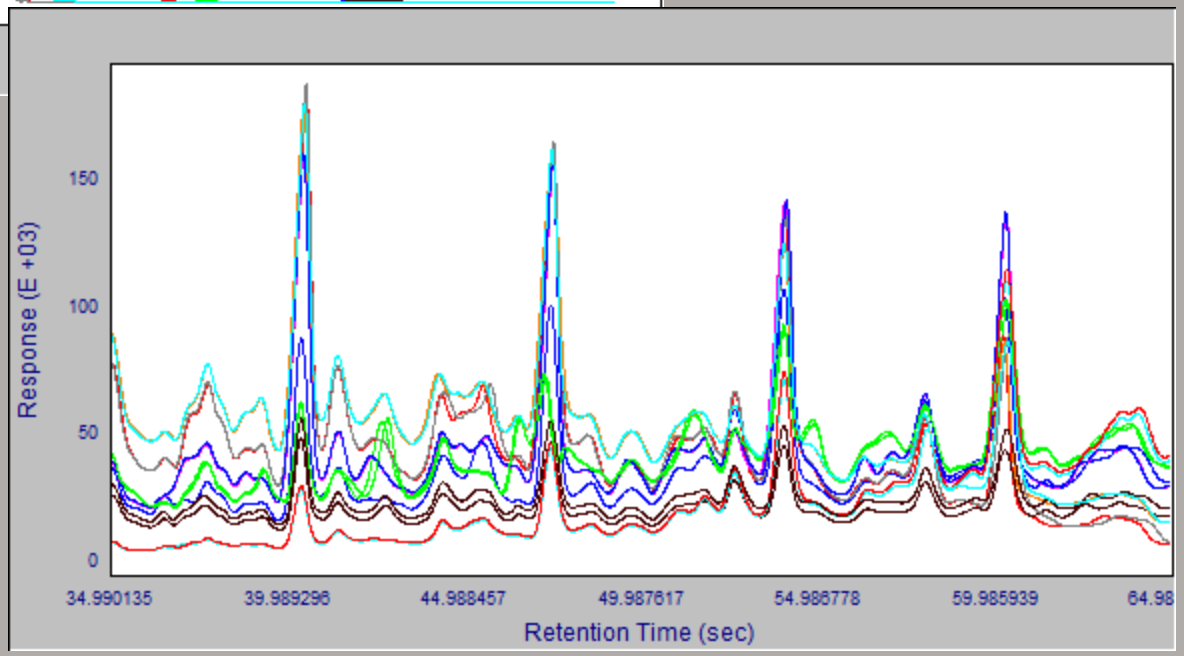
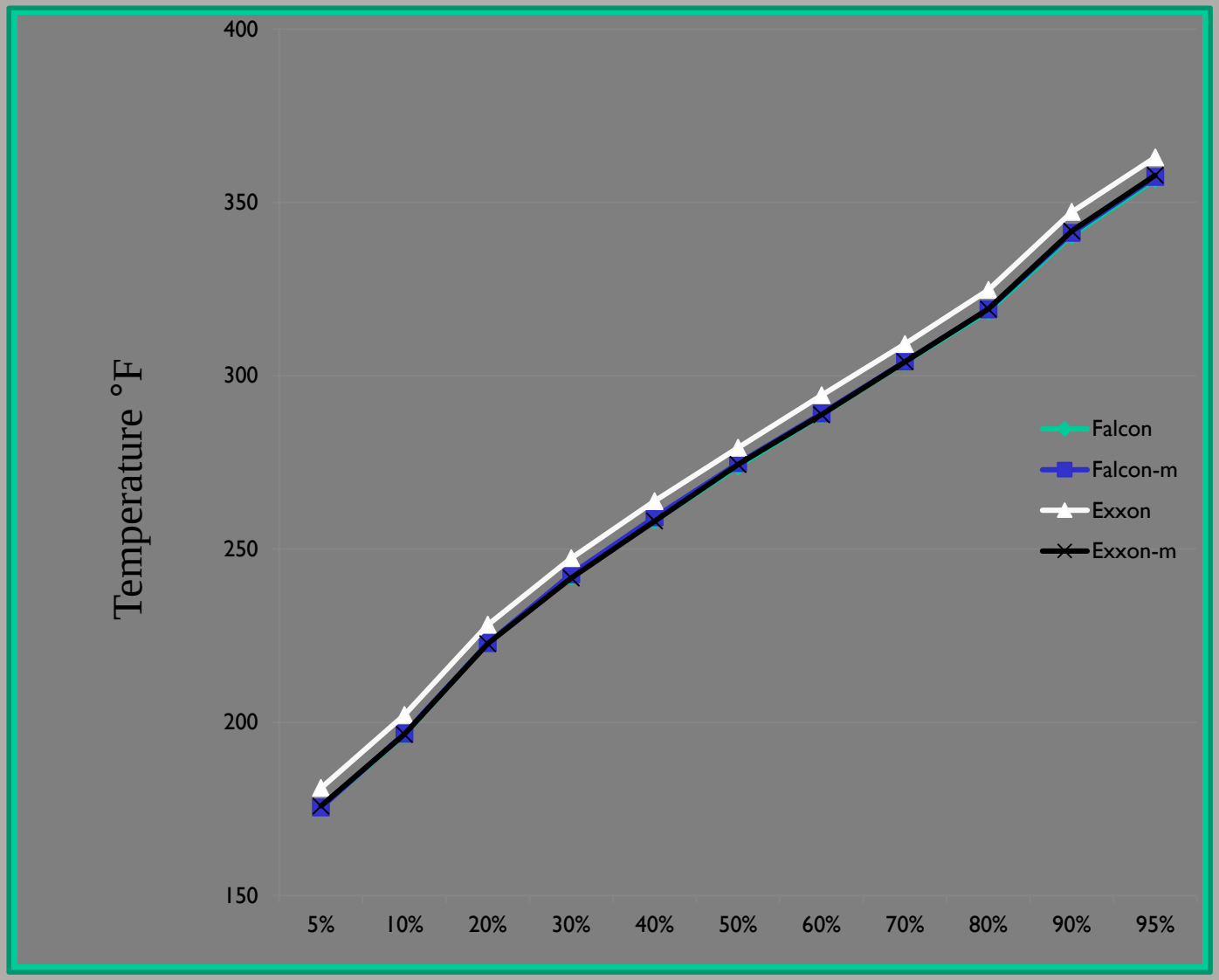
Location 2 – Aligned to the Location 1 Standard

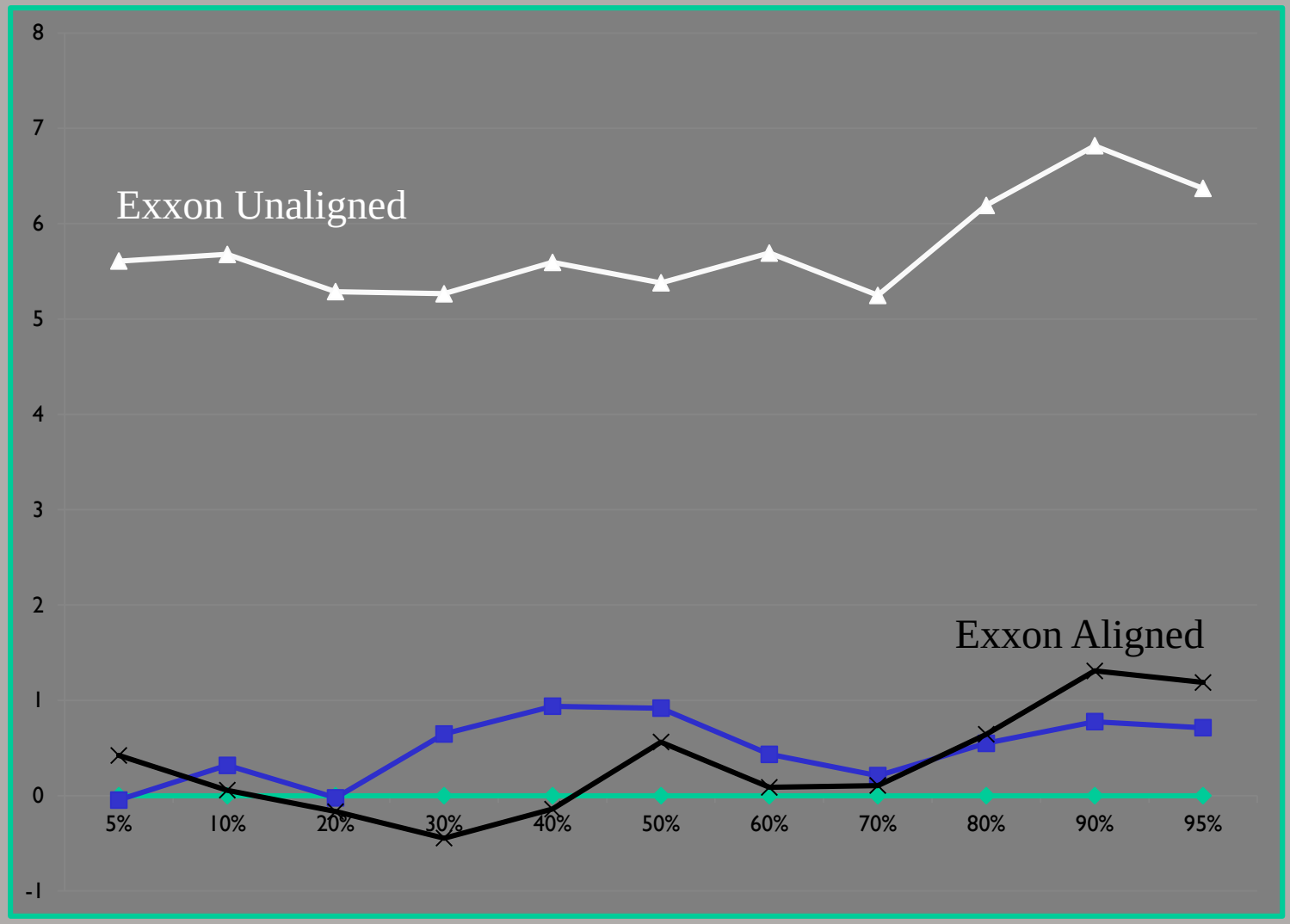




Distillation Profile



Adjusting for Out of Date Calibration



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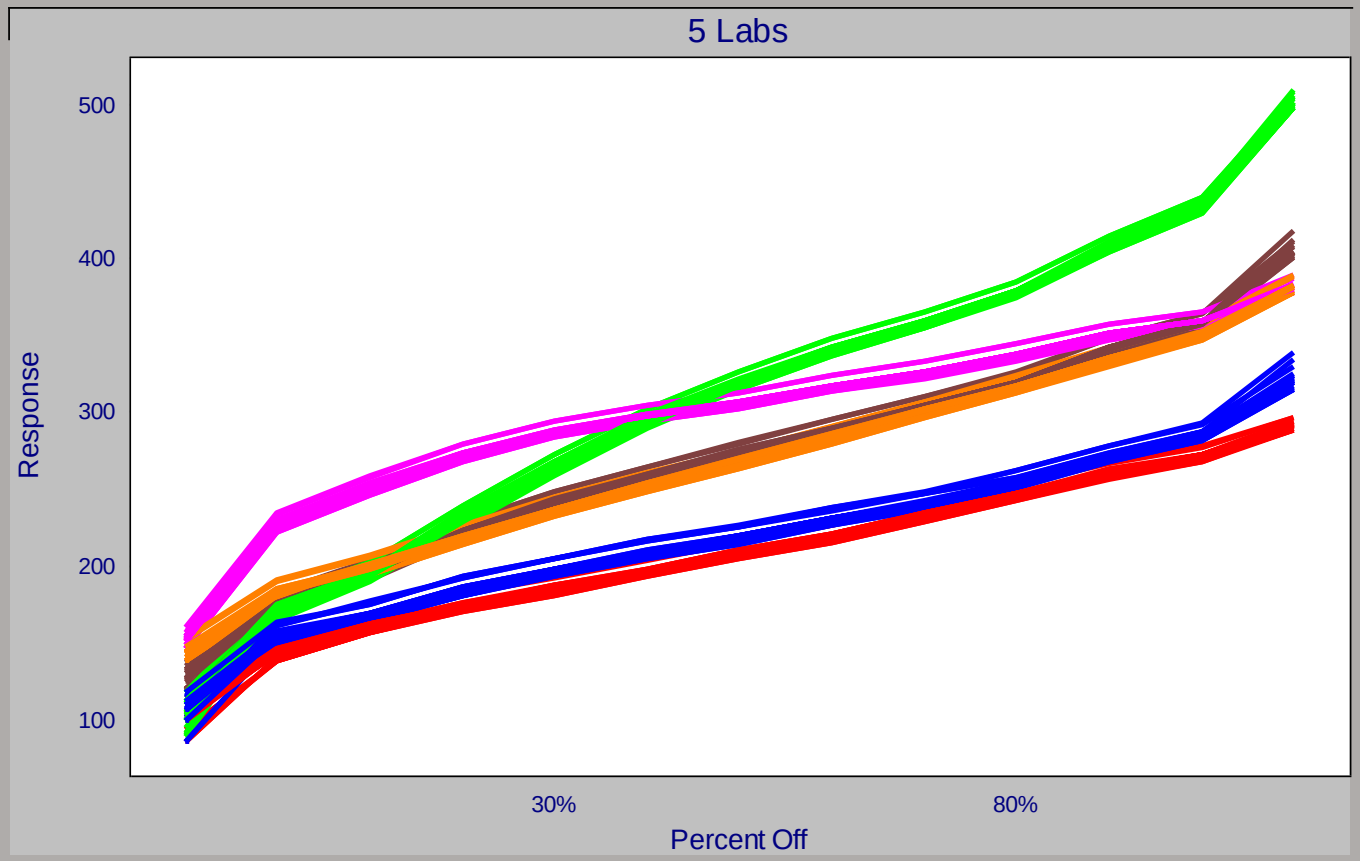
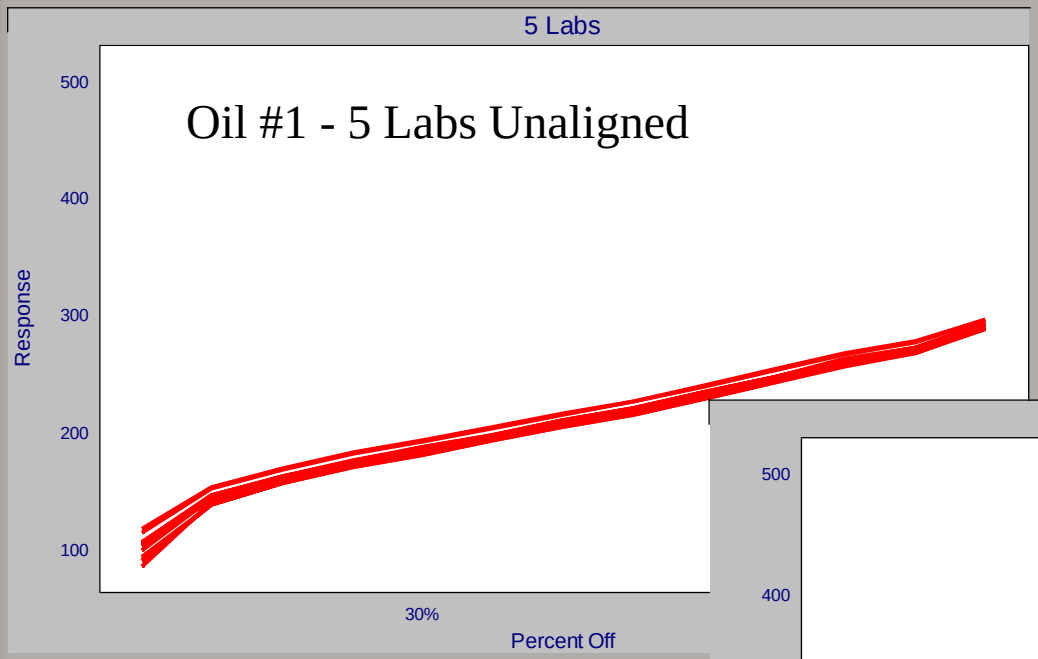
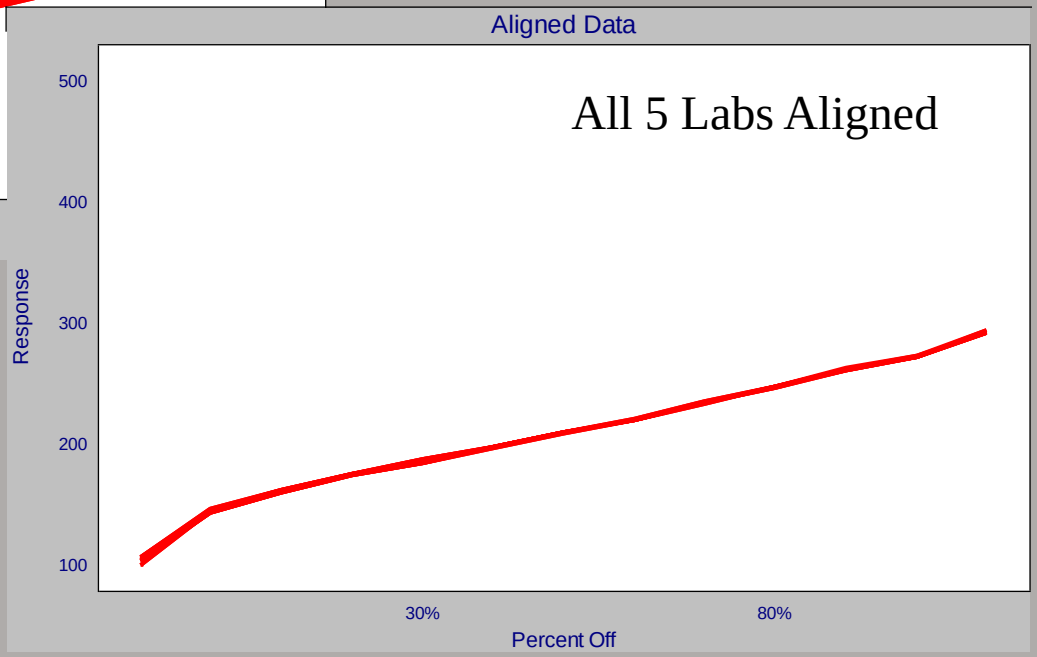
Six Different Oils, Five Labs



No Alignment

Unaligned and All 5 Labs Aligned to Location #1





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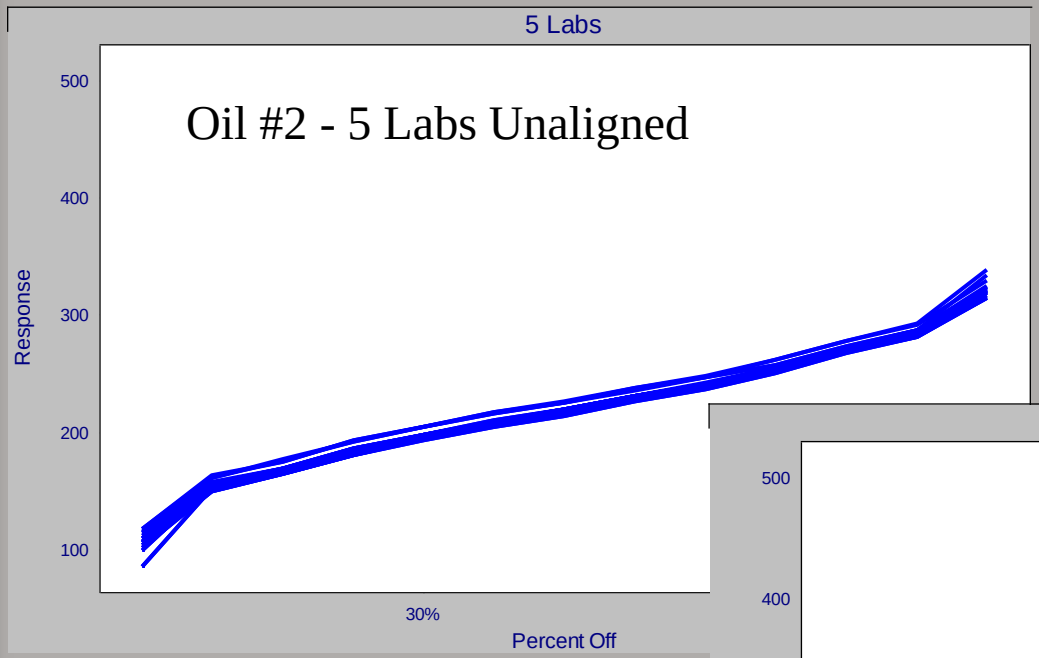

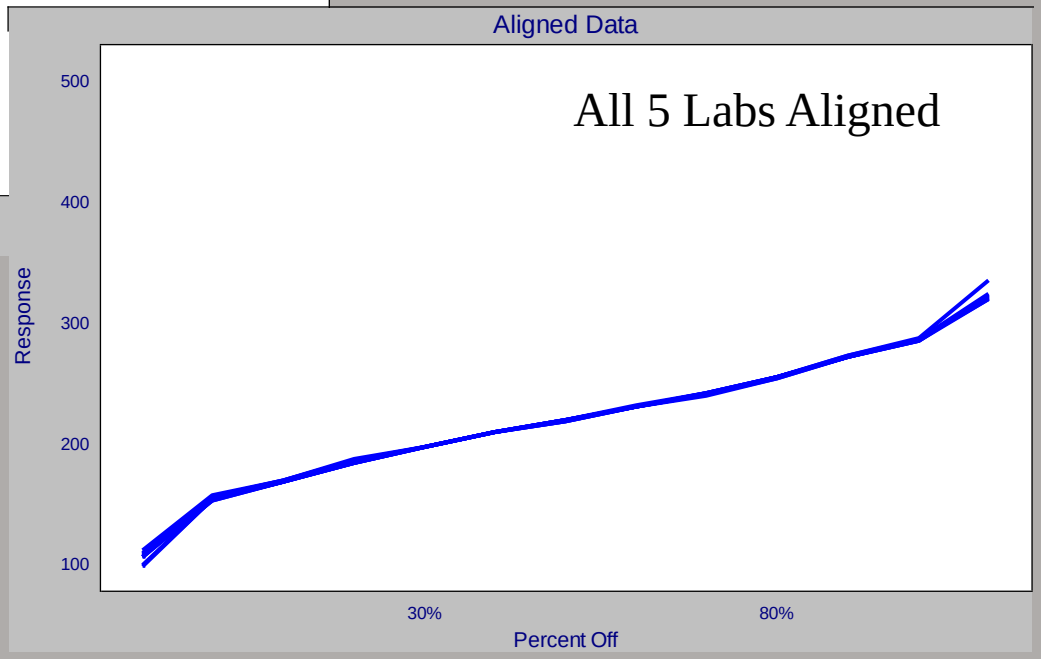

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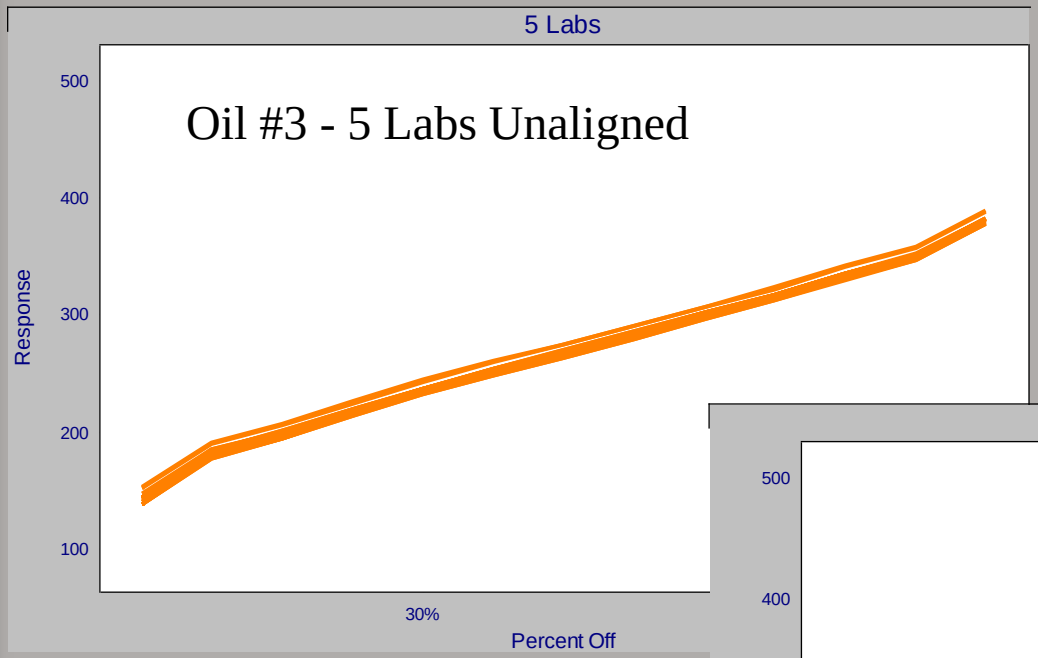

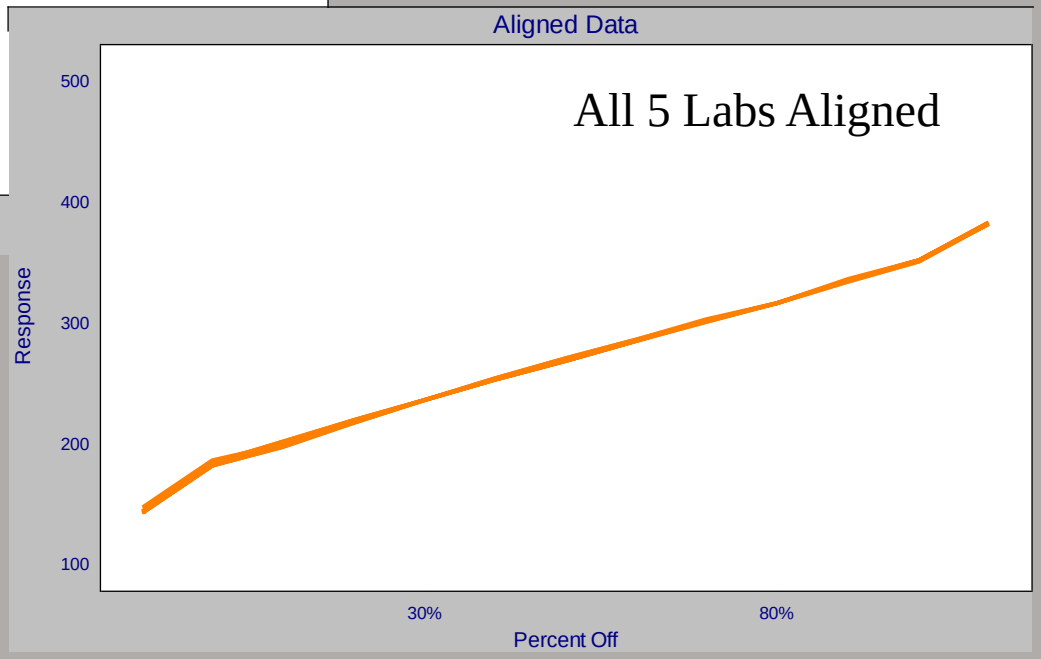

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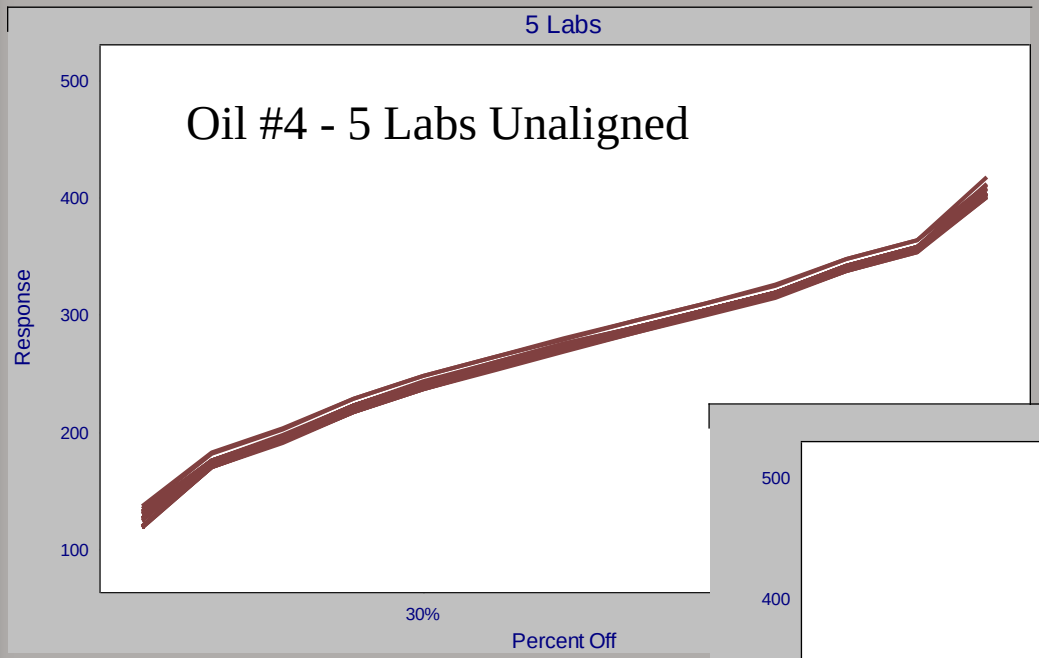

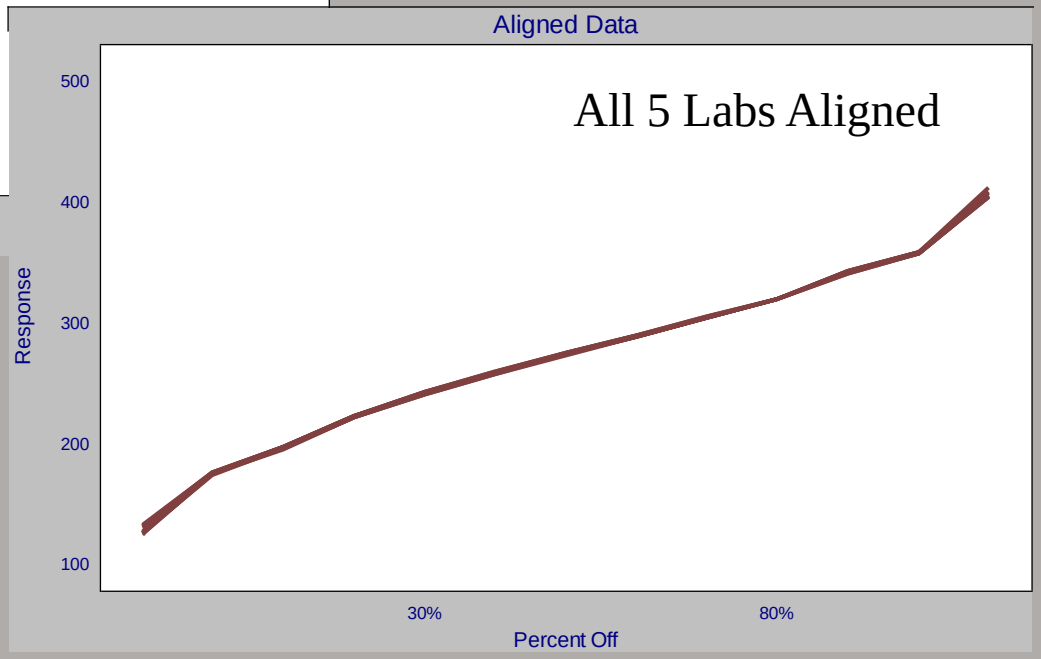

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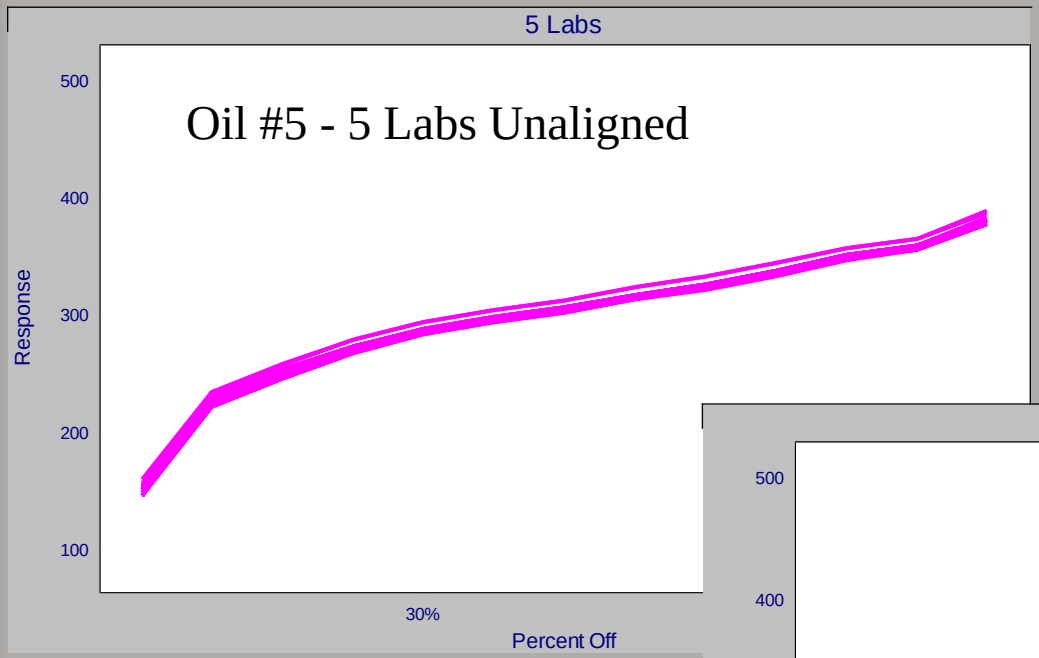

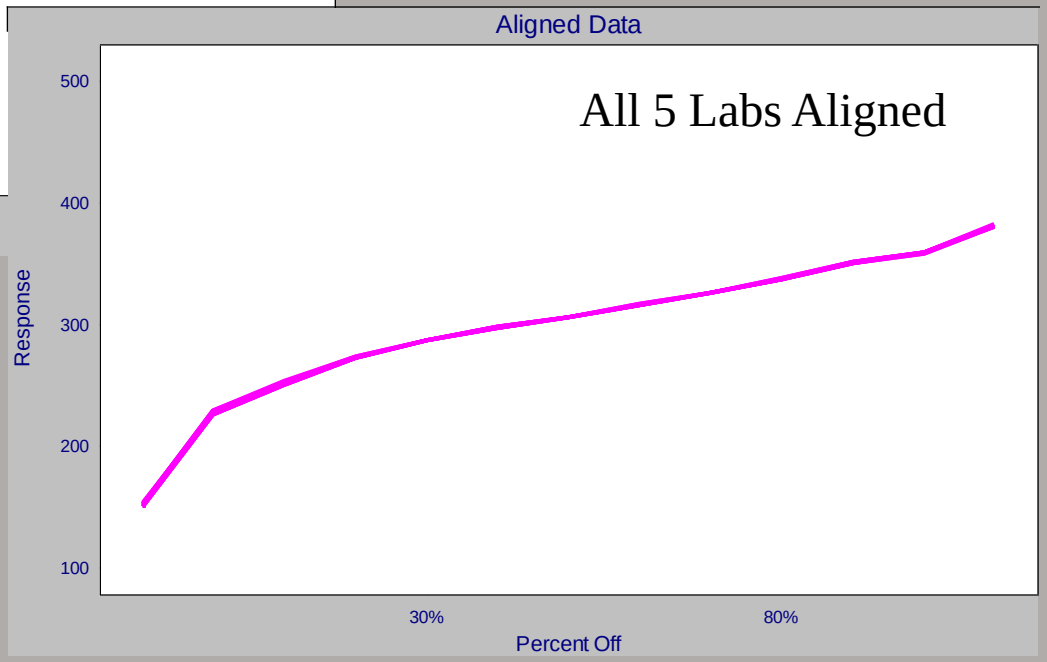

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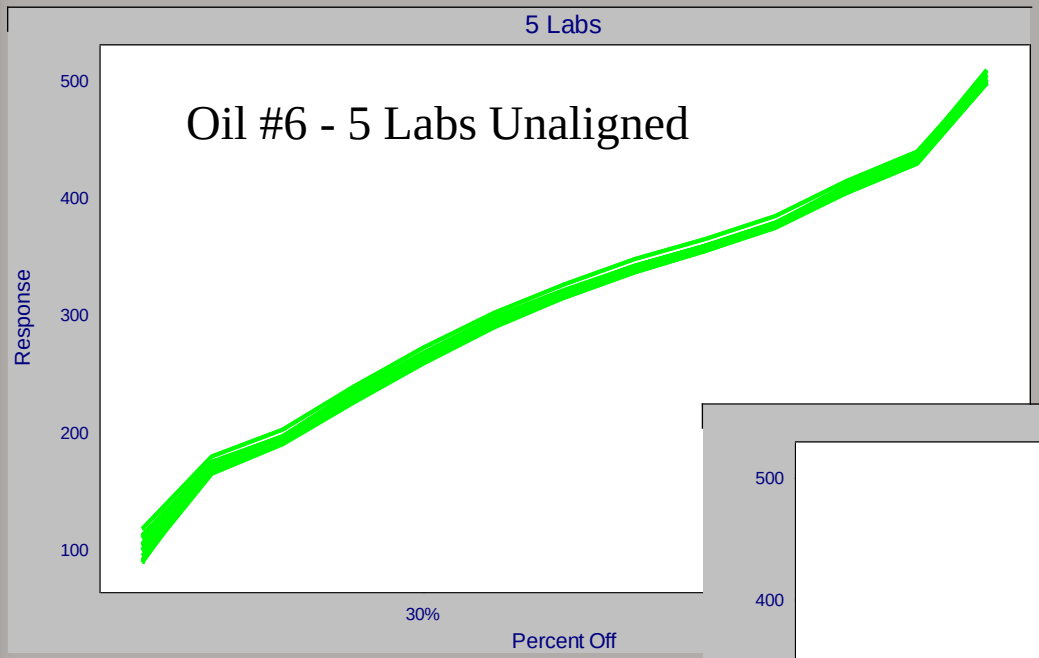

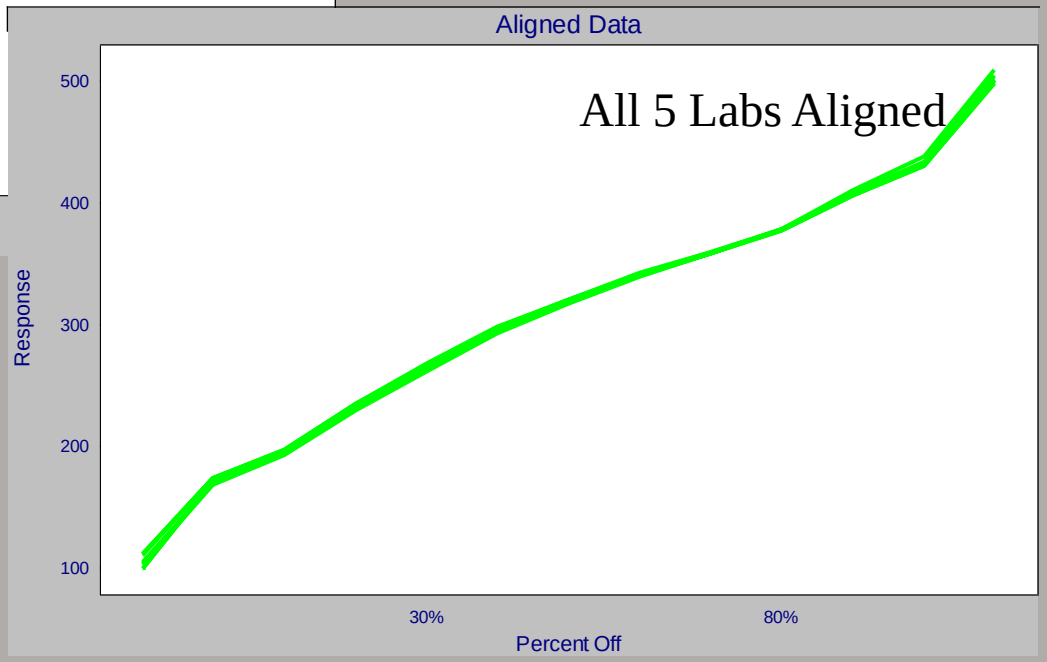

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Continuous data interpretation *PLUS* validation of a multivariate instrument

We can correct retention times to match an application-specific relevant sample

You can use this to make all instruments performing a similar task to look identical (Plug and Play)

This raises the possibility of having a universal calibration

At the least, the frequency with which we really need to run calibration standards is significantly lower that what is currently being done.

Acknowledgements

- Robert Lorenz, Chevron
- John Crandall, Falcon
- ASTM 7798 ILS Laboratories