FALCON

ANALYTICAL SYSTEMS & TECHNOLOGY

Fast Gas Chromatography using Heated Headspace Gas Auto Sampling Techniques: Polyethylene Pellets, Product Purity Analysis

Matt Holliday, Presenter – Derrick Saul, Joe Perron - Falcon Analytical

Abstract

Fast Gas Chromatography using Heated Headspace Gas Autosampling Techniques: Polyethylene Pellets, Product Purity Analysis

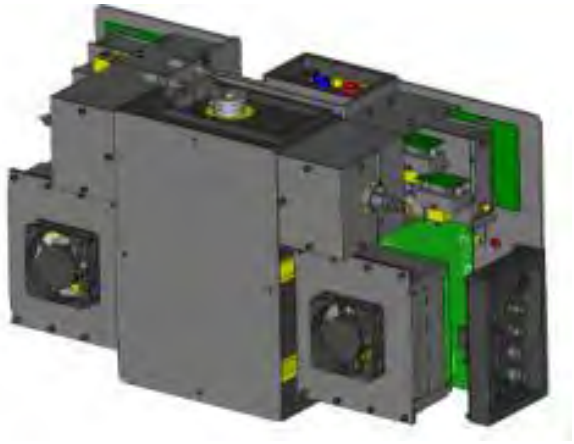
Matt Holliday - Falcon Analytical

Sampling is often the most difficult part of an analytical method even for micro and Fast Gas Chromatography. In some cases the analytes of interest cannot be separated and measured with a column system that can survive the balance of the sample matrix. Purity analysis of Polyethylene Pellets is an excellent example. The solution is to heat the pellets and drive the target analytes into the headspace gas. The autosampler using a gas tight syringe can then sample and introduce the resultant sample into the GC.

This paper will describe the system and the method developed for this analysis.

General Analytical Design

- Sample introduction is just as important as the analytical technique used.
- Difficulties with sample introduction include, but are not limited to:
  - Analyte/Matrix column phase incompatibility
  - “Non-Injectable” sample matrix (this case)
  - Sample extraction/preparation may degrade target analytes, may not be effective, or may not be practical



Falcon Analytical's CALIDUS™ CS Paired with the PALARUS™ RSI Autosampler

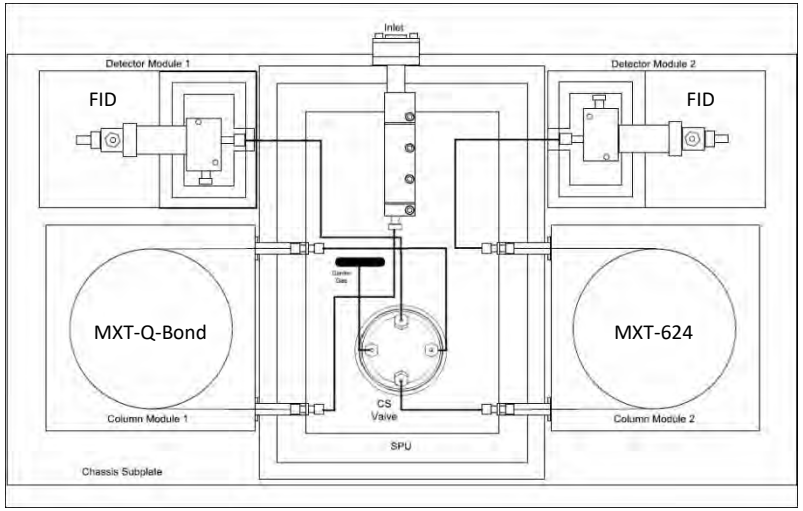
- Based on the PAL XYZ robot platform
- Modular system
- UHP purge gas input
- Magnetic vial transfer
- Variable speed, temperature, and duration agitator
- Interchangeable tool – Headspace, Liquid, and SPME injections possible with the same Auto Sampler
- Supports a wide range of Injection volumes
- Virtual interface terminal (physical terminal interface available)

PALARUS Operation

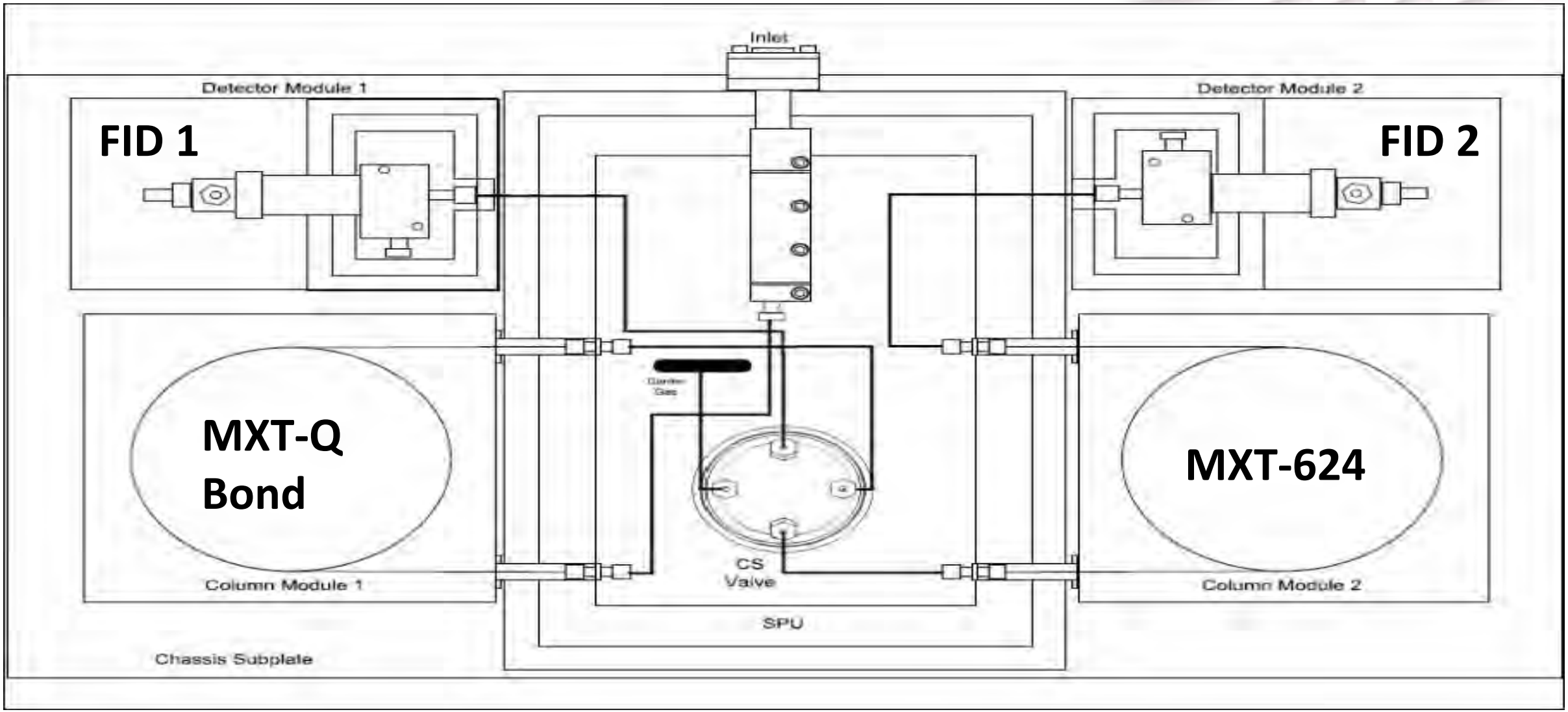
- Automated vial movement & agitation
  - Controlled by XML within Chromperfect data acquisition software
- Pre/post-injection purge
- Fully adjustable injection volume, depth, and speed
- Fully adjustable vial agitation temperature, speed, and duration
- Differences from traditional headspace sampling
  - No vial pressurization
  - Mobile Syringe vs. Stationary Syringe

The CALIDUS CS

- Sample Processing Unit (SPU) – Single Split/Splitless Injector
- Program Temperature Column Modules (PTCMs)
  - Column 1 – 8m MXT-Qbond, 320µm id, 10µm df
  - Column 2 – 8m MXT-624, 250µm id, 1.4µm df
- Detector Modules (DMs) – Flame Ionization
- Column Switching Valve – “Heart-cut” configuration



The CALIDUS CS



Requested Method Parameters

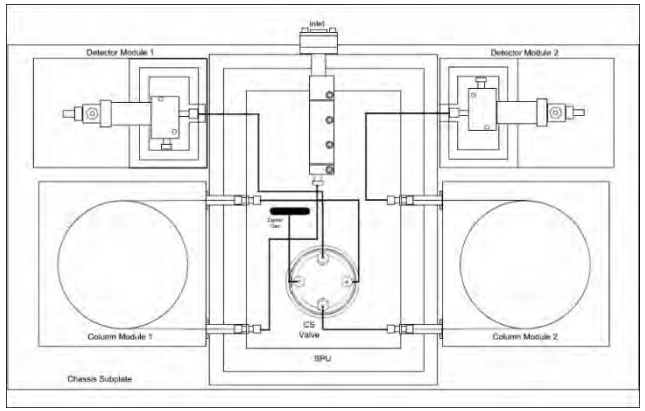
- Headspace Injection
  - Sample Matrix and compound list not conducive for any type of sample preparation.
- Target Analyte List
  - Compounds range from C_1-C_{10}
    - Specific area of interest – C_6 elution range
- Requested Detection Limits – “As Low As Possible”
- GC Run Time - <10min (Traditional run time 45 minutes)

Method Development – Challenges

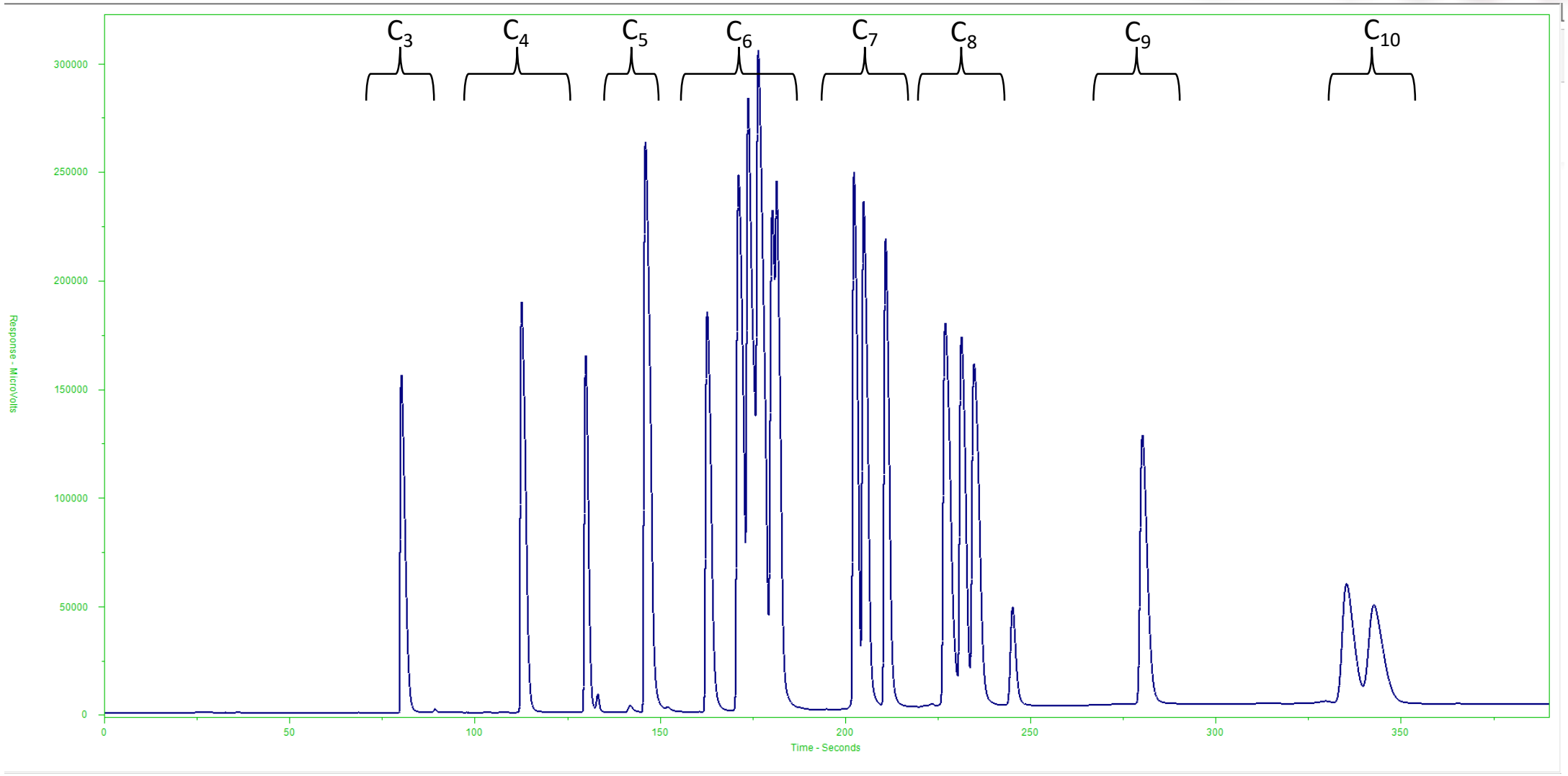
- Target analyte list
  - Comprised of compounds that are in both gas phase and in liquid phase at STP
- Availability of “live” samples
- Provided (liquid phase) standard
  - Mix of alkanes, alkenes, ketones, and alcohols
    - Compound names excluded at customer’s request
  - Contained an unlisted C_6 isomer
  - Most components at 5%, one at 2% and one at 3%
- Secondary standard used to supplement compound list (gas phase components) – Refinery Gas #2 (RFG#2)

Method Development – Phase 1

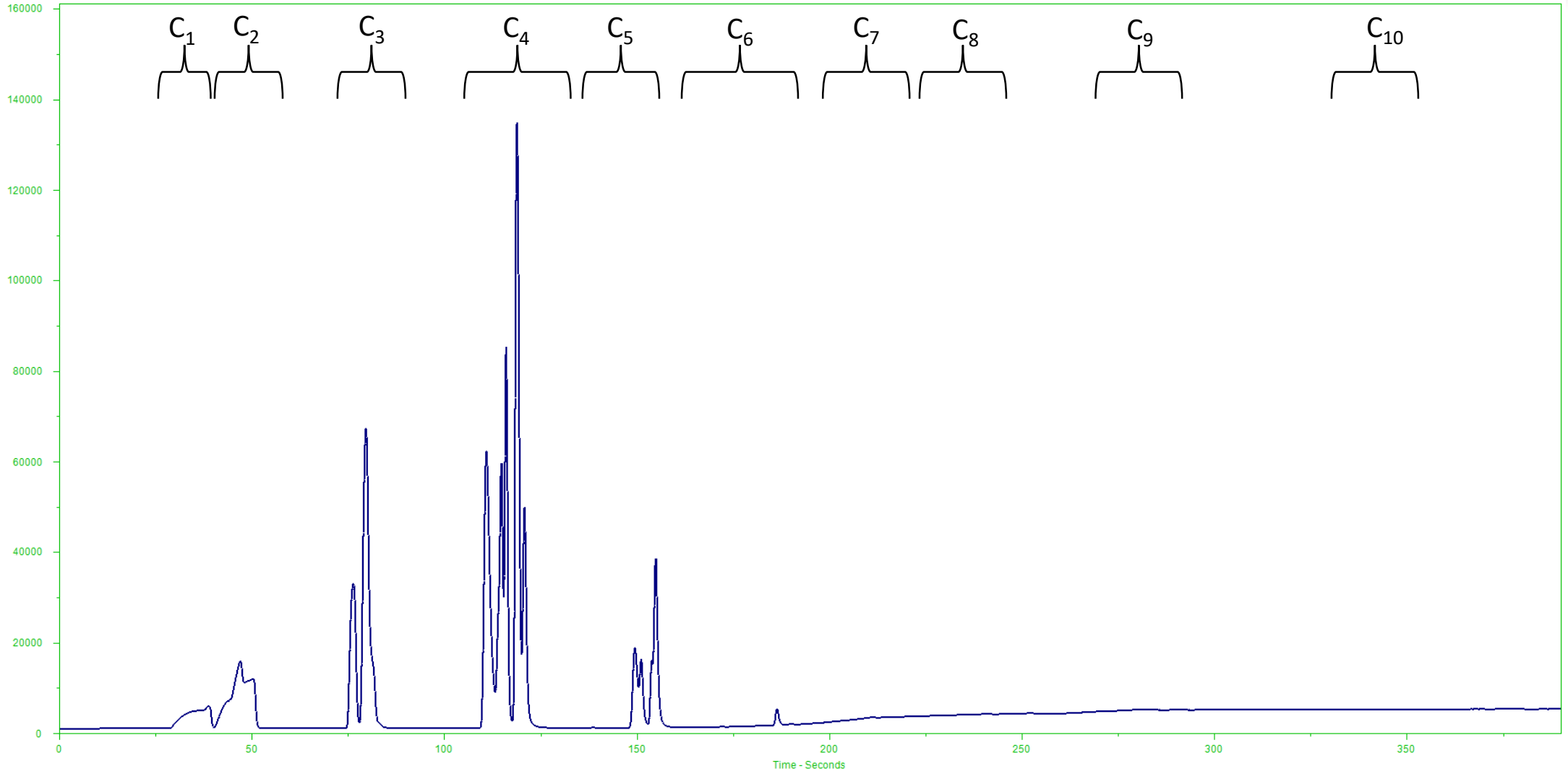
- GC Configuration
  - Due to the requested compound list, Calidus CS in “Heart-Cut” (HC) configuration was selected
  - The C_6 elution region to be HC to the secondary column for additional separation
  - FID DM selected to facilitate detection limit request
- Initial Testing
  - Provided liquid sample, in conjunction with RFG#2 to establish elution order and resolution



Method Development – Phase 1
Liquid Standard Chromatogram – Qbond only



Method Development – Phase 1
RFG#2 Standard Chromatogram – Qbond only

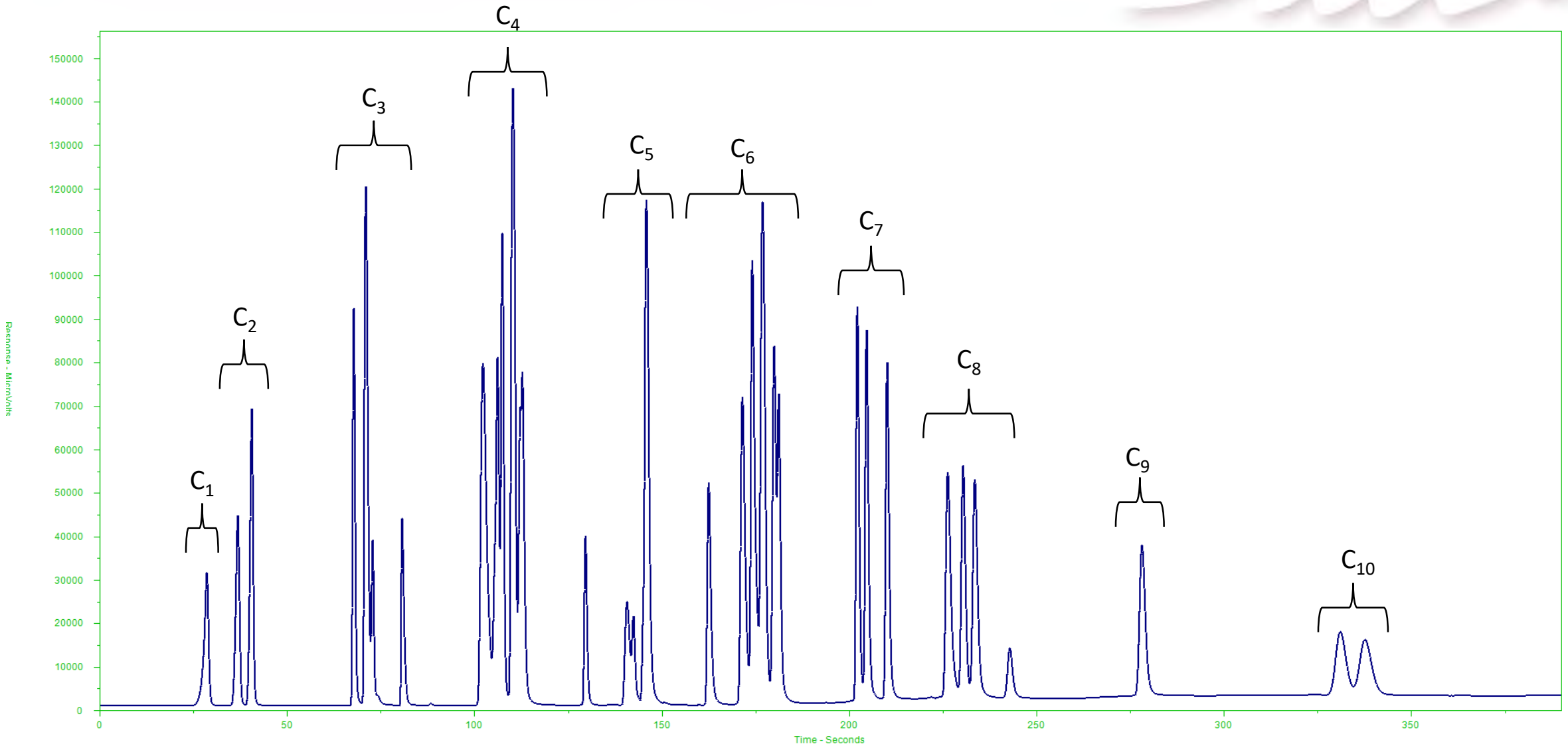


Method Development – Phase 2
Resolution of C_6 region

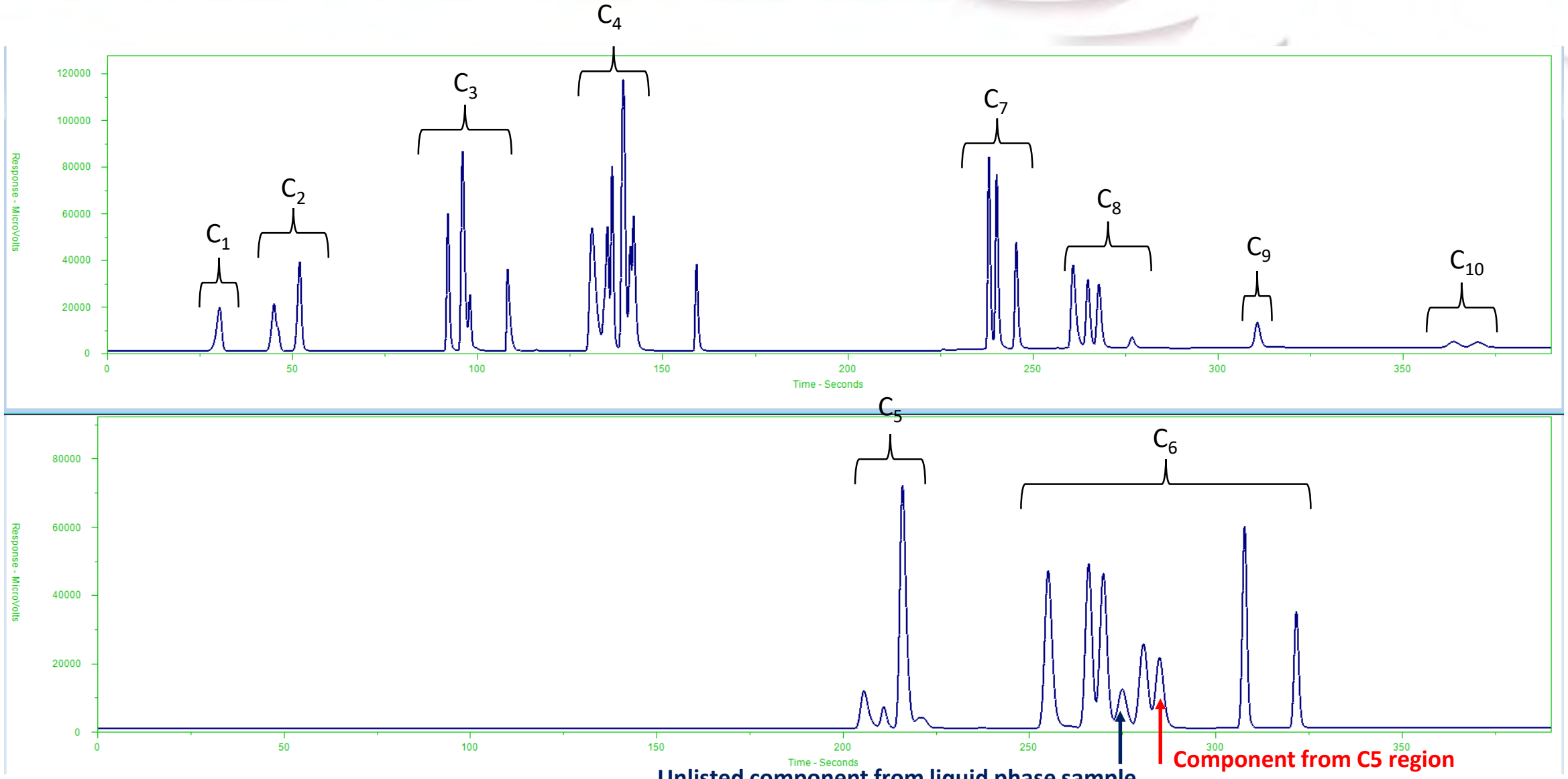
- Elution Times from Qbond used to determine HC window
  - C_6 region HC to MXT-624 to improve resolution
    - MXT-624 run with an independent temperature profile to increase resolving power
    - MXT-624 eluent plumbed to FID #2 (ch. b)

  New Standard created (INT#1)
  - Standard consists of a mix of RFG#2 and Liquid phase sample
  - Components range in concentration from ~100ppm to ~700ppm
  - RFG#2 contains more components than required (specifically in the C_4 region)
    - C_4 region compounds of interest show acceptable resolution
- INT#1 highlighted a need for more resolution of C_5 region
  - C_5 region added to HC window

Method Development – Phase 2
Chromatography – INT#1 on Qbond no HC



Method Development – Phase 2
Chromatography – INT#1 with HC

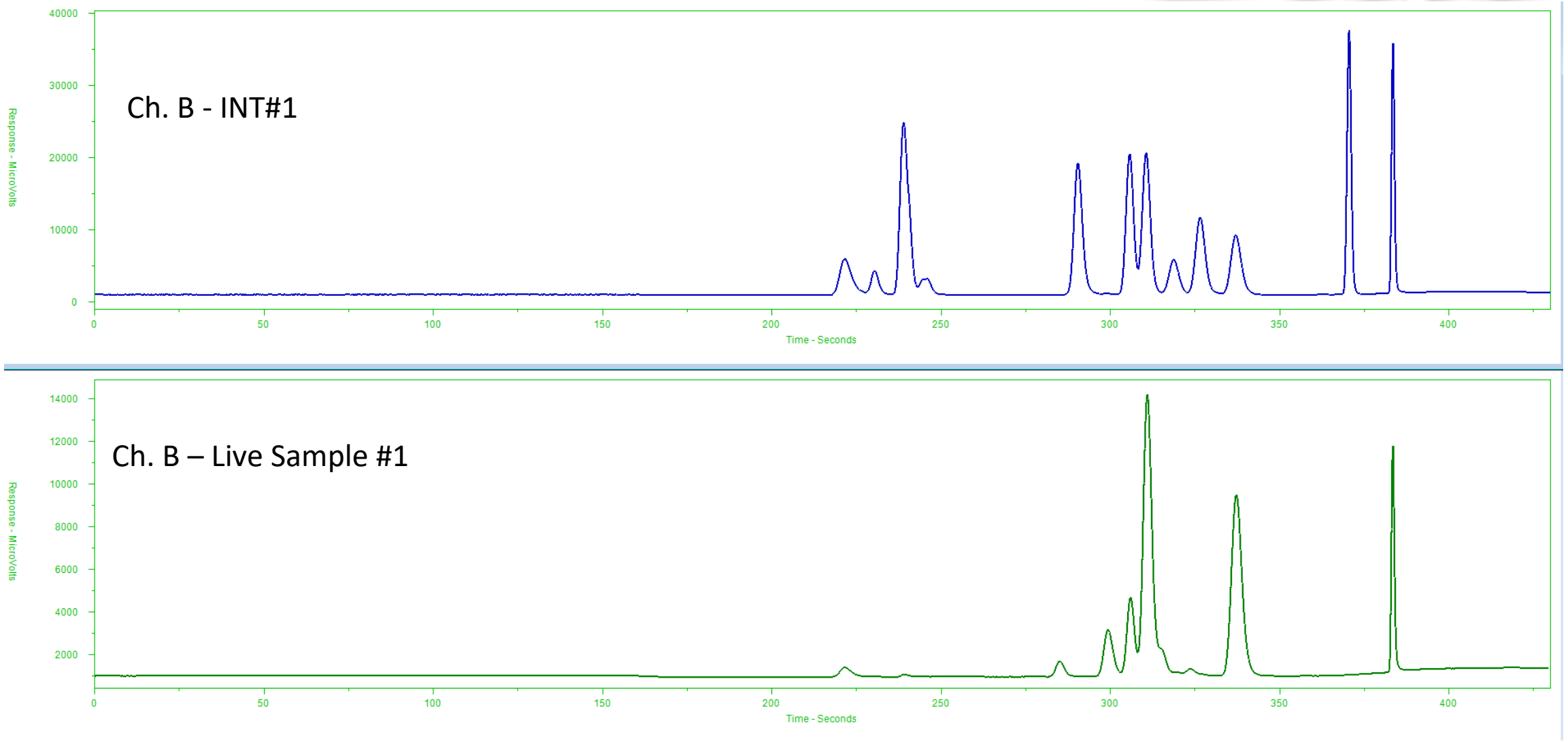


Method Development – Phase 3

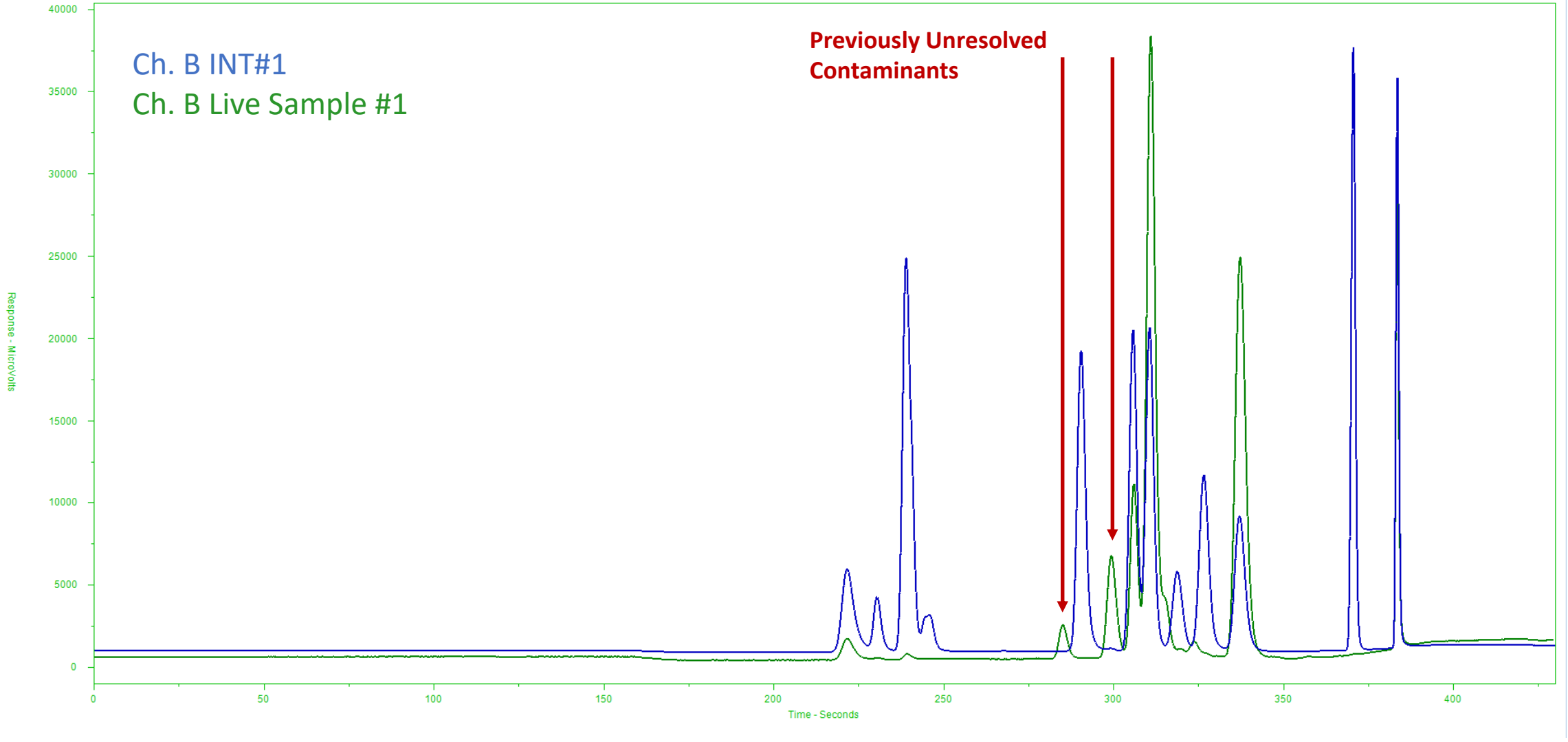
More Resolution for C_6

- C_6 region resolution chromatography
  - Column 2 (MXT-624) temperature ramp profile optimized
  - Pressure profile optimized
- Two previously unresolved contaminants found
  - Compounds were not detected by current analytical method

Method Development – Phase 3
Chromatograms - Stacked



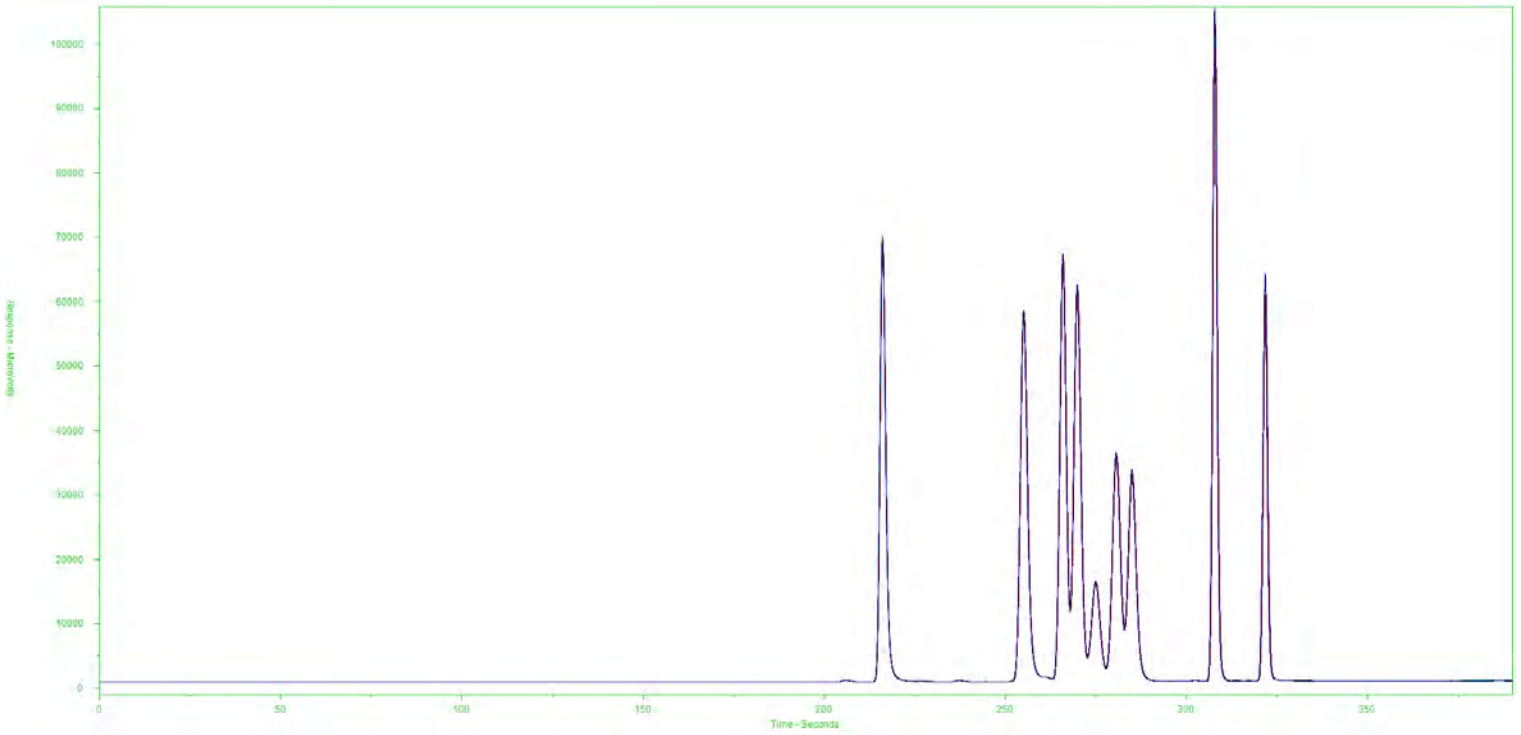
Method Development – Phase 3
Chromatograms - Overlaid



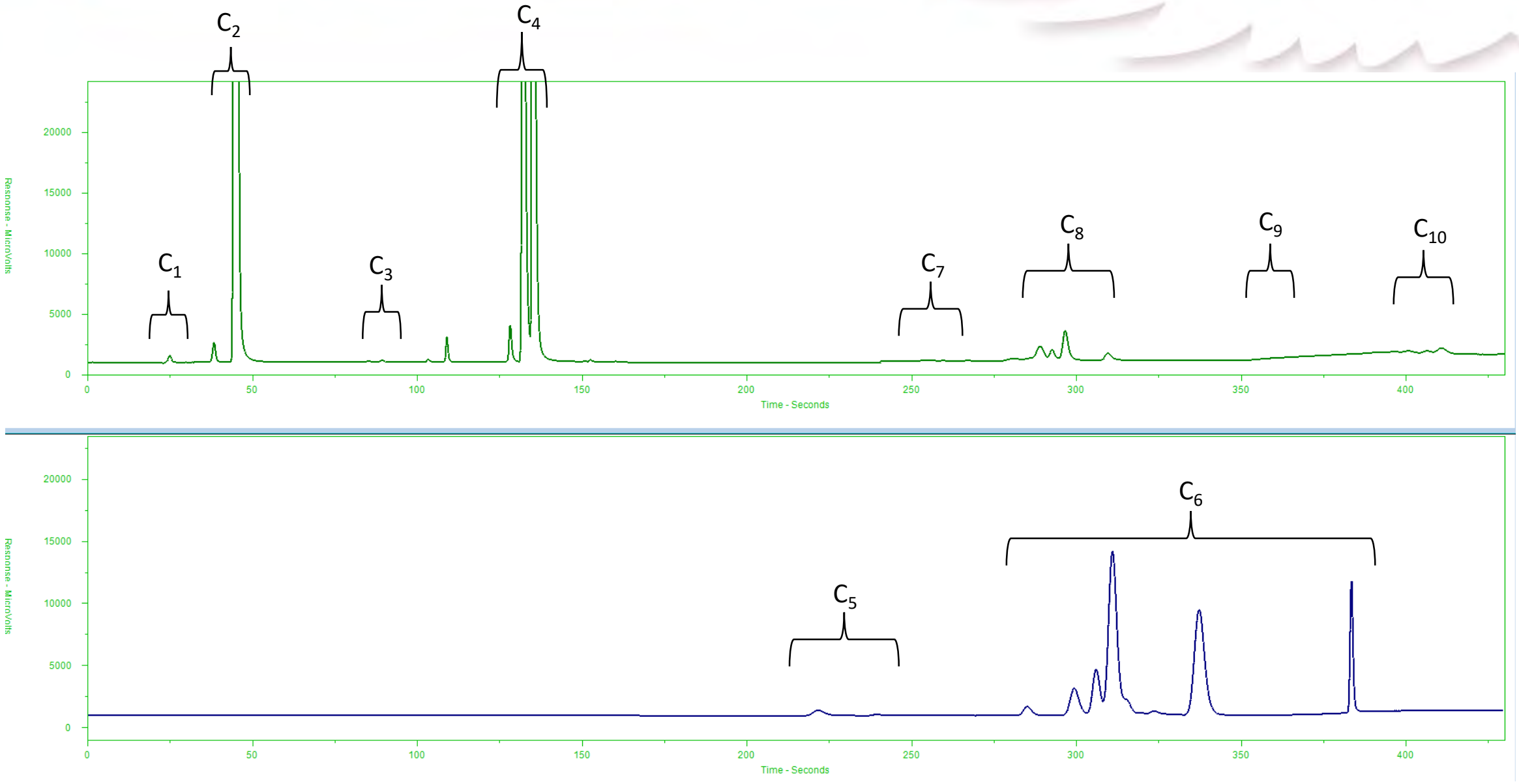
Method Development – Final Testing
Repeatability and Linearity

Channel A		
	Area	Retention Time
Average %RSD	2.9	0.11
Max %RSD	3.8	0.23
Min %RSD	1.2	0.06
Channel B		
	Area	Retention Time
Average %RSD	2.4	0.03
Max %RSD	2.8	0.06
Min %RSD	2.1	0.01

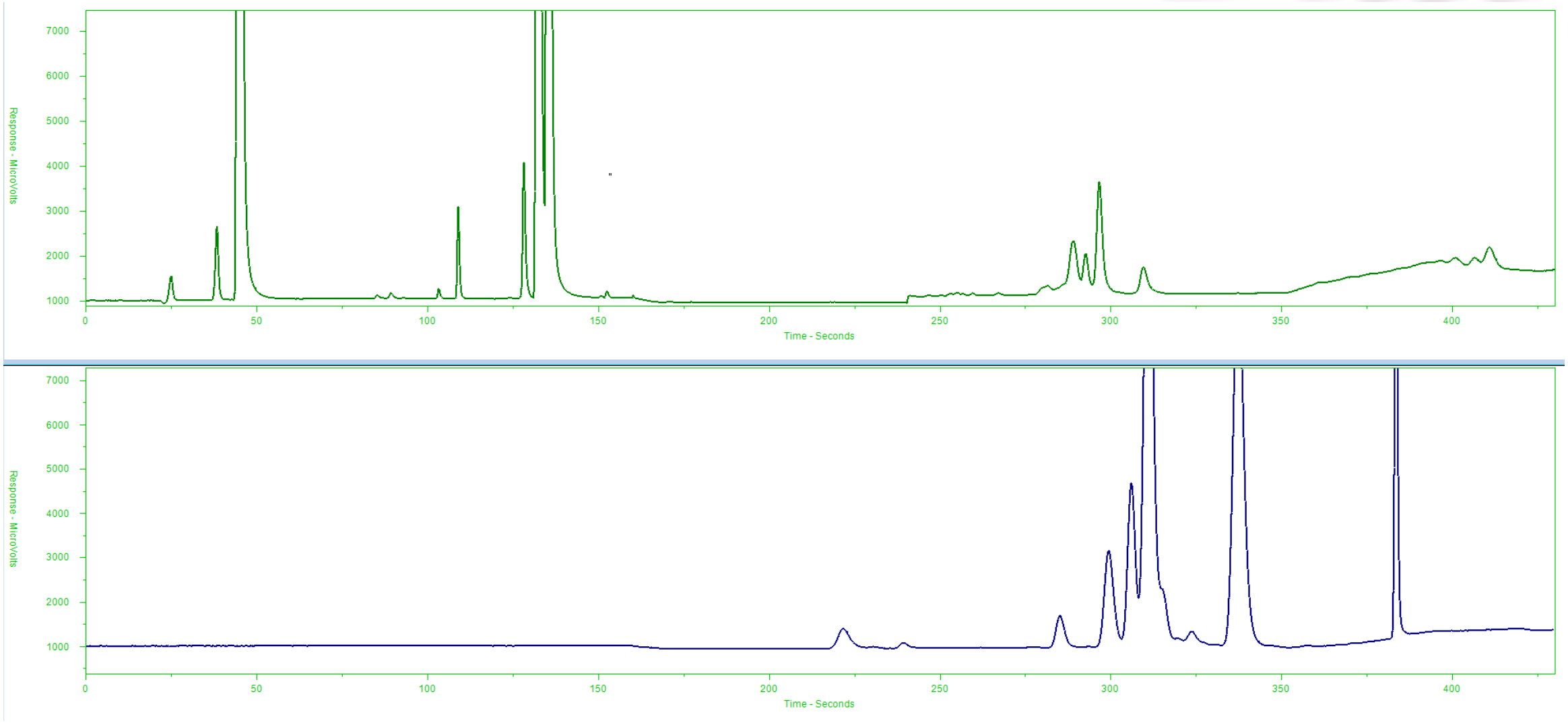
Seven “Live” Sample Runs Overlaid



Method Development – Final Testing
Live Sample #1

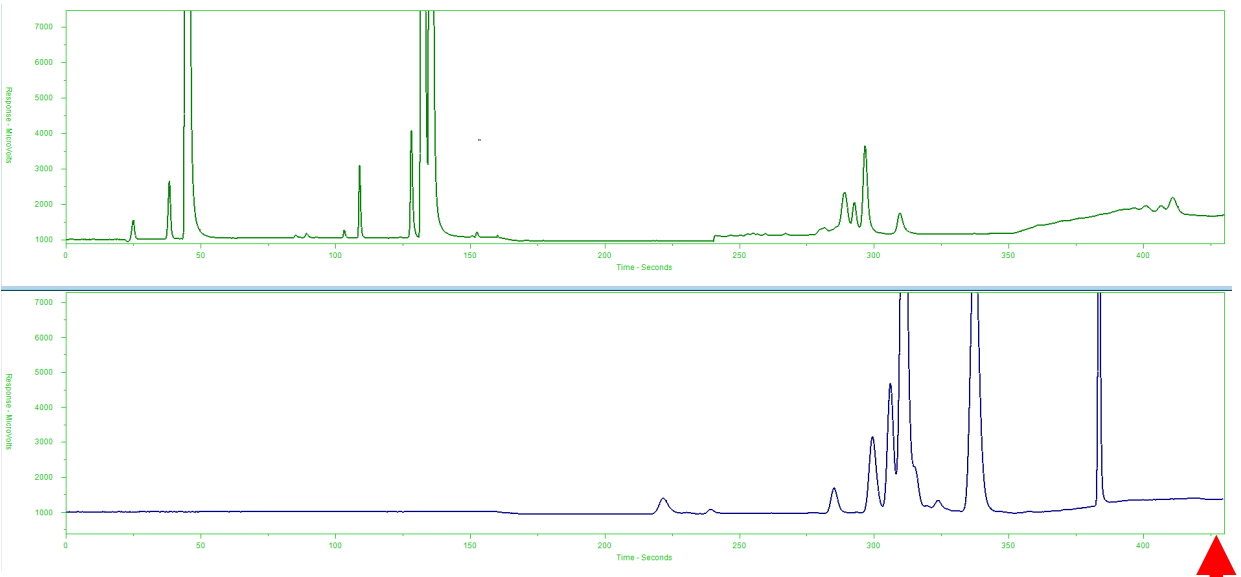


Method Development – Final Testing
Live Sample #1 - Zoomed



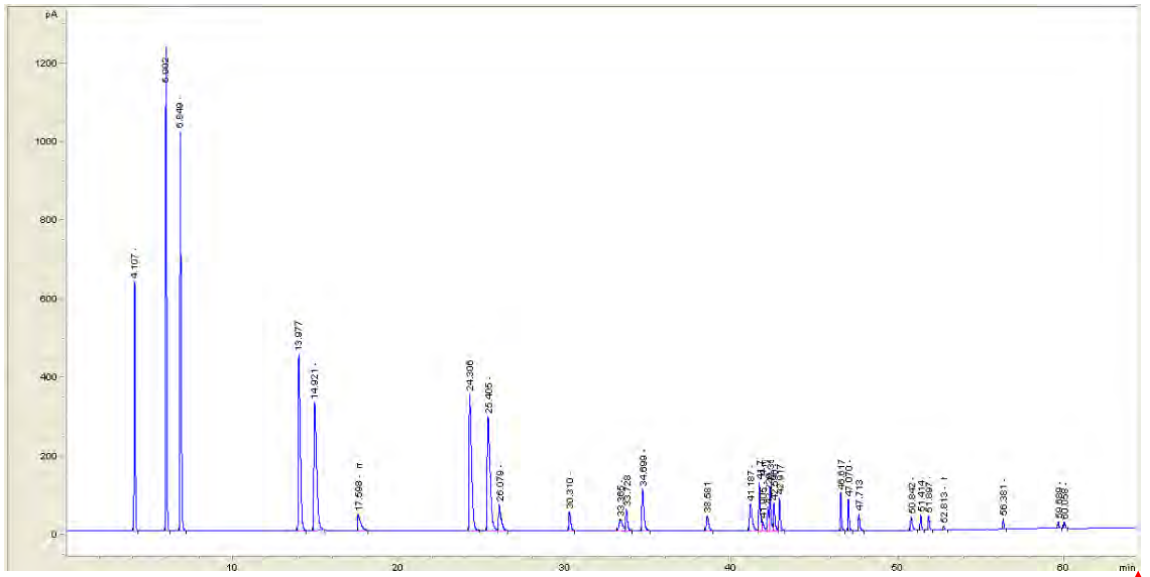
Old Method vs. New Method

New Method



7.5 Minutes

Old Method



64 Minutes

Advantages vs. Traditional Headspace

- Advantages:
  - Versatility
  - Speed
  - Simple, Reliable Design
  - Conserves Benchspace
  - Enables Mobile Headspace Analysis

Other Potential Applications

- Monomers in Polymer Pellets
  - Various
- Ripening Agents in Food Industry Applications
  - Ethylene in Apples
- Residual Solvents in Pharmaceuticals
  - USP, General Chapters Residual Solvents
- Low Boiling Environmental Contaminants in Soil/Water
  - RSK-175 Methane, Ethane, Ethylene in Water
  - SW846 8015 Alcohols in Soil/Water
- And Many More!

Thank You

- Any Questions?
- Matt Holliday
- Chromatography Application Engineer
- Falcon Analytical