# Fast Gas Chromatography in the Refinery Quality Control Laboratory

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# Abstract

**Fast Gas Chromatography in the Refinery Quality Control Laboratory – 2:30-2:50**

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Fast GC is now developed and proven to the extent that it is in routine use in refinery quality control. The new method D-7798 has been proven to be 2 to 3 times more precise and having far less bias than the older standard method D-2887. The Inter-Laboratory Study (ILS) done simultaneously with a D-2887 ILS program on the same samples provided an excellent means for comparison. While the speed of analysis certainly helps with throughput and productivity, speed is not the key benefit. Better precision leads to tighter process control, better products and lower costs. This paper will show the comparison of data between the two methods from the simultaneous ILS and discuss the impact better precision and bias parameters have on daily operations.

# Refinery QA/QC Labs

- Locations
  - Main Laboratory
  - Field Laboratory
  - In Plant Laboratory

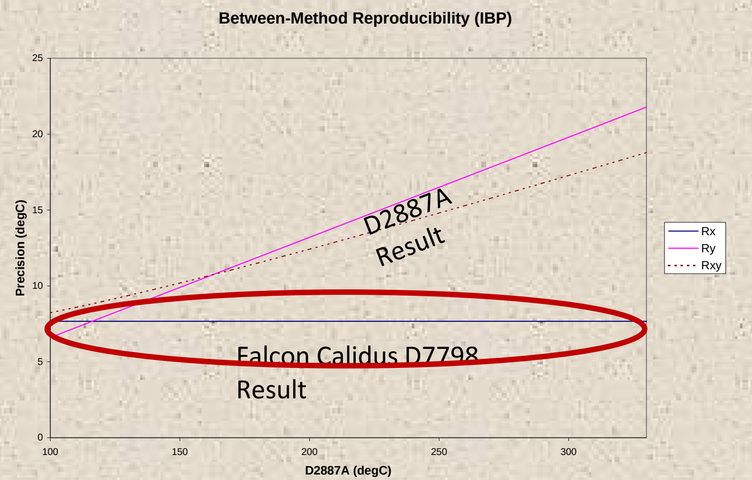
- Roles
  - Product Release
  - Process/Engineering Support
  - Troubleshooting

# Impact of Fast GCs on Throughput

- Refinery QA/QC laboratories are a critical step for product release.
- Conventional wisdom is that you can get only 2 of these 3 attributes; Fast, Right, or Cheap.
- Since getting the measurement Right is of primary importance, you either have longer cycle times or much higher costs (i.e. multiple high cost capital equipment, extra manpower and facility costs).
- Micro and fast GCs upend this wisdom since a good system can maintain or increase the labs throughput without sacrificing the accuracy of the measurement.
- With good micro and fast GCs, you can get better precision with little or no bias on a much larger number of materials than otherwise possible.
- Thus, one can get improved decisions and even explore new applications of this technology.

# Proven Technology

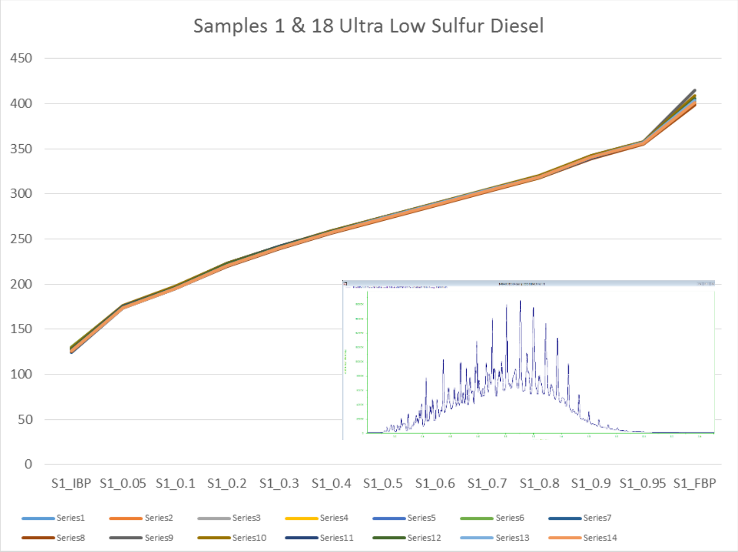
- Demonstrated by ASTM's D2887/D7798 Interlaboratory Study
- Both are Simulated Distillation methods incorporating Gas Chromatography covering the boiling point range from about 100ºF to 1000ºF ($C_5$-$C_{44}$)
- Statistical comparison of the results shows
  - D7798 is 2-3 times more precise than D2887
  - No appreciable boiling range bias from C5 to C44 (outlier at the 99.5% point explained by one unit of 7 HW problem) with D7798
- All points to Ultrafast ASTM D7798 as a better workhorse method using Calidus and Palarus (better precision, better accuracy, tighter control, less cost, more profit.

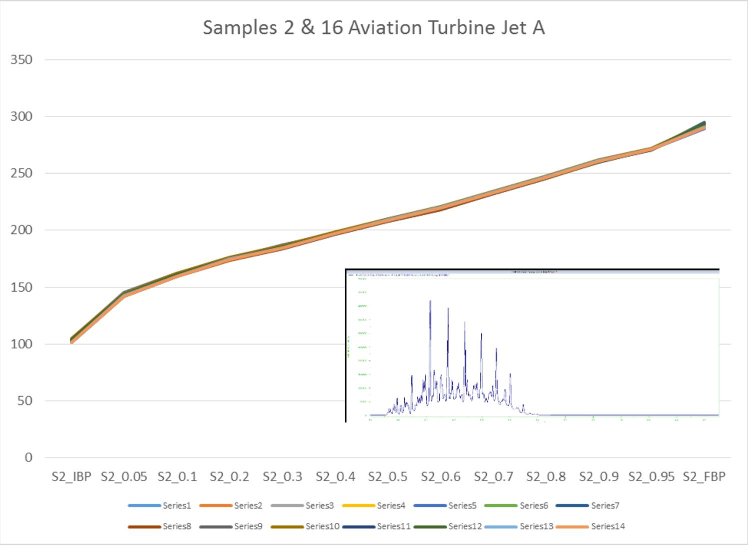


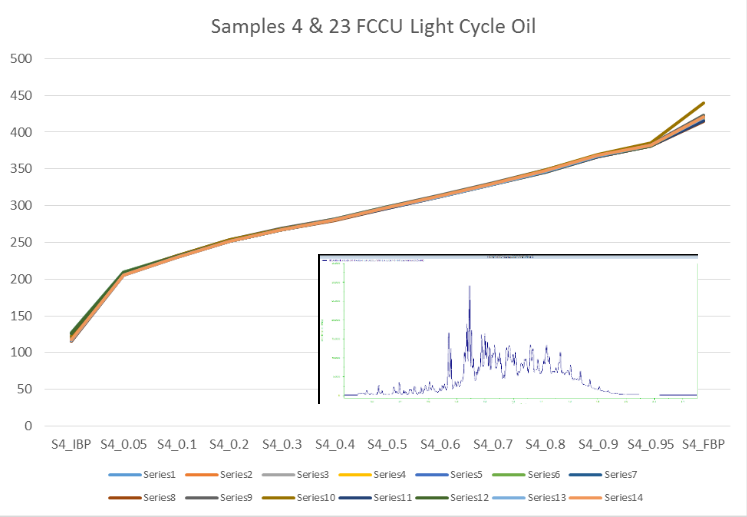

| | method X | method Y | | | |
|---|---|---|---|---|---|
| | D7798 | D2887A | R_x | R_y | R_xy |
| S2_IBP | 102.65 | 103 | 7.671 | 6.80 | 8.33 |
| S5_IBP | 105.49 | 108.7 | 7.671 | 7.17 | 8.53 |
| S8_IBP | 105.88 | 112 | 7.671 | 7.39 | 8.65 |
| S6_IBP | 119.85 | 128.6 | 7.671 | 8.49 | 9.29 |
| S4_IBP | 121.35 | 127 | 7.671 | 8.38 | 9.23 |
| S1_IBP | 127.03 | 128.3 | 7.671 | 8.47 | 9.28 |
| S11_IBP | 142.93 | 142.6 | 7.671 | 9.41 | 9.86 |
| S7_IBP | 151.02 | 153.4 | 7.671 | 10.12 | 10.32 |
| S3_IBP | 230.96 | 229.7 | 7.671 | 15.16 | 13.80 |
| S10_IBP | 246.43 | 246.2 | 7.671 | 16.25 | 14.60 |
| S12_IBP | 288.33 | 294 | 7.671 | 19.40 | 16.95 |
| S9_IBP | 330.05 | 332.1 | 7.671 | 21.92 | 18.87 |

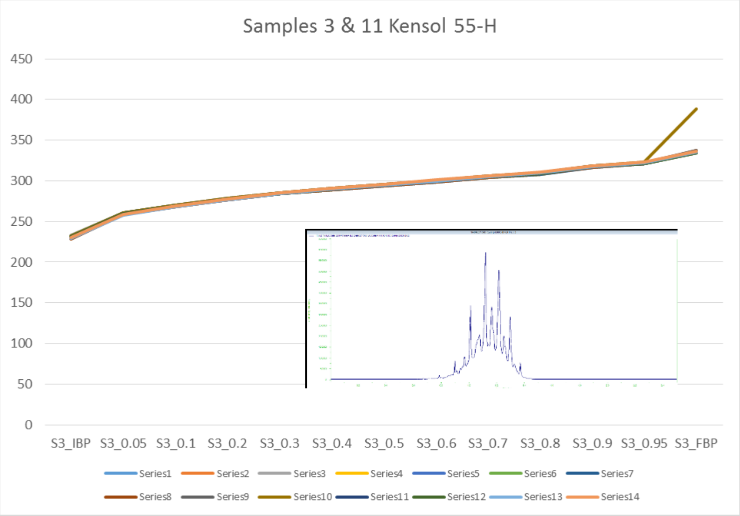
# Demonstrated Reproducibility

- Multiple samples analyzed in a blind study



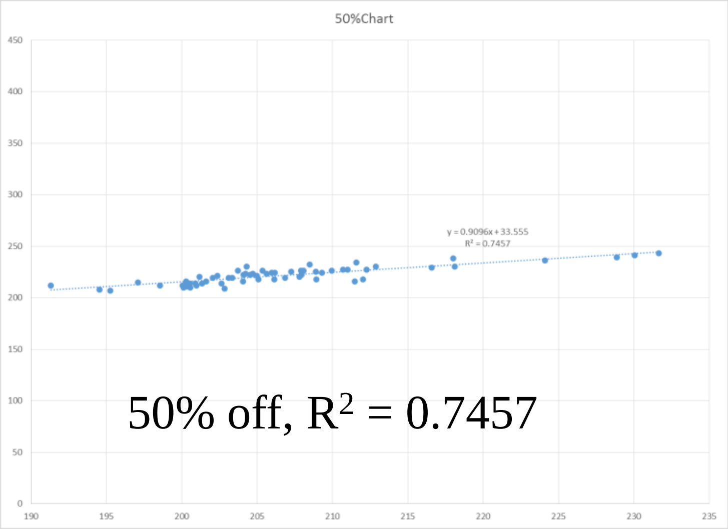



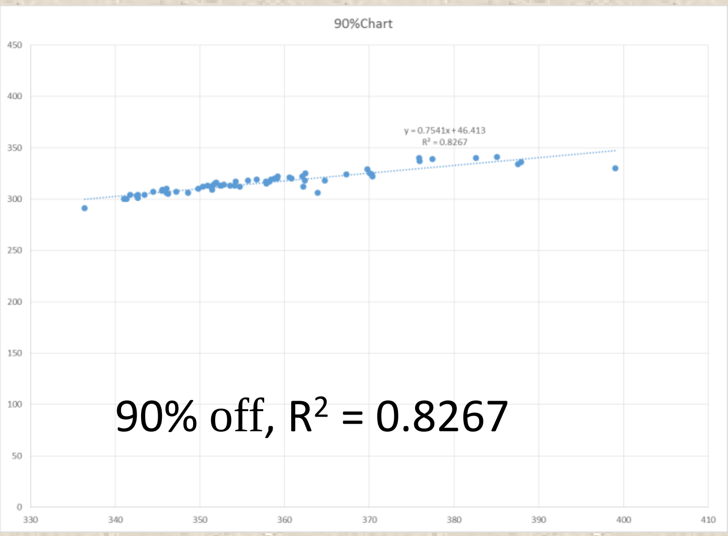



# Benefits for High Value Products

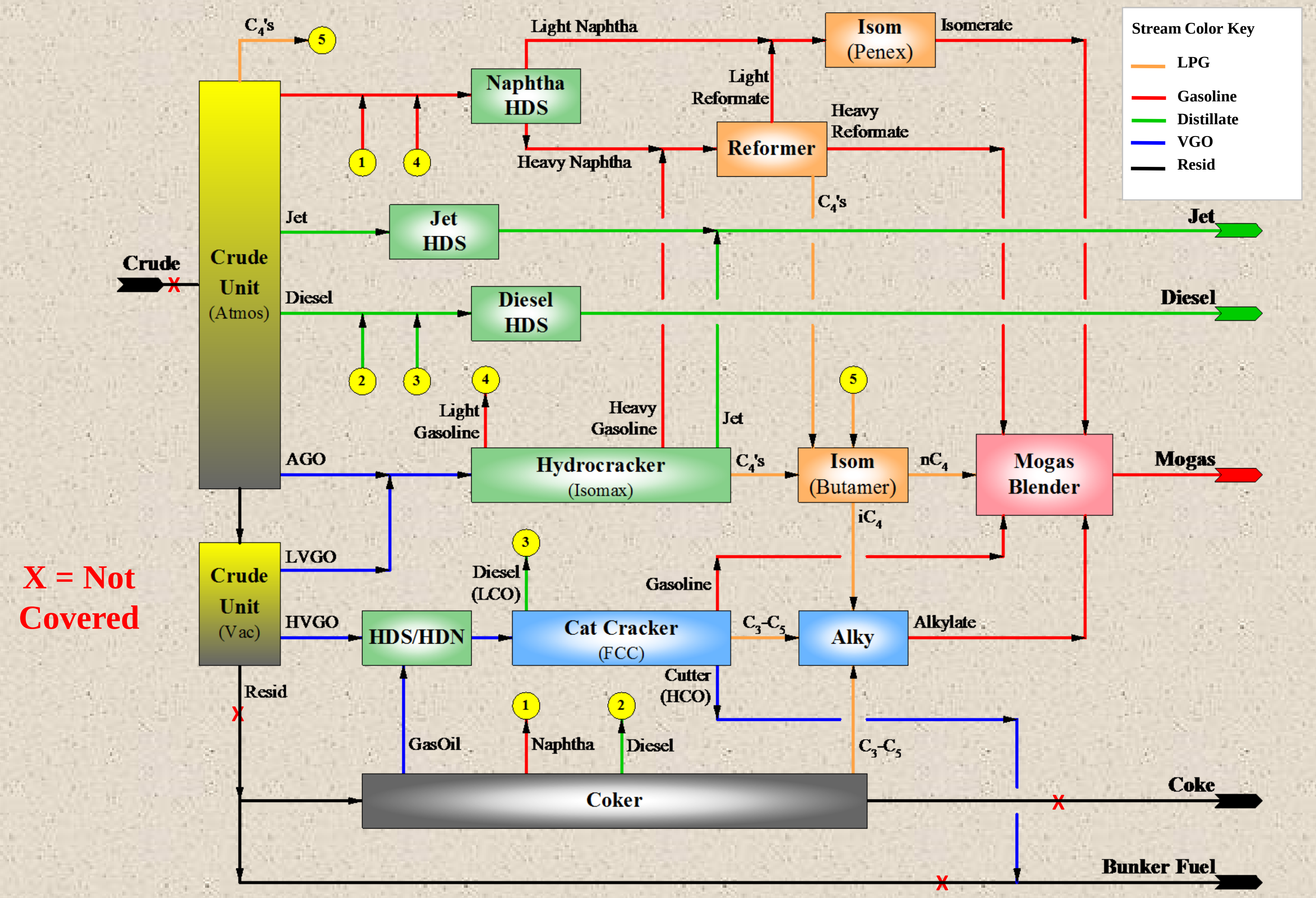
- High value products include light transportation fuels and lube oils (all within the ASTM D7798 method range).
- Gasoline sales may require different blends depending on local regulations.
- Since contractual requirements specify ASTM D-86 distillation, correlations are needed to convert the GC based alternative (ASTM D-3710) to D-86 equivalence.
- A gasoline blender running D-3710 with a Calidus system has been in service for almost 3 years with no problems.  The key issue is the robustness of the correlation.
- Benefit – higher throughput for COAs and reduced product giveaway (est. $1MM/mo)



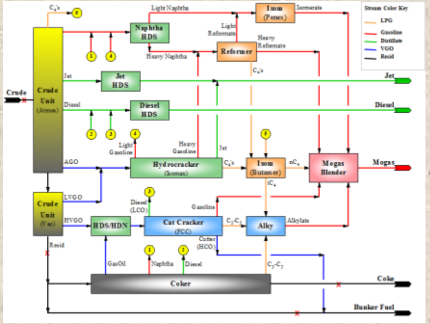



# Calidus GC Applications Cover Most Refinery Streams

## Feeds, Intermediates and Products



# One Refiner’s Experience



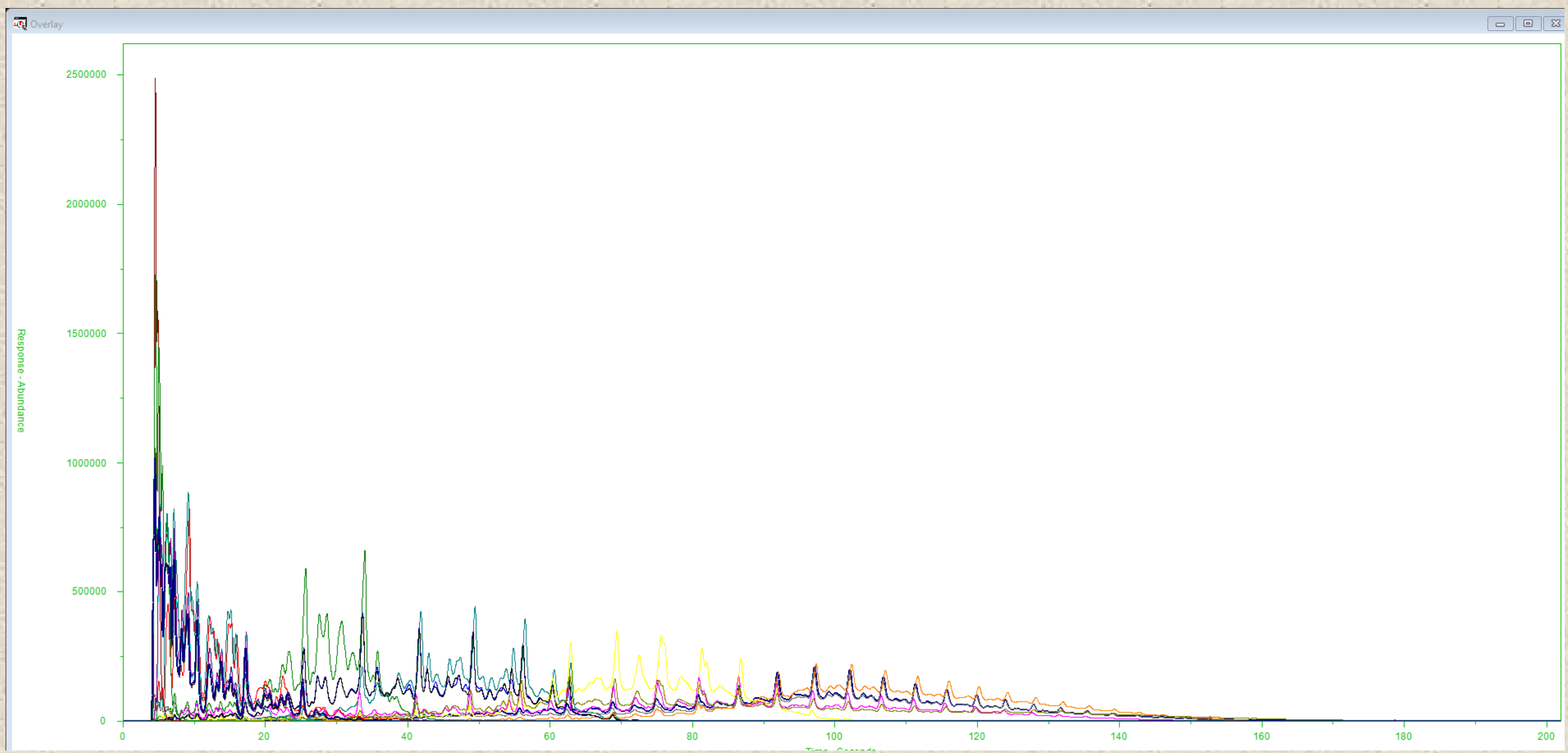

- ASTM D7798 being used throughout the refinery as indicated in the previous slide

- More than 20 samples/day are run for process control

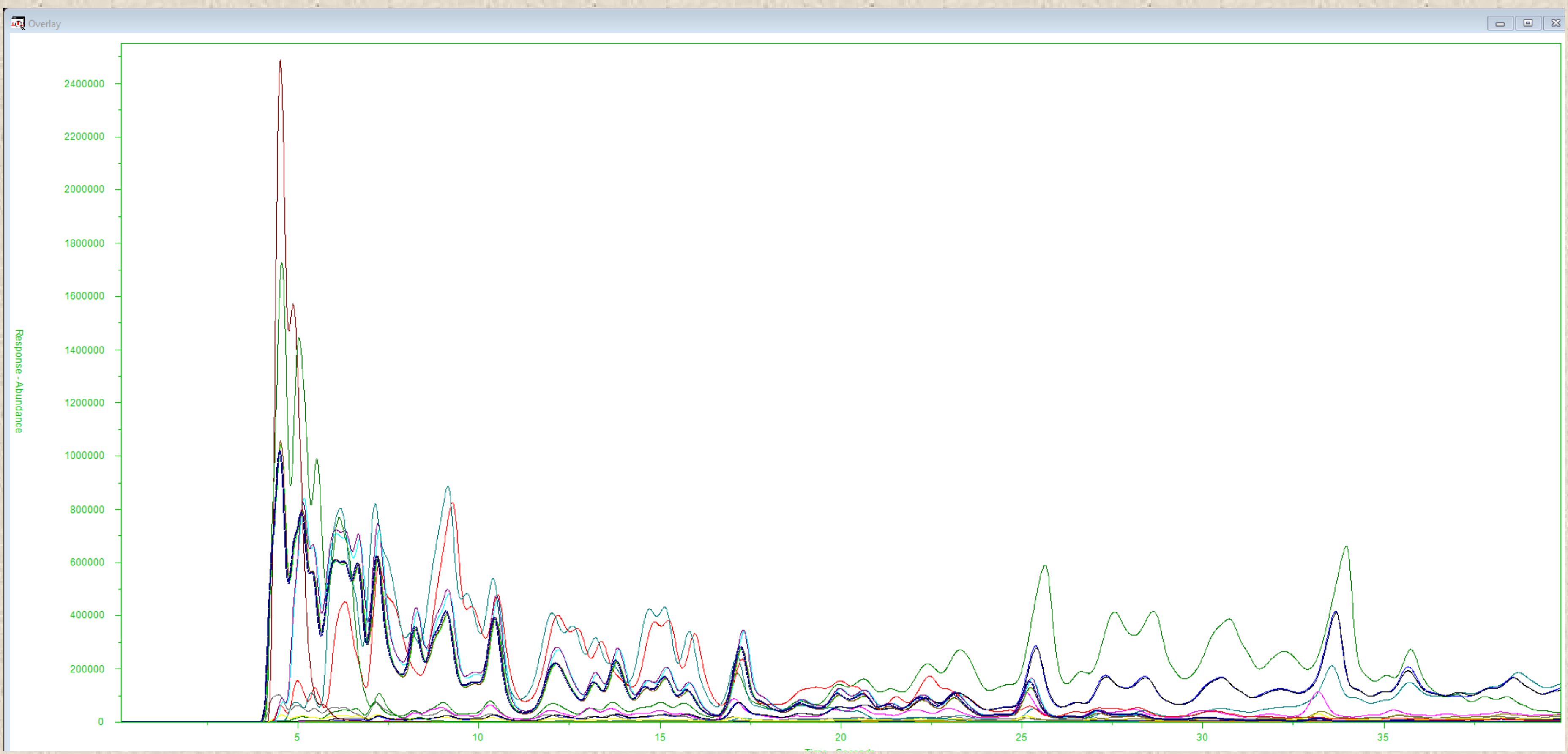
- Processes being controlled using the Calidus 95% cutpoint (D-86 is still run on about ½ of the samples to build confidence)

- BUT the Process Controls settings are set using D7798 for a wide variety of streams.

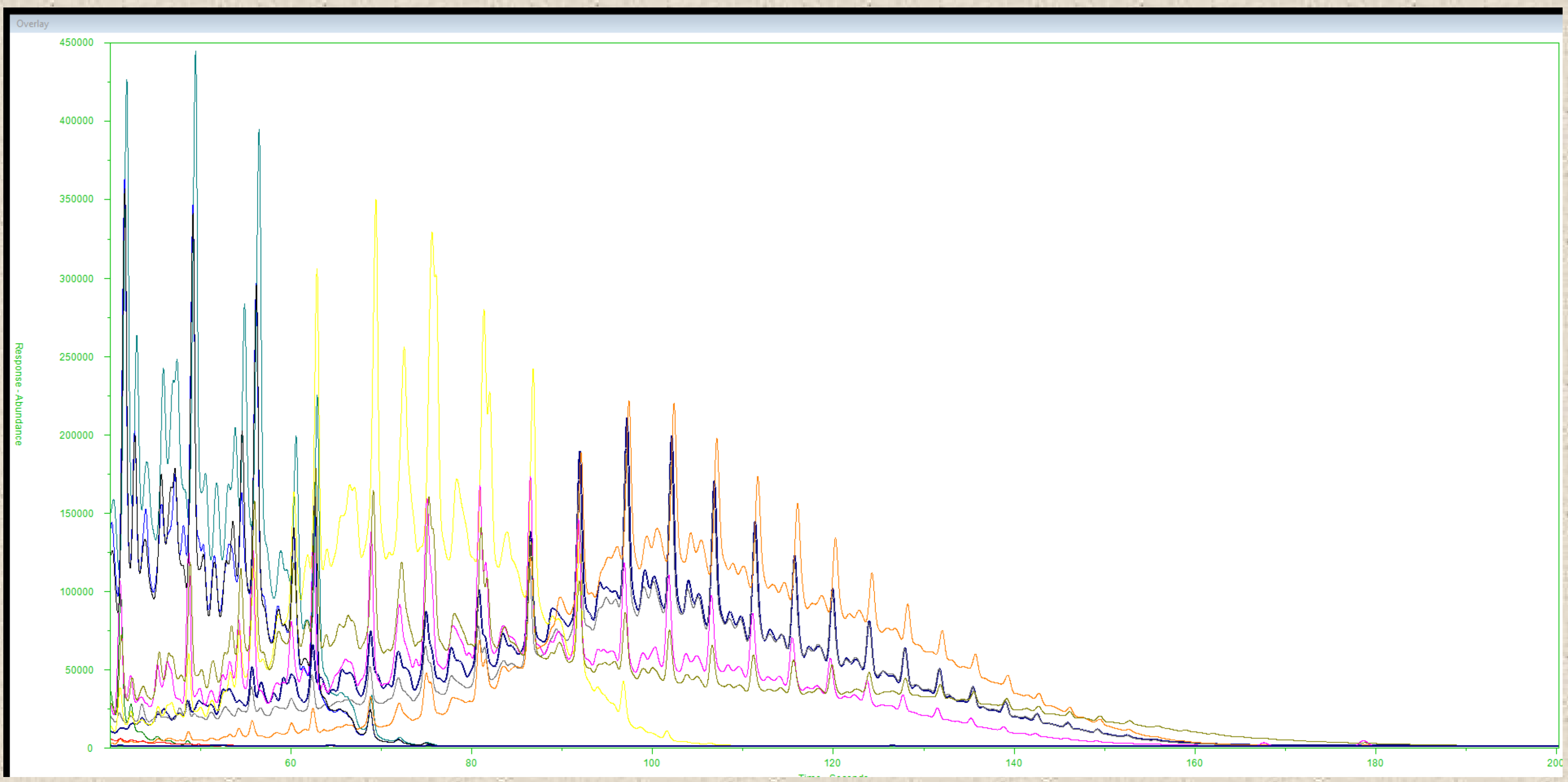
# Single Example Chromatograms Overlaid



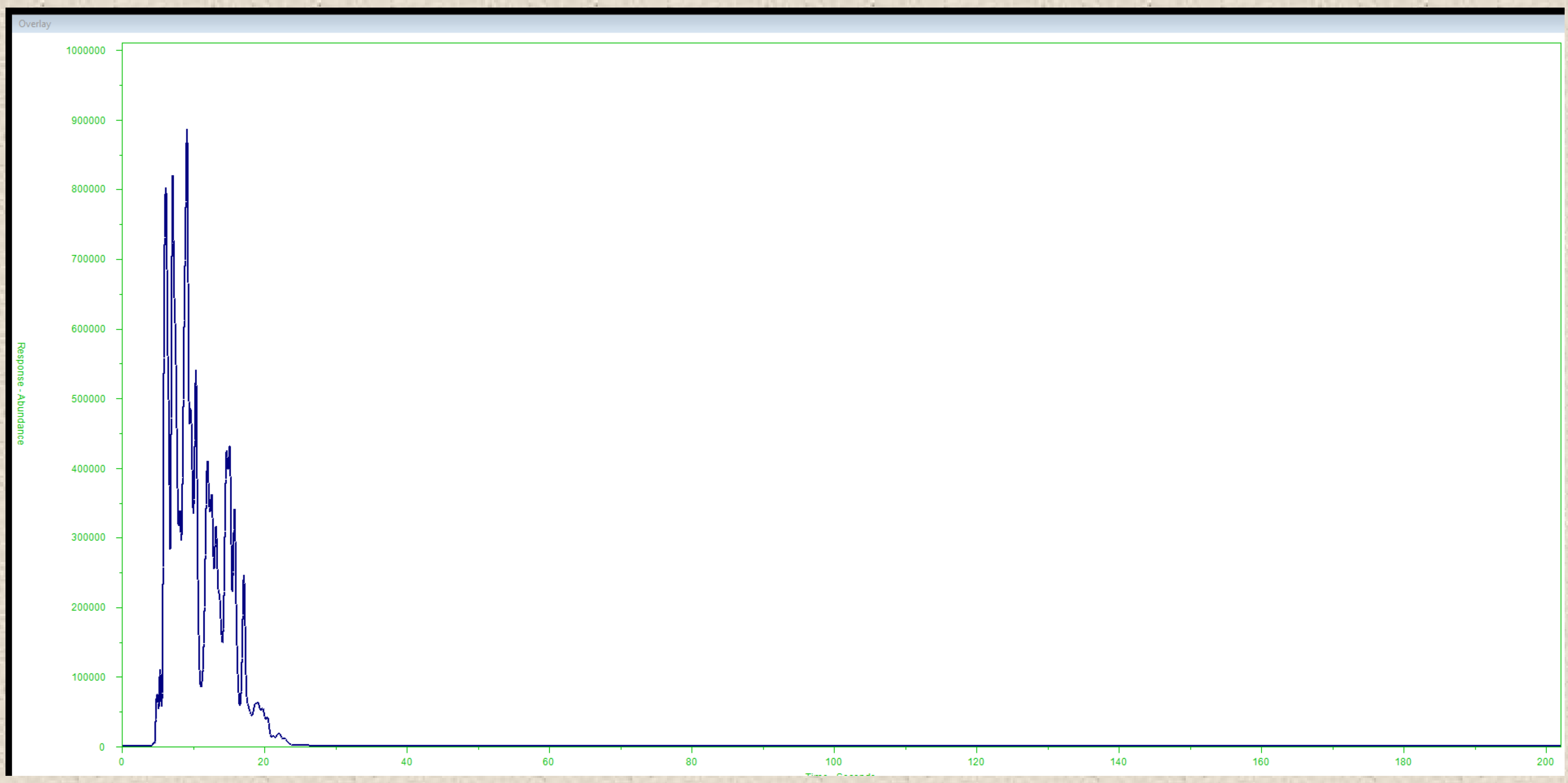
# To 40 Seconds



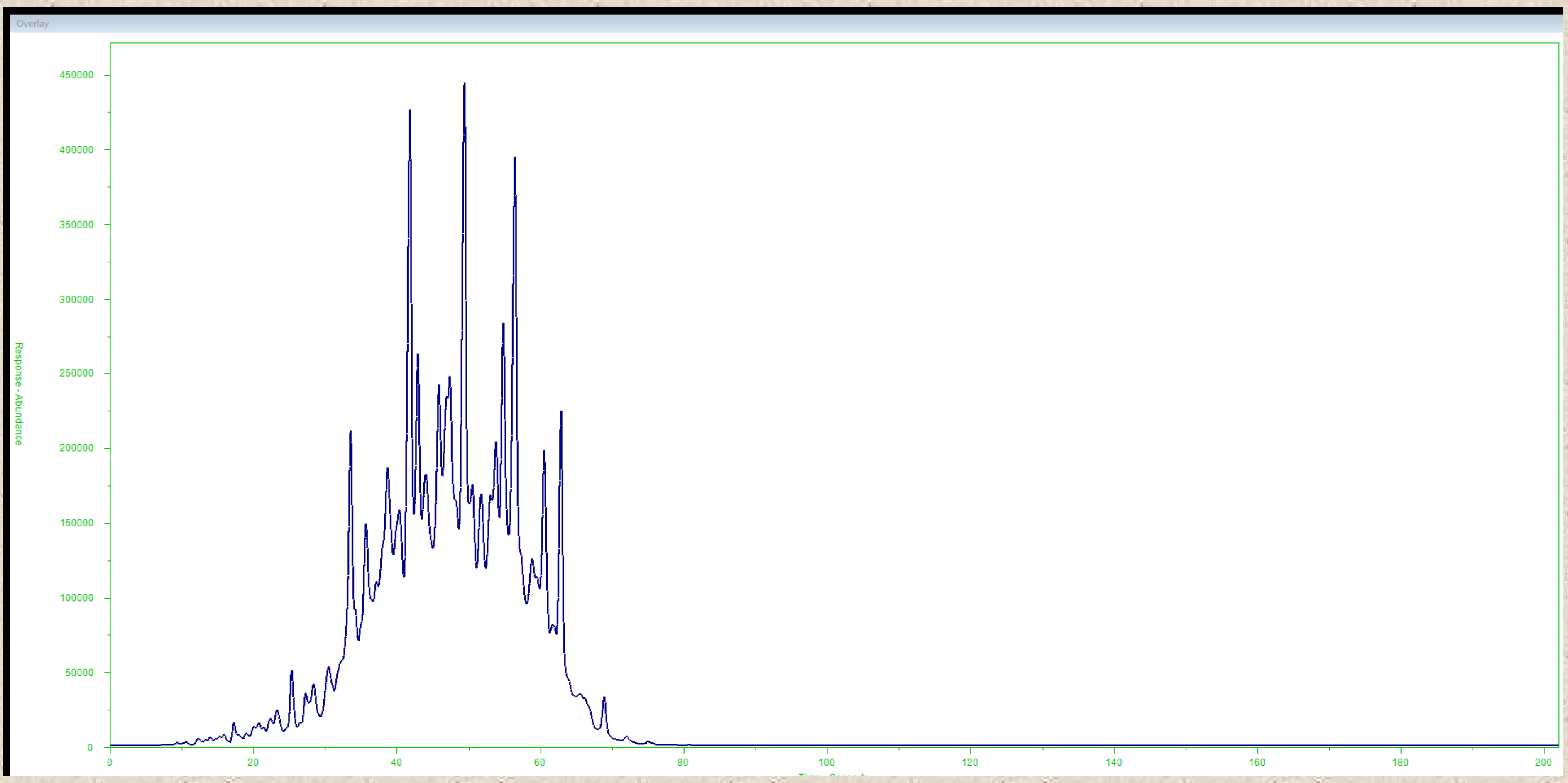
# 40 Seconds to End



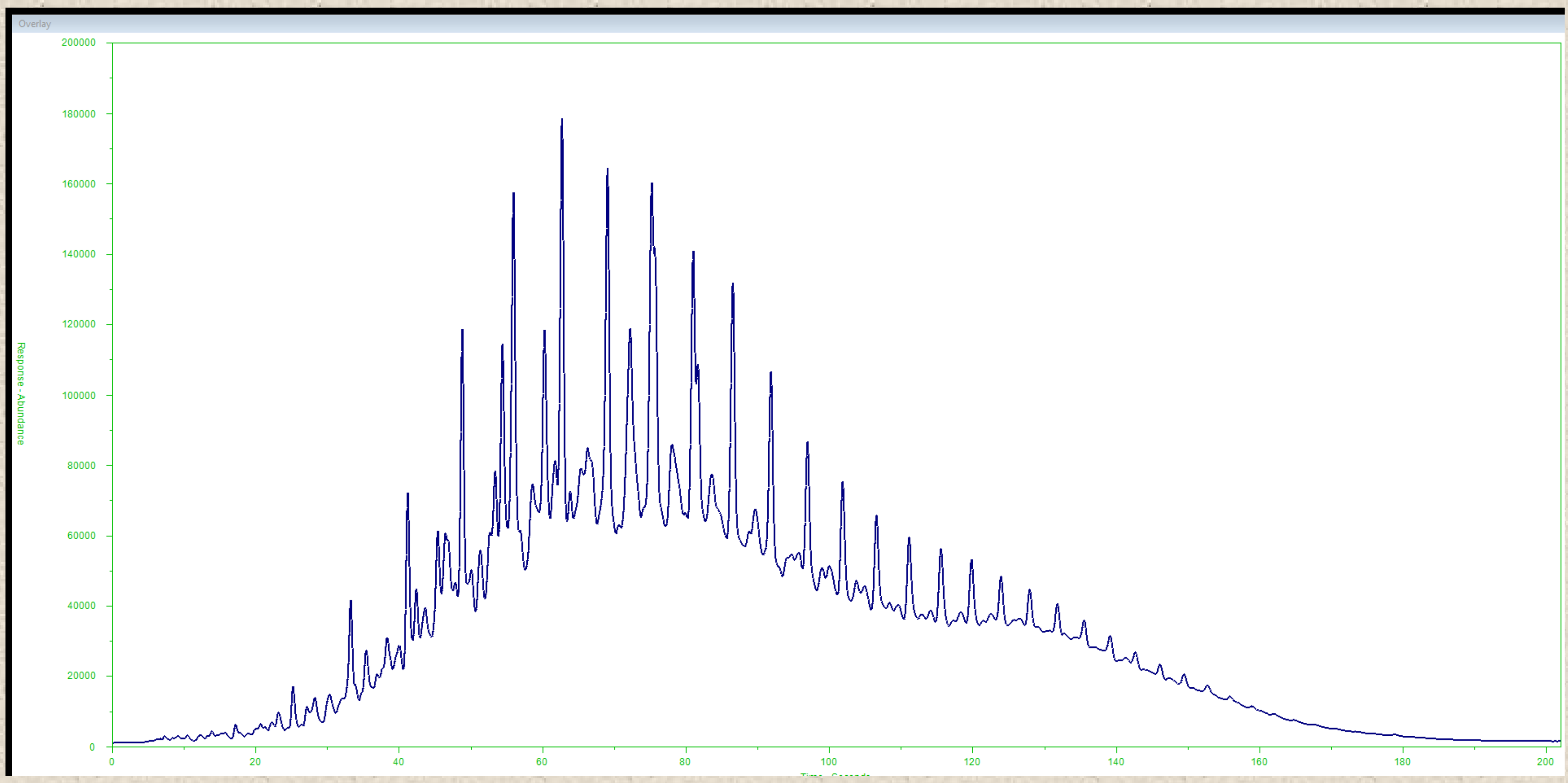
# Low, Narrow Boiling Range Example



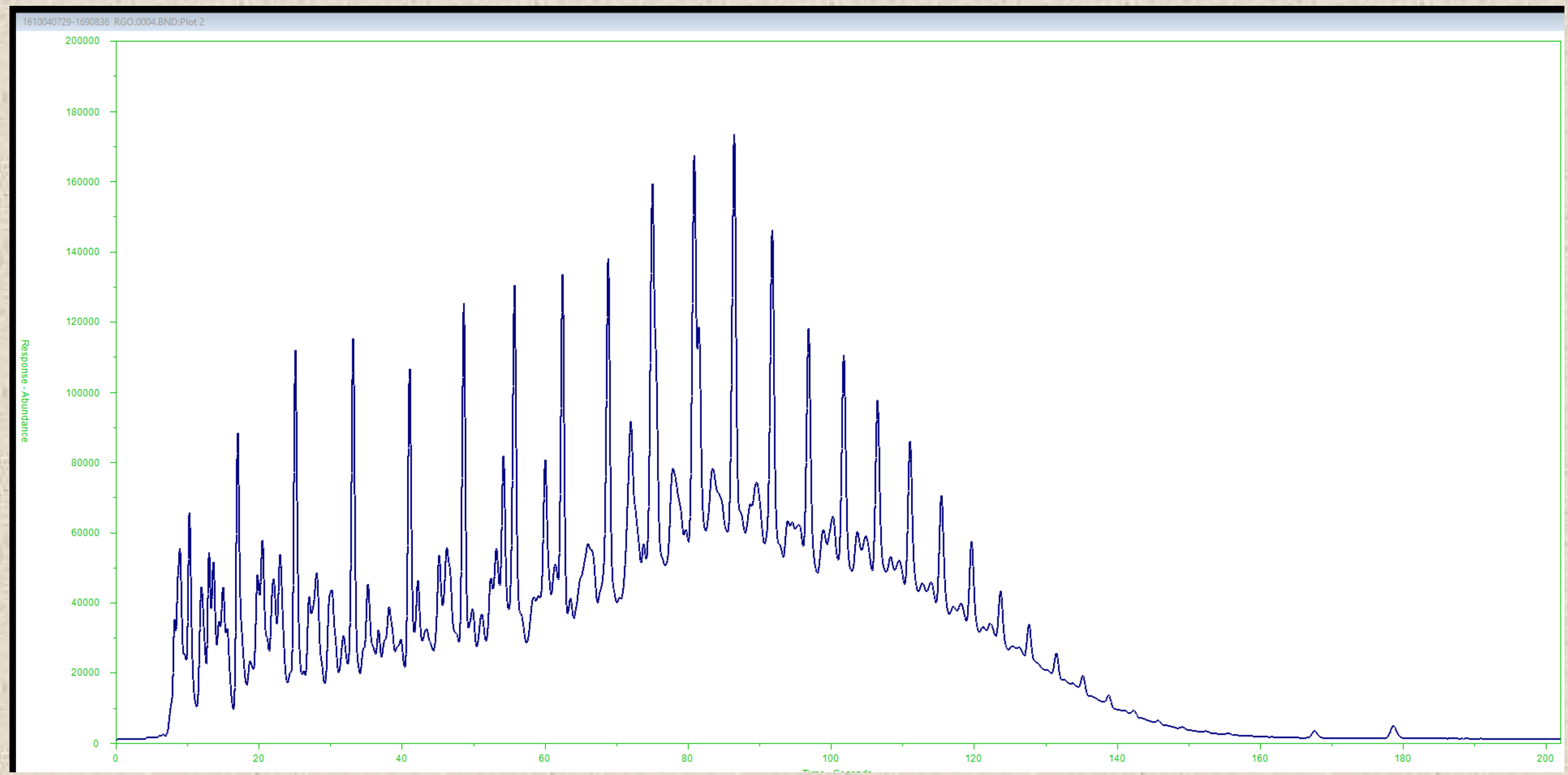
# Medium, Broader Boiling Range Example



# Very Broad Boiling Range Example



# Reference Gasoil Check Sample Example



# Economic Benefits

- Economics difficult to quantify like fuel product “give away” but
  - Tighter controls resulting from better precision is quite valuable
    - Ability to blend closer to the required specification
    - Reduced processing energy consumed
    - Reduced recycle/rework
    - More consistency in the fuel blending pool components
    - Improved decisions on which streams to process/blend where
- Greater product throughput for increased revenues and higher profits
- Smaller footprint means more bench top or analyzer shelter space. Space is both costly and at a premium in Labs or in the plant.
- Speed and precision for quicker turnaround
- A reduction in manpower and utility cost (i.e. power and consumables)

# Next steps

- Instrument/Analyzer Pairs and Data Equivalency
  - IF process GC and Lab GC results are equivalent then
  - Routine testing in the lab can be eliminated
    - Except for “spot checks”
    - The path for certification to inventory or the pipeline becomes realistically possible
- See Joe Perron’s paper at 3:20 for more information

# Acknowledgements

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