

**FALCON**

*ANALYTICAL SYSTEMS & TECHNOLOGY*





# Recent Advances: An Overview of Fast GC, Sensitive GC and Even Simply Faster GC than the Traditional

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## ABSTRACT

Gulf Coast Conference

January 17, 2018

Fast gas chromatography has been deployed “from the winery to the refinery to the wellhead” as previously reported at GCC. The value of rapid response has been demonstrated in the lab, at-line, online and even by the roadside. However, recent applications expand the technology even more to include product purity at the 99.99% plus levels. Environmental applications using both direct injection and pre-concentration trapping have been used to achieve limits of detection downwards from the parts per million level to parts per billion and even parts per trillion. Also, demand for higher resolution capability have been met with longer column possibilities up to 16 meters for a total of 32 meters with two modules. This paper will be a visual overview of the expanded capabilities of fast GC since Gulf Coast Conference 2016.





Definitions:  
Fast Gas  
Chromatography &  
Micro Gas  
Chromatographs



- Fast Gas Chromatography is any GC analysis where the cycle time is at least 10 times faster than the currently accepted state-of-the-art.

Paraphrasing Dr. Jerry Clemons' PhD thesis from long ago

- Micro Gas Chromatograph is any GC where internal volumes are measured in microns, not millimeters and cycle times are measured in seconds, not minutes.

Proposed by Falcon during ASTM D7798 standard method development

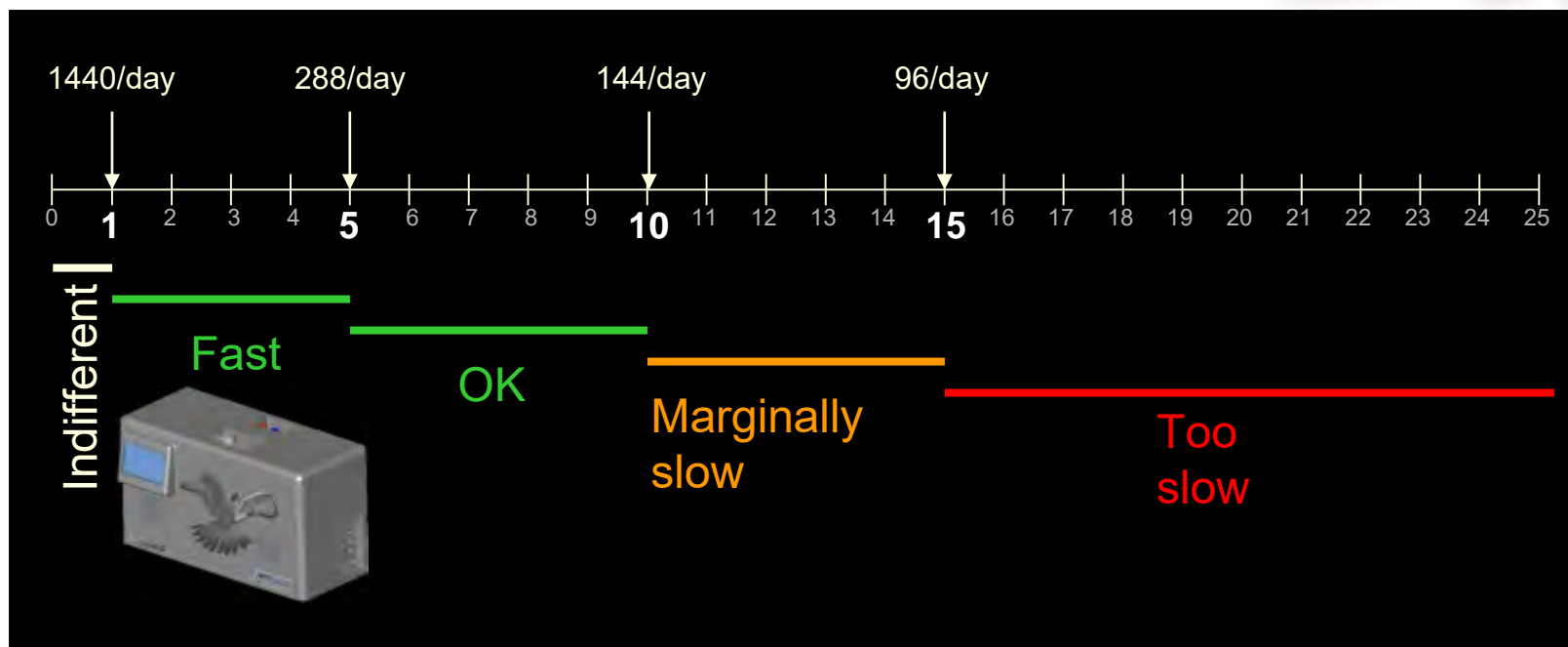
- These definitions are not mutually exclusive
  - Lower dead volume & thermal mass allow shorter columns with acceptable resolution and

**SPEED**

# Speed, Selectivity, Sensitivity

It is a balancing act.

easier, smaller,  
**faster**, smarter,  
and greener

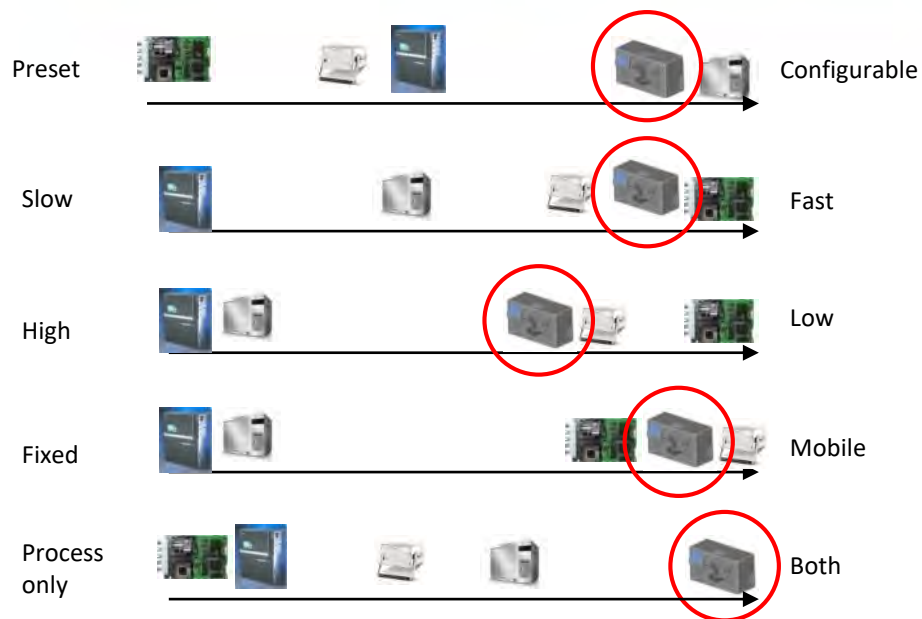


If we are really going to use GC for **control**, speed means under 10 minutes for most applications.

*Poll of Process Users*



# Technology Positioning



*Flexibility*

*Speed*

*Power consumption*

*Portability*

*Suitable for lab and process*



*Speed of Analysis (use to control the process)*  
*Application Coverage (common instrument platform)*  
*Form Factor (size, weight, footprint)*  
*Cost (price, maintenance, periphery)*

The applications flexibility combined with a more-compact footprint allows Falcon to occupy a middle ground and appeal to laboratory, process and the transportable crowd.

CALIDUS™  
Intellectual  
Property



US08414832B1

**(12) United States Patent**  
Roques et al.

**(10) Patent No.:** US 8,414,832 B1  
**(45) Date of Patent:** Apr. 9, 2013

**(54) FAST MICRO GAS CHROMATOGRAPH SYSTEM**

**(70) Inventor:** Ned Roques, Lewisburg, WV (US); John Crandall, Lewisburg, WV (US)

**(\*) Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 369 days.

**(21) Appl. No.:** 12/888,783  
**(22) Filed:** Sep. 8, 2009

**Related U.S. Application Data**

**(60) Provisional application No. 61/095,075, filed on Sep. 8, 2008.**

**(51) Int. Cl.:** G01N 30/02 (2006.01); G01N 30/54 (2006.01)  
**(52) U.S. Cl.:** 422/89; 73/23.39; 73/23.4; 96/102; 96/106

**(56) Field of Classification Search:** 422/701; 422/89; 73/23.39; 23.4; 61.53; 61.57; 61.58; 95/87; 96/102; 100; 210/108.2  
See application file for complete search history.

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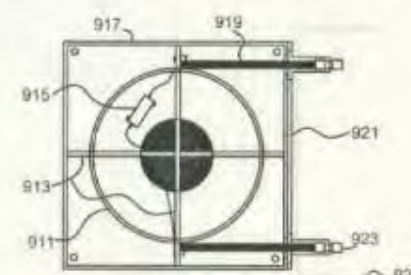
WO 02/08748	A1	6/1992	
WO 93/2008	A1	3/2008	

**(74) Attorney, Agent, or Firm:** Sheldon H Parker, Esq.

**(57) ABSTRACT**

The invention is a chromatography apparatus which comprises at least one capillary column, which has a coil assembly of column material and a small diameter wire coated with an electrically insulating high temperature material encased within a high temperature sheath. The small diameter wire is at least one electrically conductive element co-linear with the column material. Also provided is means for directly resistively heating the at least one capillary column, and means for controlling the temperature of the capillary column. Additionally, the apparatus includes an oxygen gas generating inlet, a hydrogen inlet, an analyte port and a flame region, oxygen delivery means for delivering oxygen through the oxygen inlet to the flame region, a hydrogen and analyte delivery system for delivering hydrogen and analyte to the flame region, and a detector arranged in series flame exit.

**21 Claims, 8 Drawing Sheets**



US08336366B2

**(12) United States Patent**  
Roques et al.

**(10) Patent No.:** US 8,336,366 B2  
**(45) Date of Patent:** Dec. 25, 2012

**(54) TRANS-CONFIGURABLE MODULAR CHROMATOGRAPHIC ASSEMBLY**

**(75) Inventors:** Ned Roques, Lewisburg, WV (US); John Crandall, Lewisburg, WV (US)

**(73) Assignee:** Falcon Analytical, Lewisburg, WV (US)

**(\*) Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 365 days.

**(21) Appl. No.:** 12/817,137  
**(22) Filed:** Jun. 16, 2010

**(65) Prior Publication Data**  
US 2010/0256922 A1 Oct. 7, 2010

**Related U.S. Application Data**

**(63) Continuation-in-part of application No. 12/555,783, filed on Sep. 8, 2009.**

**(60) Provisional application No. 61/095,075, filed on Sep. 8, 2008.**

**(51) Int. Cl.:** G01N 30/02 (2006.01)  
**(52) U.S. Cl.:** 73/23.39  
**(58) Field of Classification Search:** 73/23.39  
See application file for complete search history.

**(56) References Cited**

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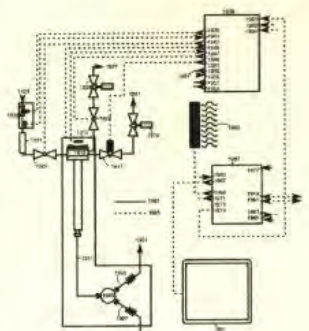
**(\*) cited by examiner**

**Primary Examiner** — Hezron E Williams  
**Assistant Examiner** — Rodney T Frank  
**(74) Attorney, Agent, or Firm** — Sheldon H. Parker, Esq.

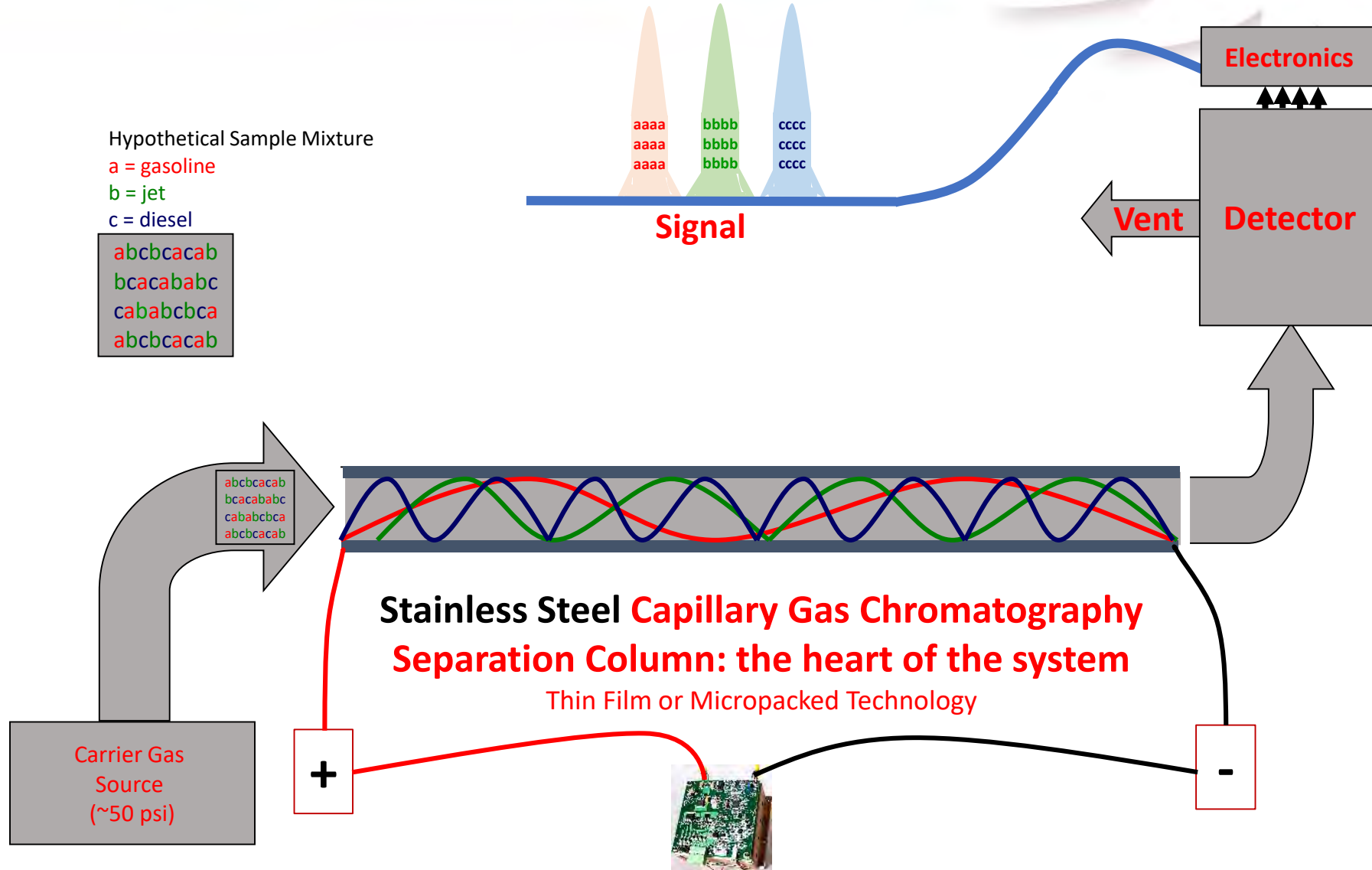
**(57) ABSTRACT**

A trans-configurable modular chromatograph assembly is provided with a core unit, at least one column module, and at least one detector module. The core unit includes a controller module having a first computer processing unit, an analogue to digital signal converter, and a thermally insulated enclosure. The enclosure includes a first heater member positioned to heat the thermally insulated first enclosure housing, a first analyte stream inlet, and a first analyte stream conduit. A temperature controller is programmed to maintain the thermally insulated first enclosure at a uniform temperature throughout an analysis. The at least one column module includes a computer processor, means for releasably securing the core unit to a column module, a capillary column, a capillary column heater member, and means for sensing and controlling the temperature of the capillary column. The capillary column has an analyte outlet member in fluid communication with at least one detector module. The at least one detector module has a computer processing unit, and an analogue to digital signal converter, means for releasably securing said core unit to the detector module. The detector module includes detector member within a thermally insulated enclosure.

**15 Claims, 9 Drawing Sheets**

# How does CALIDUS Ultrafast GC work?



# The Calidus Modular GC System



- Sample Processing Module

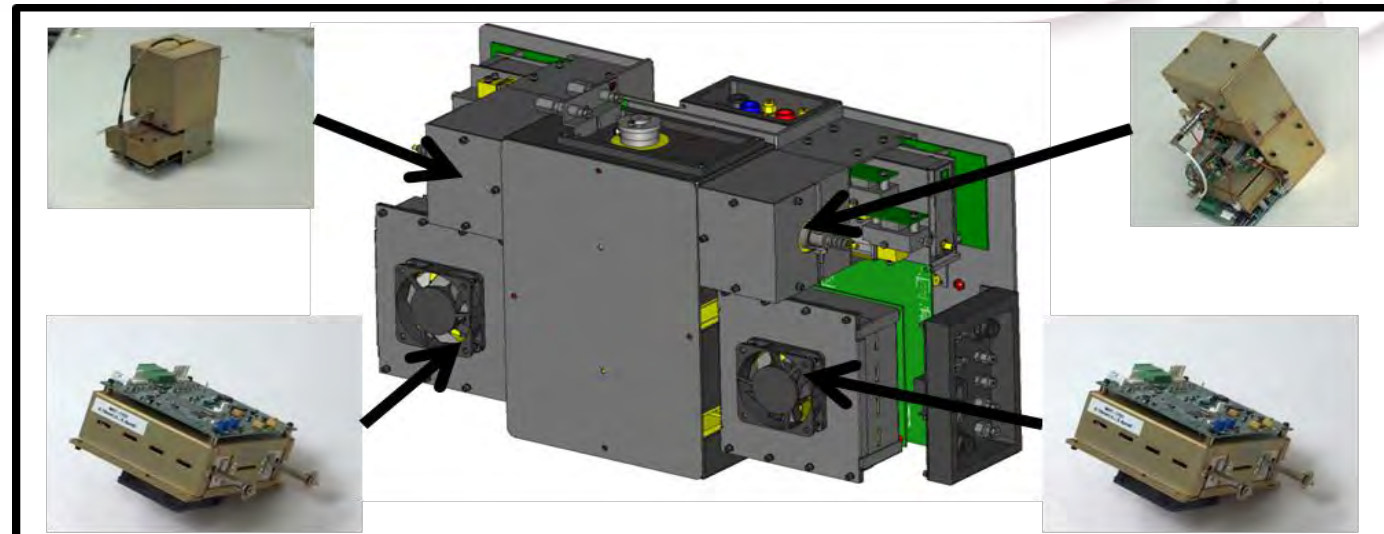
- Split/splitless injector
- Septum purge
- Inlet glass liner
- Column switching

- Column Modules

- **2 – 16** meters for **32** meters total
- 180 – 530 micron ID
- Various film thickness
- Even micropacked available

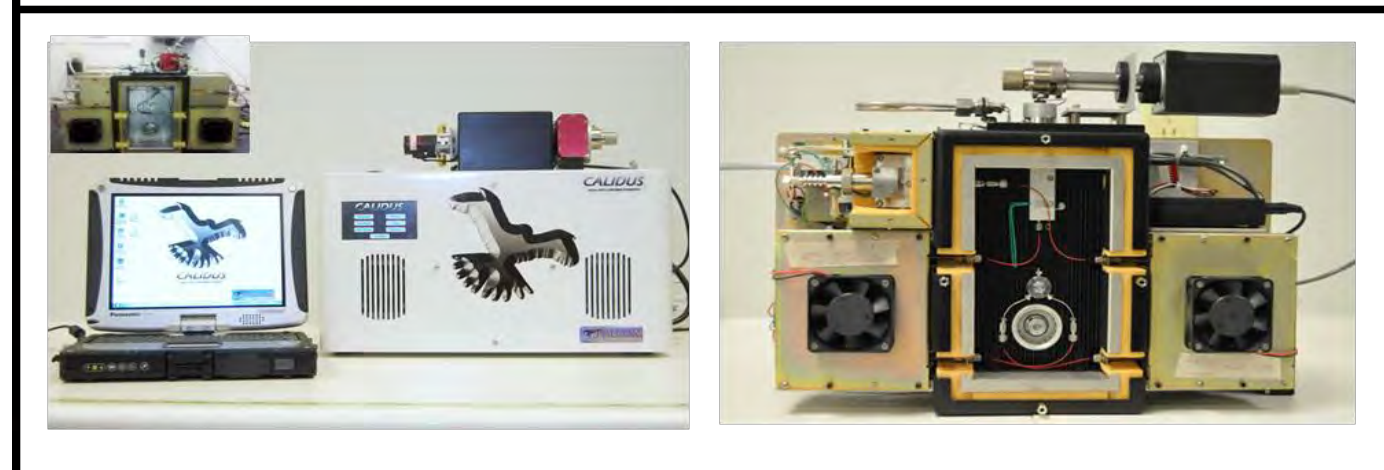
- Detectors

- Flame Ionization
- Thermal Conductivity
- Flame Photometric
- Dielectric Barrier Discharge with Helium Ionization, Electron Capture & Photo Ionization modes



Swappable  
Choice of  
Detectors

Choice of  
Columns



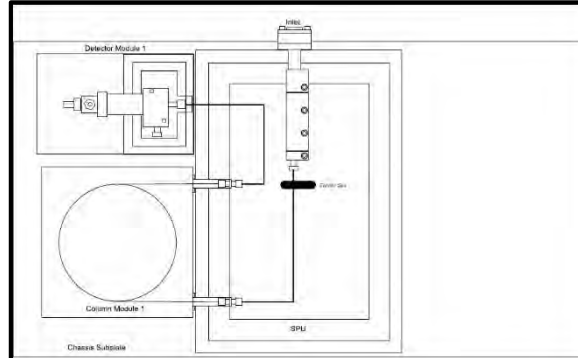
Flowing Gas  
or Liquid  
Sample GC  
System



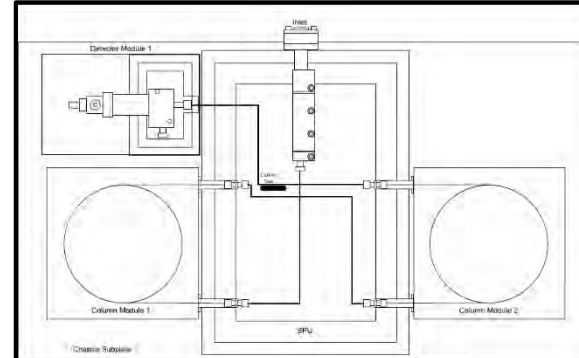
# Modules Combined into Instrument **Models**

## CALIDUS™ Modular, Ultrafast GC Systems

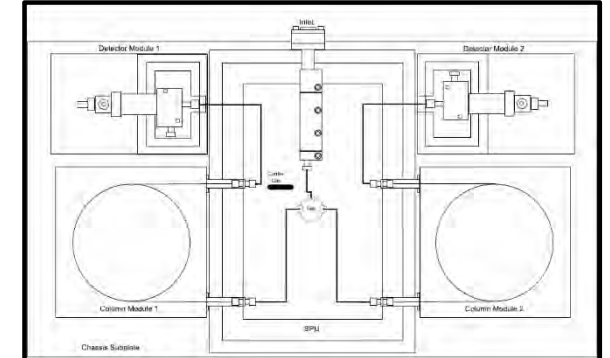
Single Split/Splitless  
Injectors with  
Septum Purge



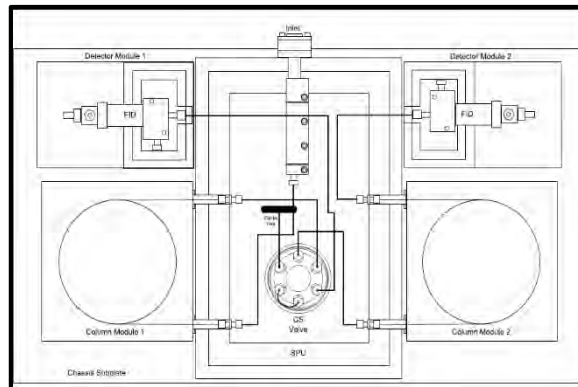
101 – single column 2m – 16m,  
single detector



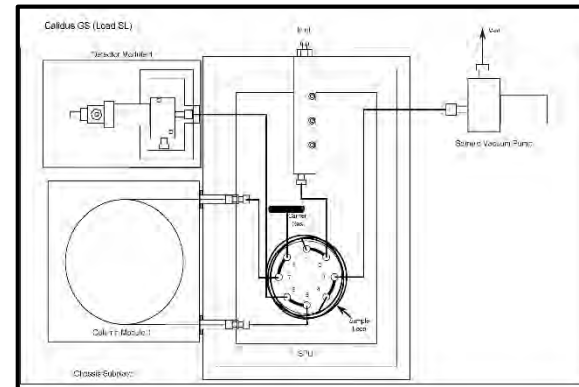
201 – single column 4m – 32m,  
single detector in series



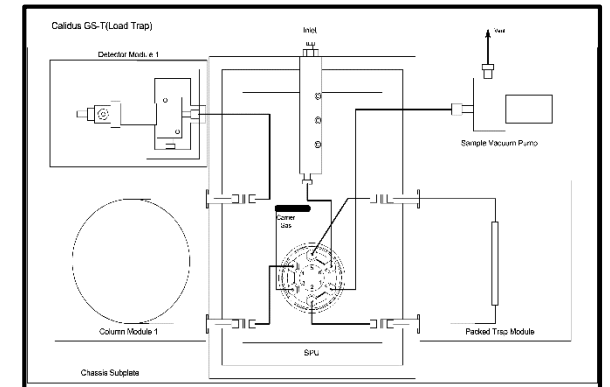
301 – dual column 2m – 16m, dual  
detector in parallel



CS– dual column 2m – 16m, dual  
detector with column switching  
valve, up to 32 meters total



GS – single column 2m – 16m, with  
large sample loop, single detector  
with sample pump



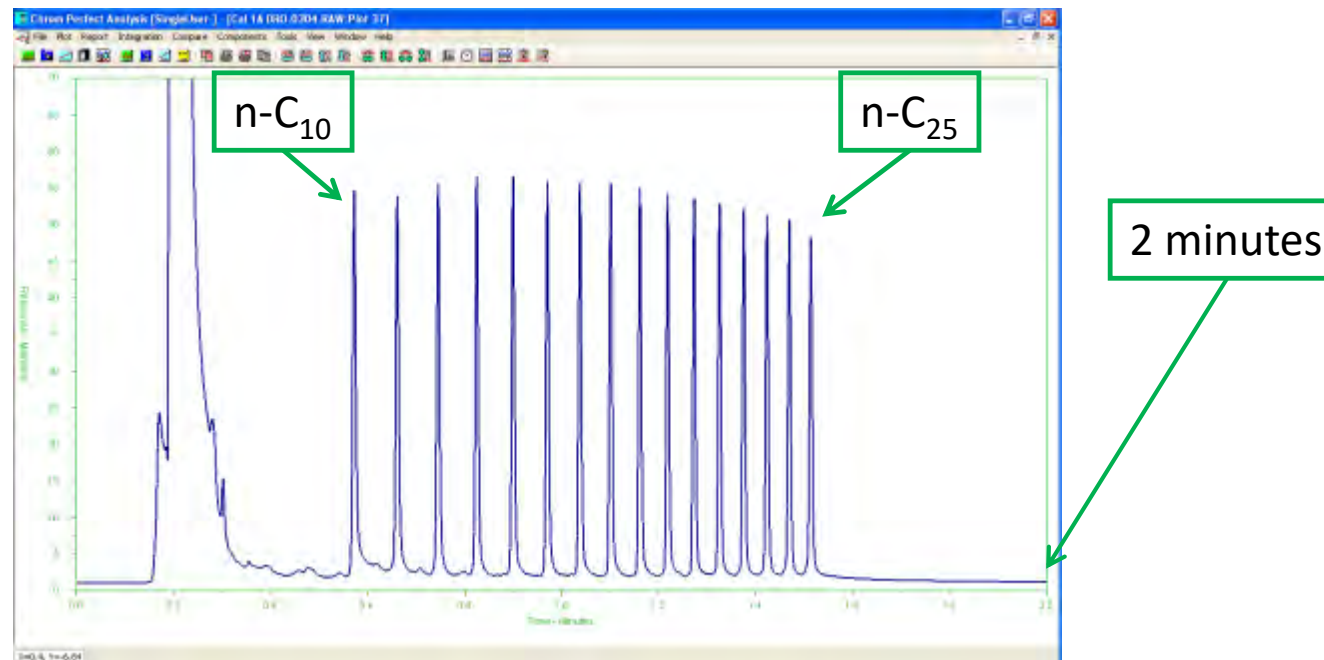
GS-T – single column 2m – 16m,  
with preconcentration trap, single  
detector with sample pump

**New**

**New**

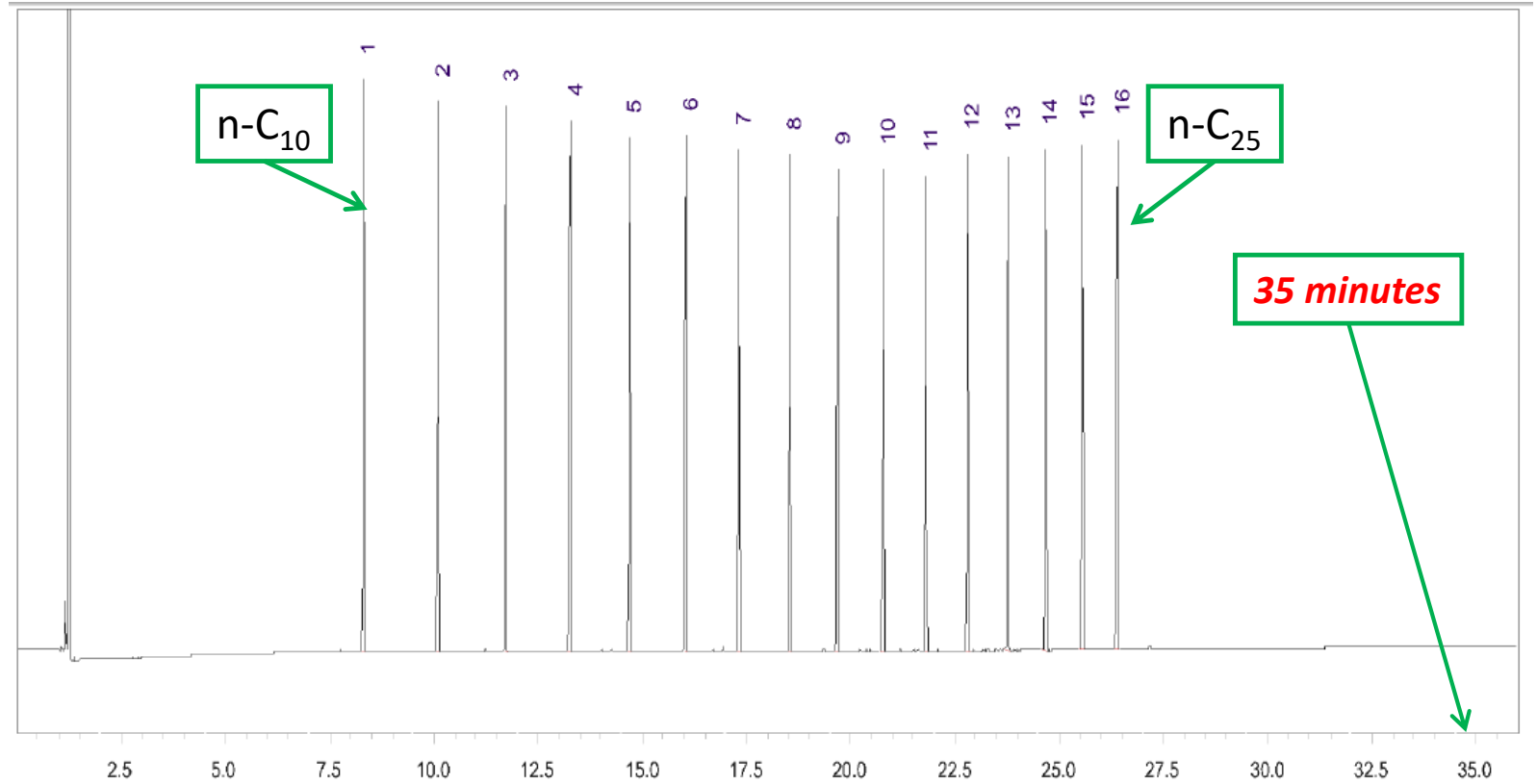
# Fast!

- Calibration standard for DRO method
- Small molecules (low boiling point) elute earlier (left), in this case starting with decane ( $n\text{-C}_{10}$ ).
- Large molecules (high boiling point) elute later (right), here ending with pentadodecane ( $n\text{-C}_{25}$ )



Chromatogram  
Shipped with n-C<sub>10</sub>  
to n-C<sub>25</sub> Alkanes  
Calibration Sample  
(Agilent GC)

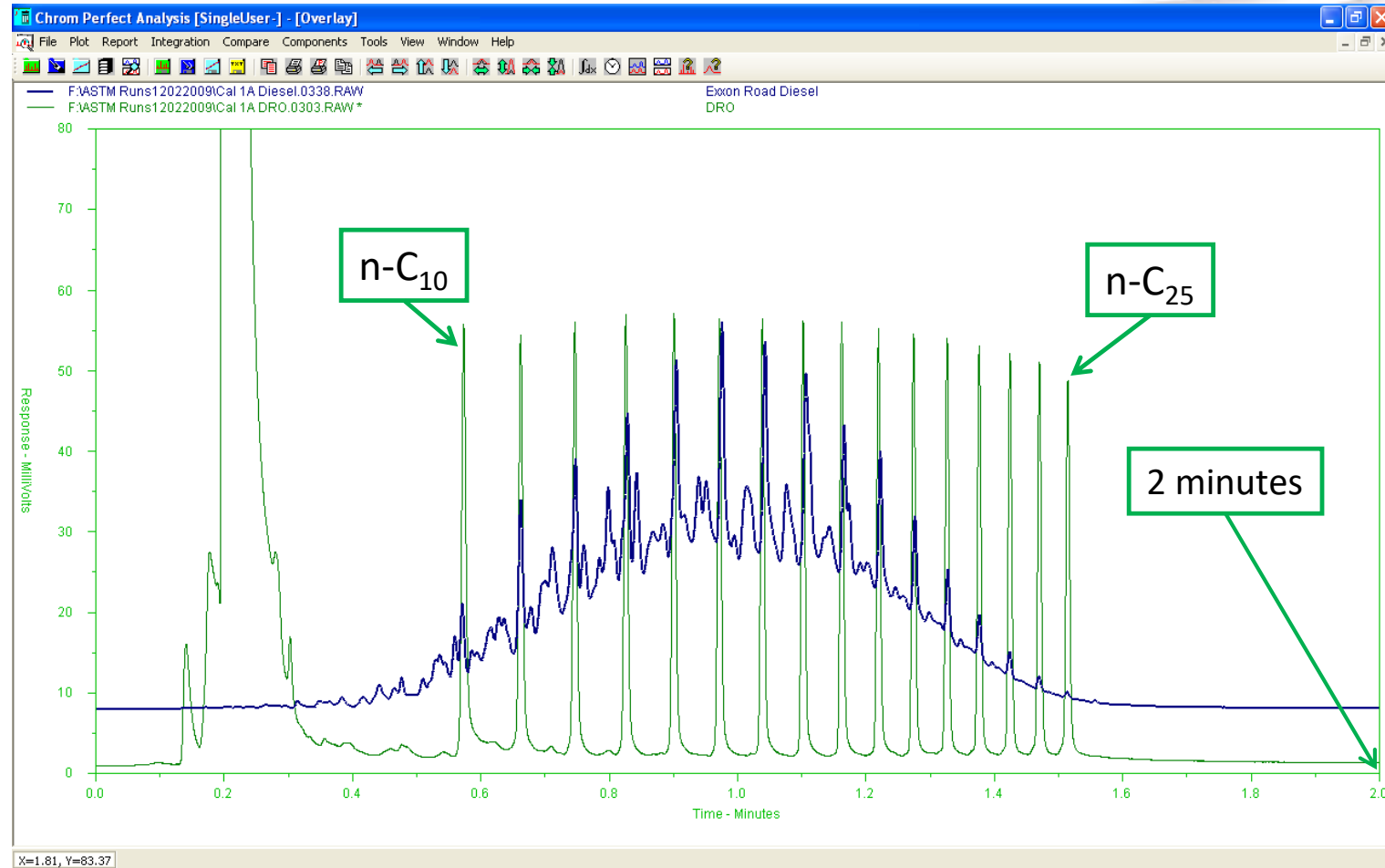
## Chromatogram Shipped with n-C<sub>10</sub> to n-C<sub>25</sub> Alkanes Calibration Sample (Agilent GC)



Retention Time in **Minutes**



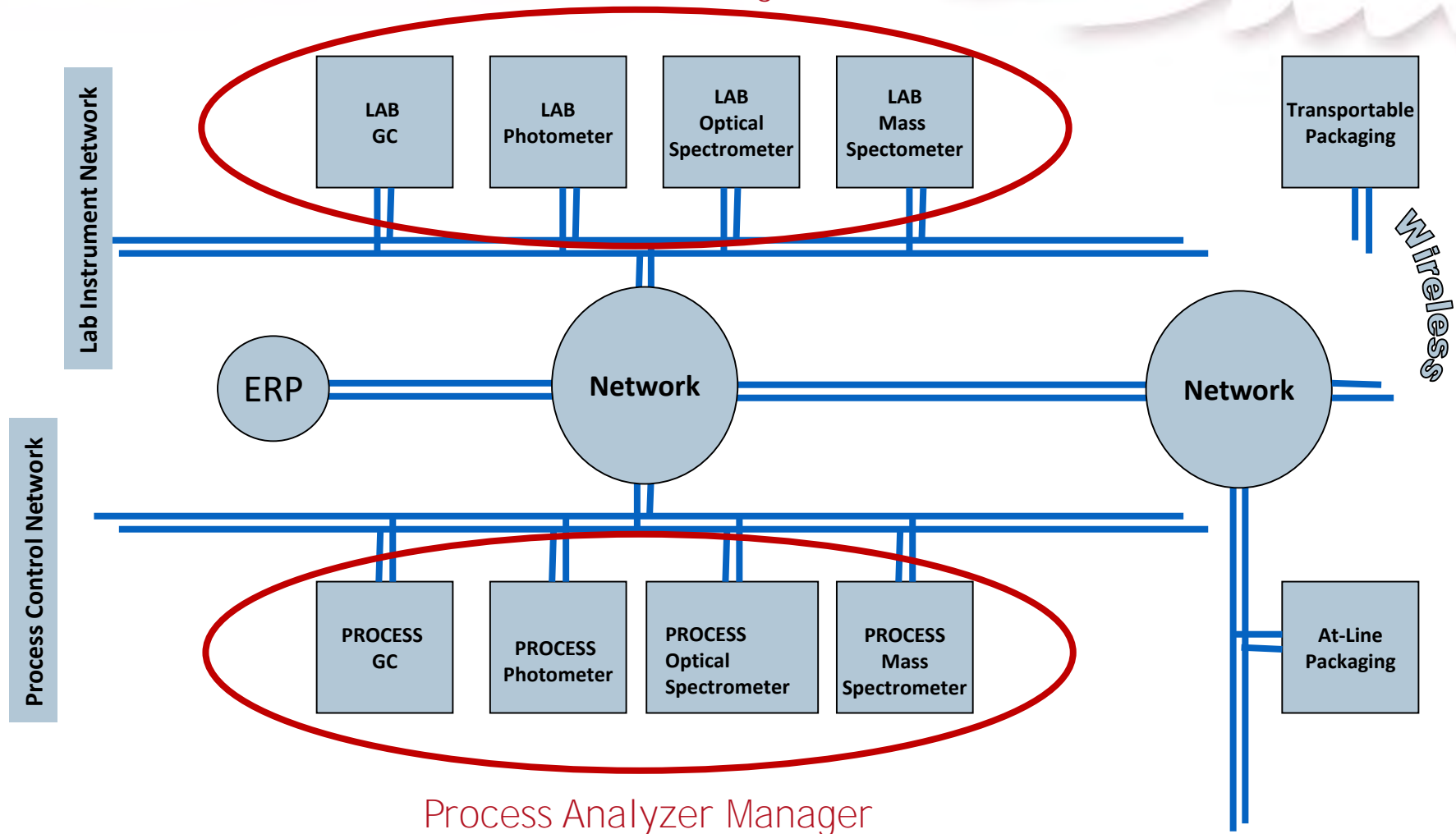
# ExxonMobil Road Diesel Overlaid n-C<sub>10</sub> to n-C<sub>25</sub> Alkanes



# Modern Processing Plant Architecture

Plant Lab Manager

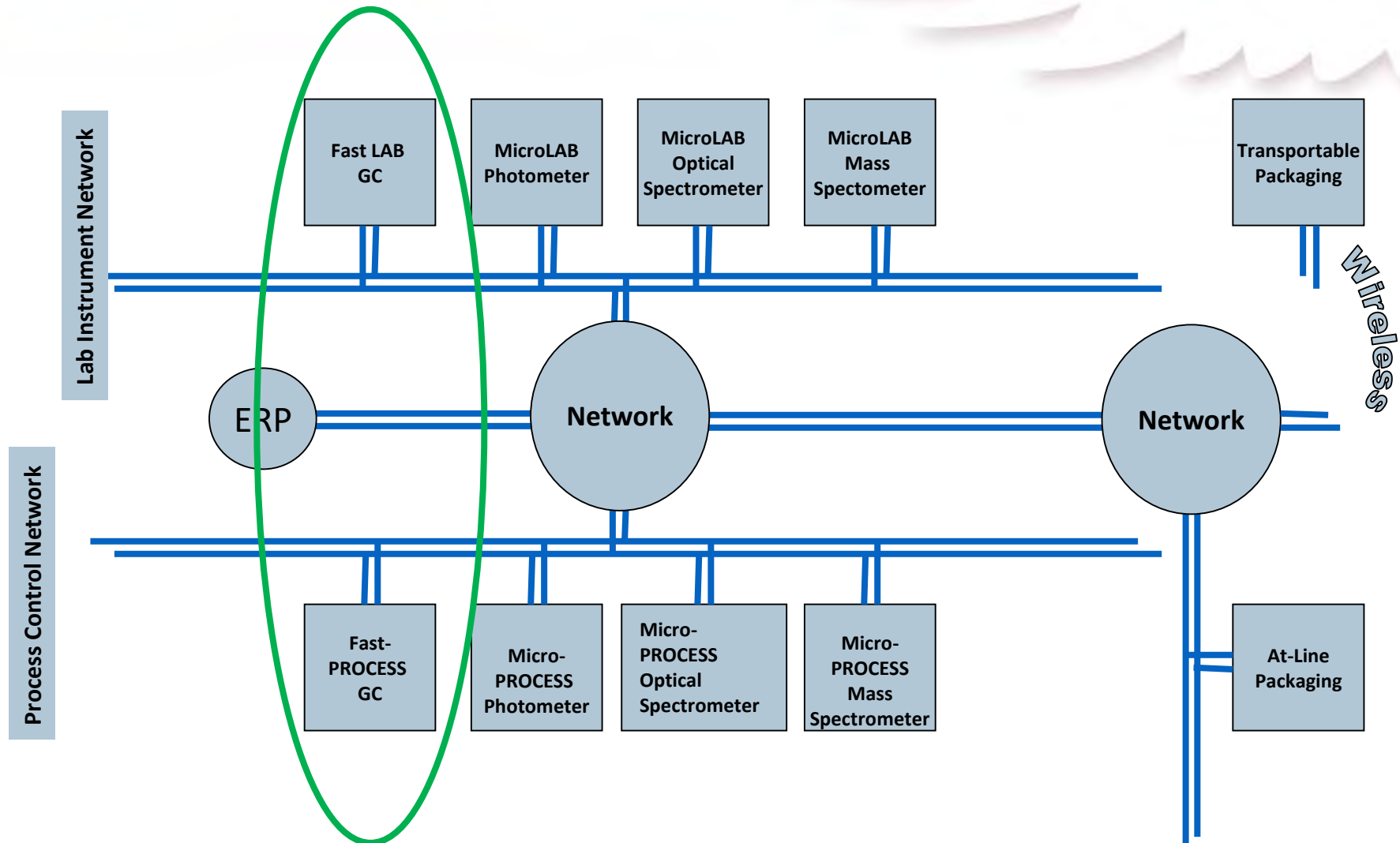
Old School



Process Analyzer Manager

# Modern Processing Plant Architecture

New Thinking,  
**ONE** manager for  
lab and process  
analysis.



Modules Make  
Instruments,  
Instruments Make  
Analyzers  
Analyzers Make System  
Solutions...

**One Solution**



# Broad Based Deployment of CALIDUS

It's just a GC... a small, very fast, extremely capable GC.

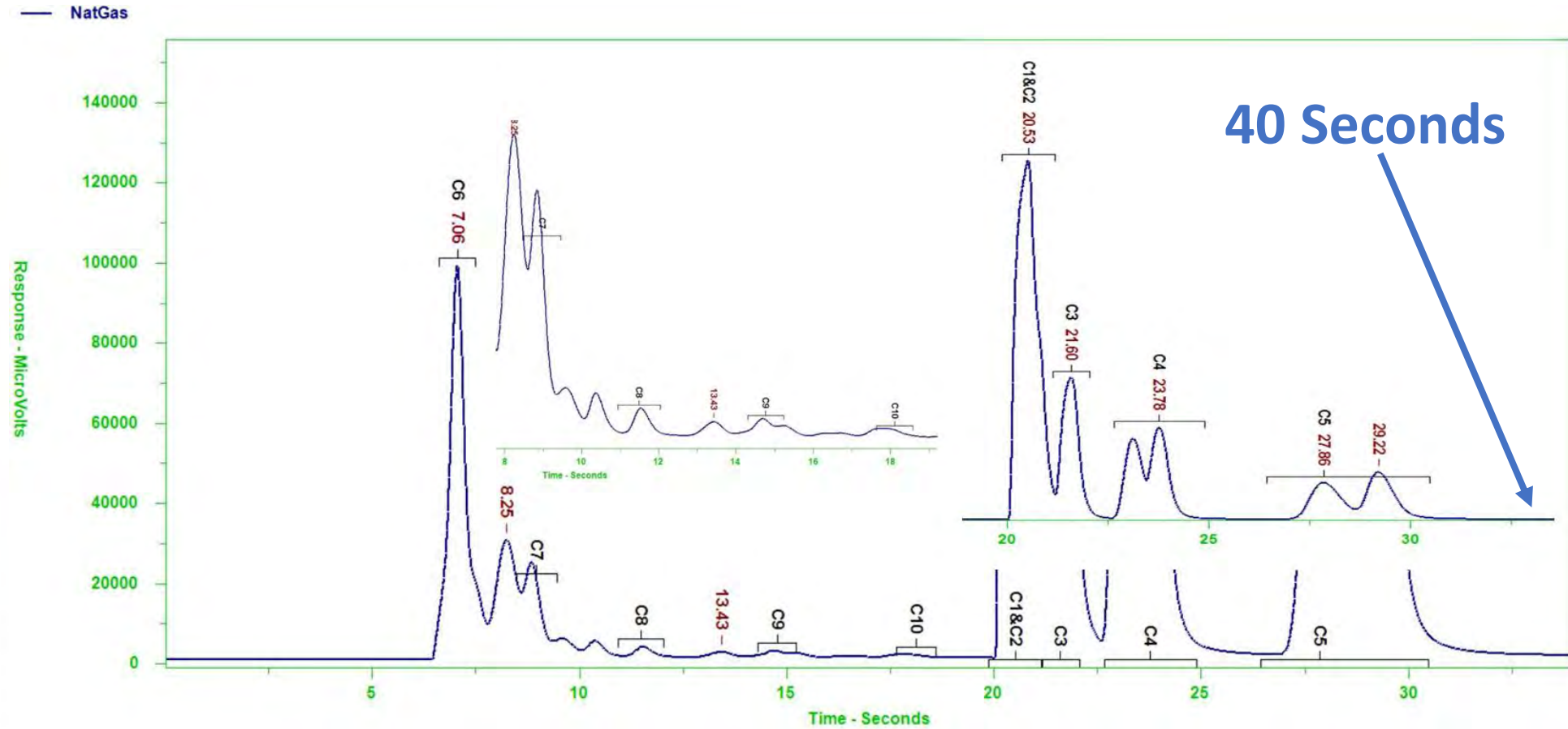






**FAST**

Hydrocarbons  
C<sub>1</sub> & C<sub>2</sub> to  
n-C<sub>10</sub>





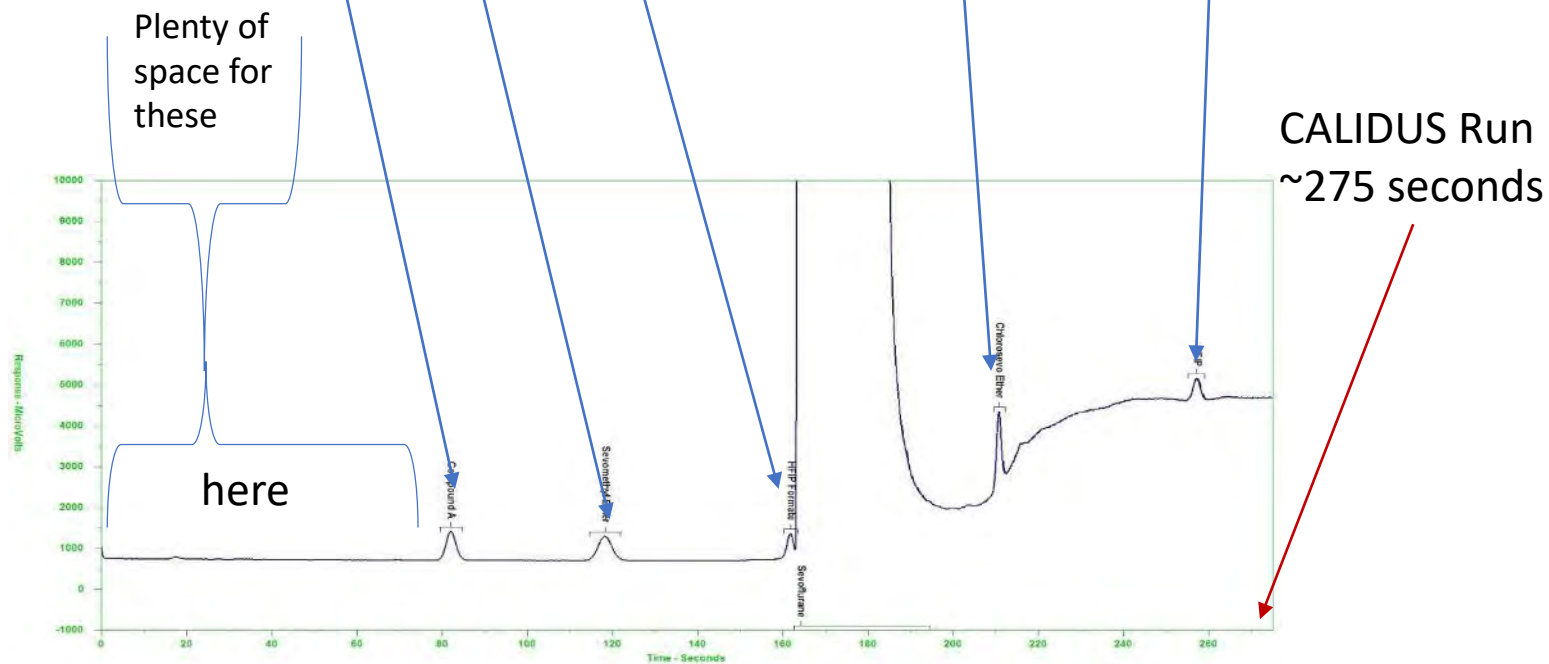
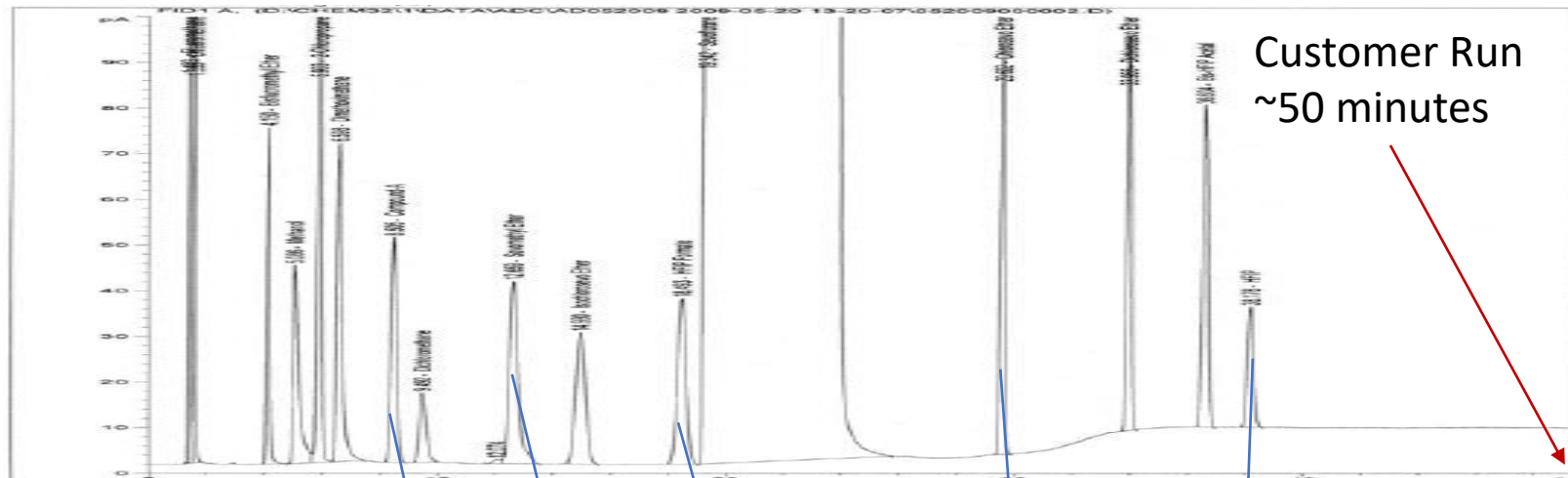
**FAST**

Pharmaceutical  
Applications

Anesthetics and residual  
solvents

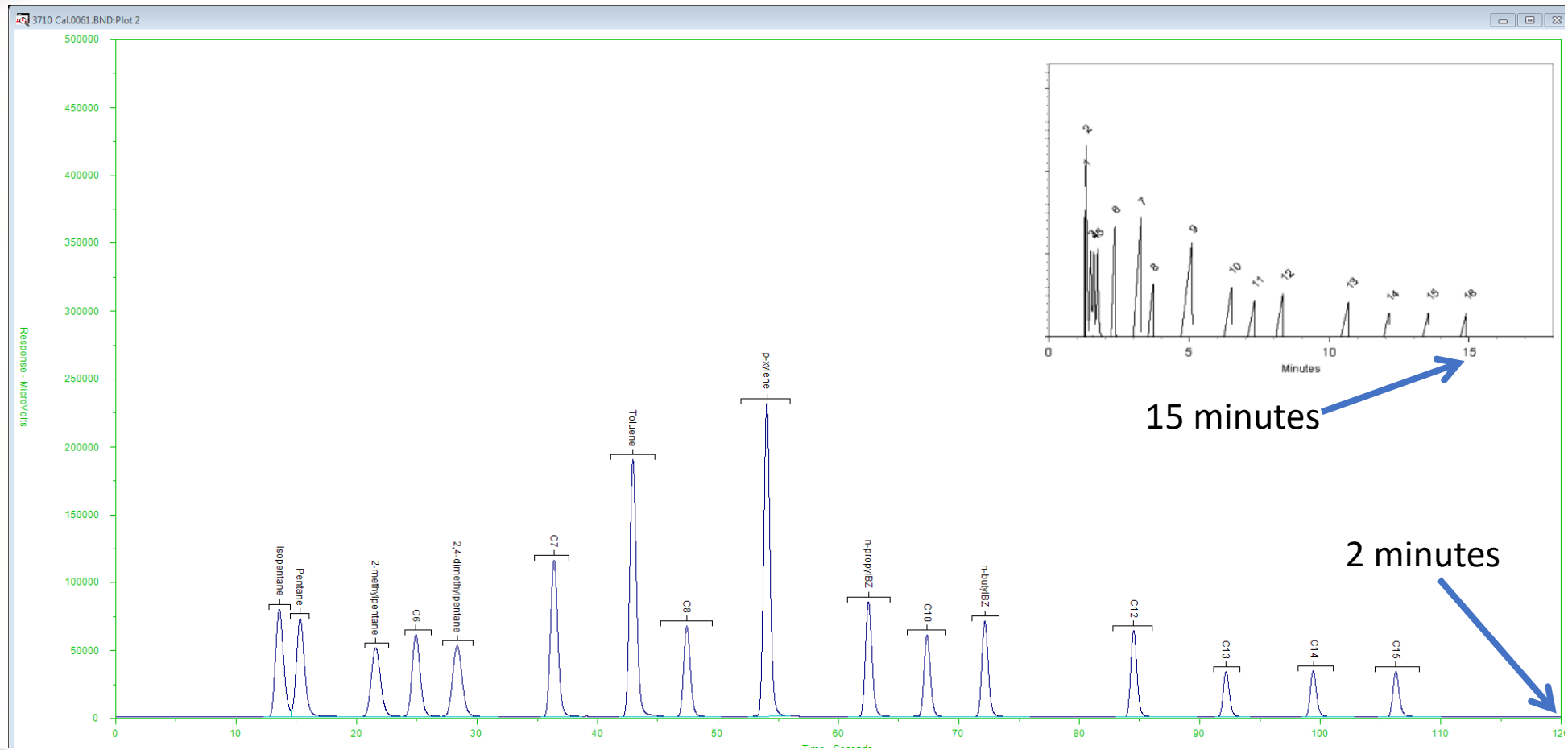


# Anesthetic “non-quantitative impurity standard”



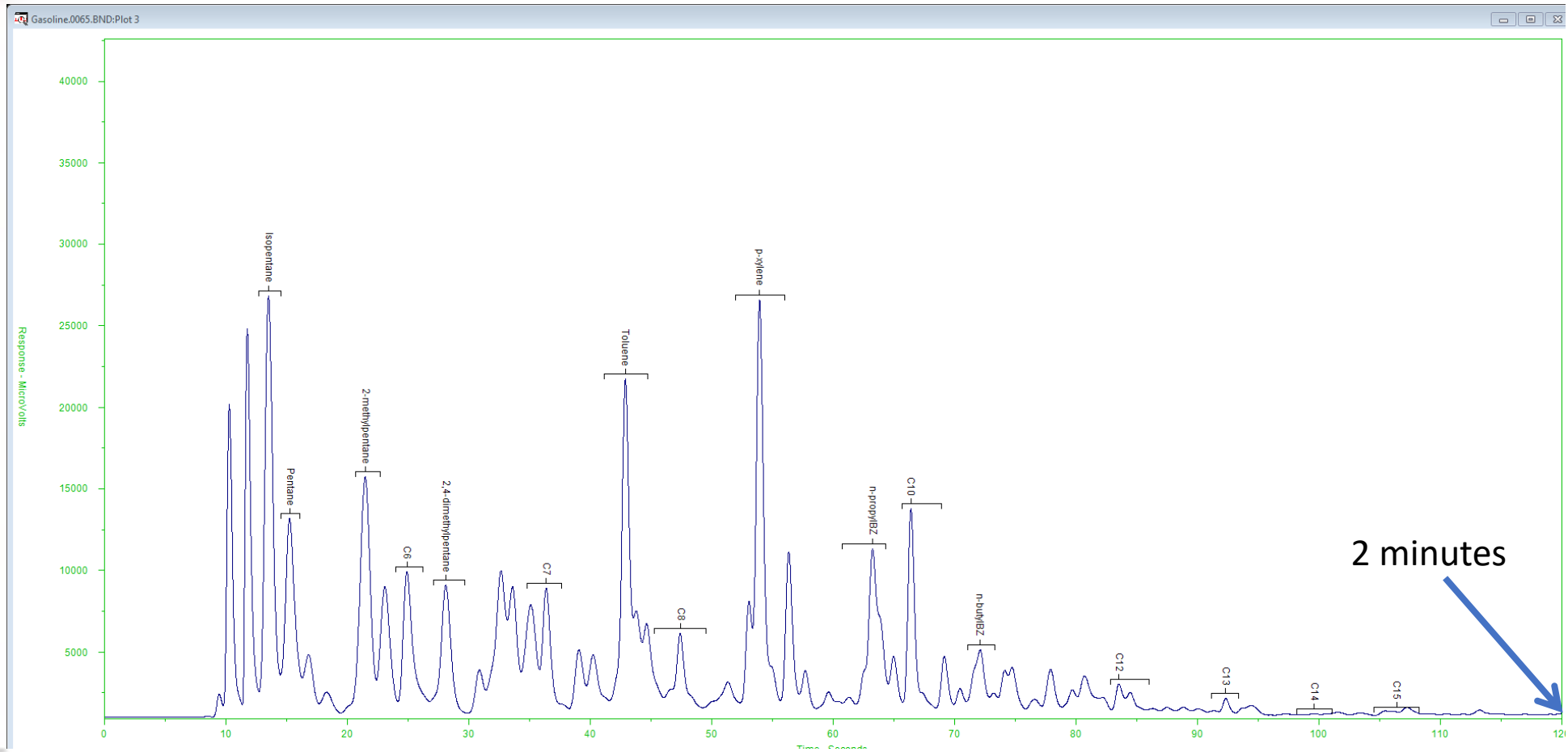
# Restek ASTM D-3710-95 Standard

**FAST**  
Gasoline  
Simulated  
Distillation



# Regular Unleaded Gasoline

**FAST**  
Gasoline  
Simulated  
Distillation





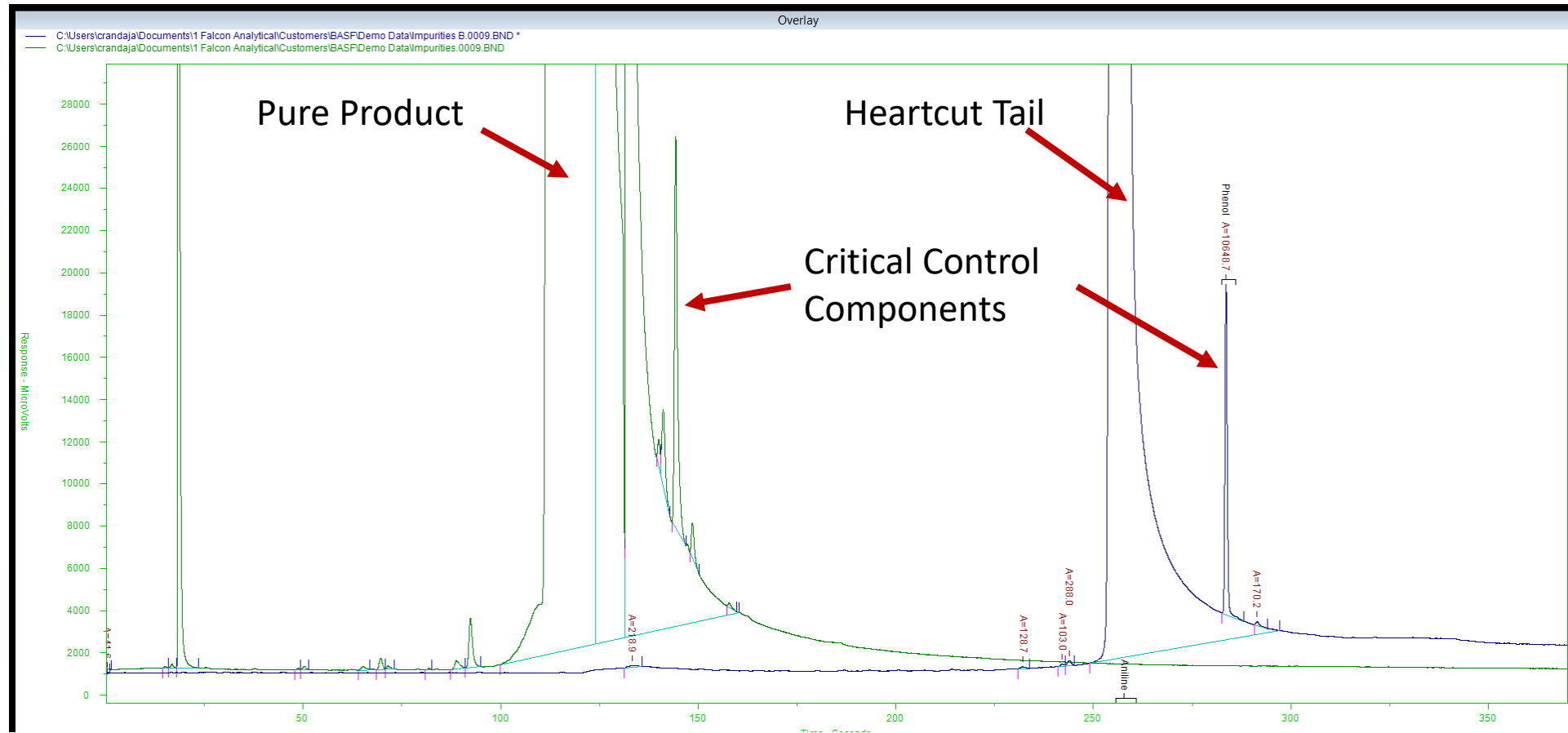
- Impurities in Pure Product

- 2 Column modules, MXT-5 & MXT-Wax
- Heartcut operated twice to get the separation
- 2 FID modules to get all the components @ low ppm levels



**FAST, Selective  
and Sensitive**

Parts per million level  
impurity measurements

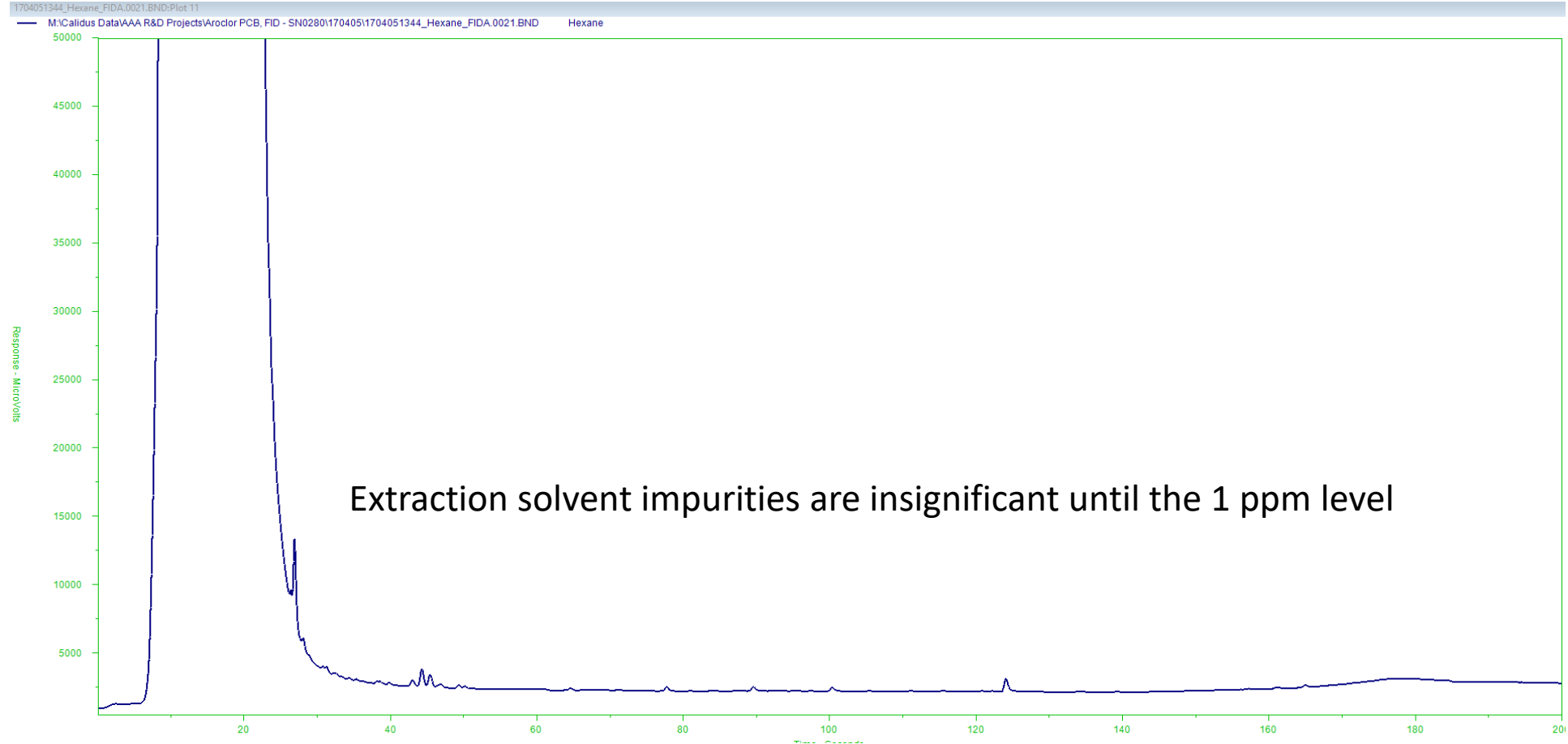


# Hexane Extraction Solvent for Aroclor



Even spectral grade solvents still have ppm level impurities, full scale at 5000 microvolts

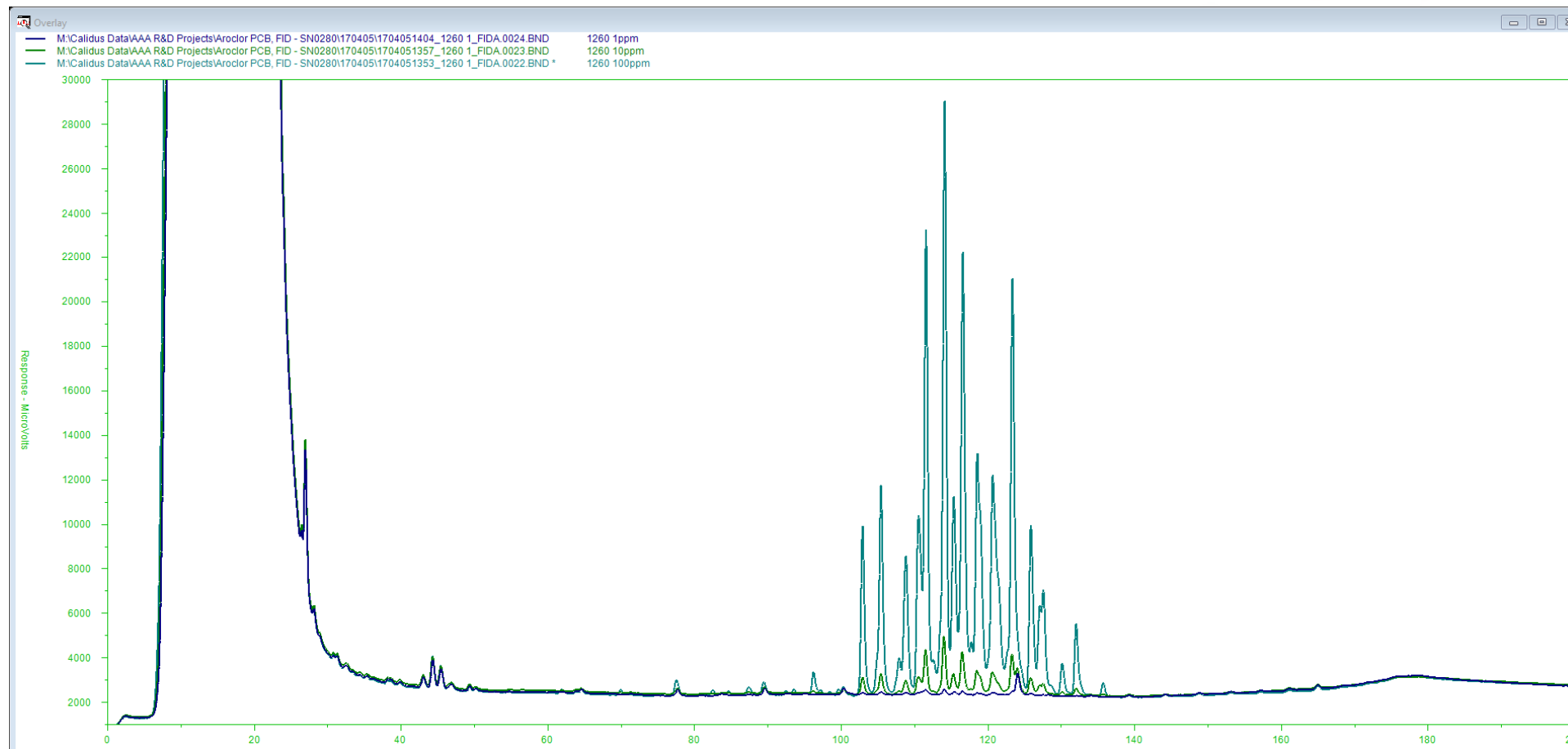
**FAST  
&  
Sensitive**



# Aroclor PCBs – 1, 10 & 100 ppm



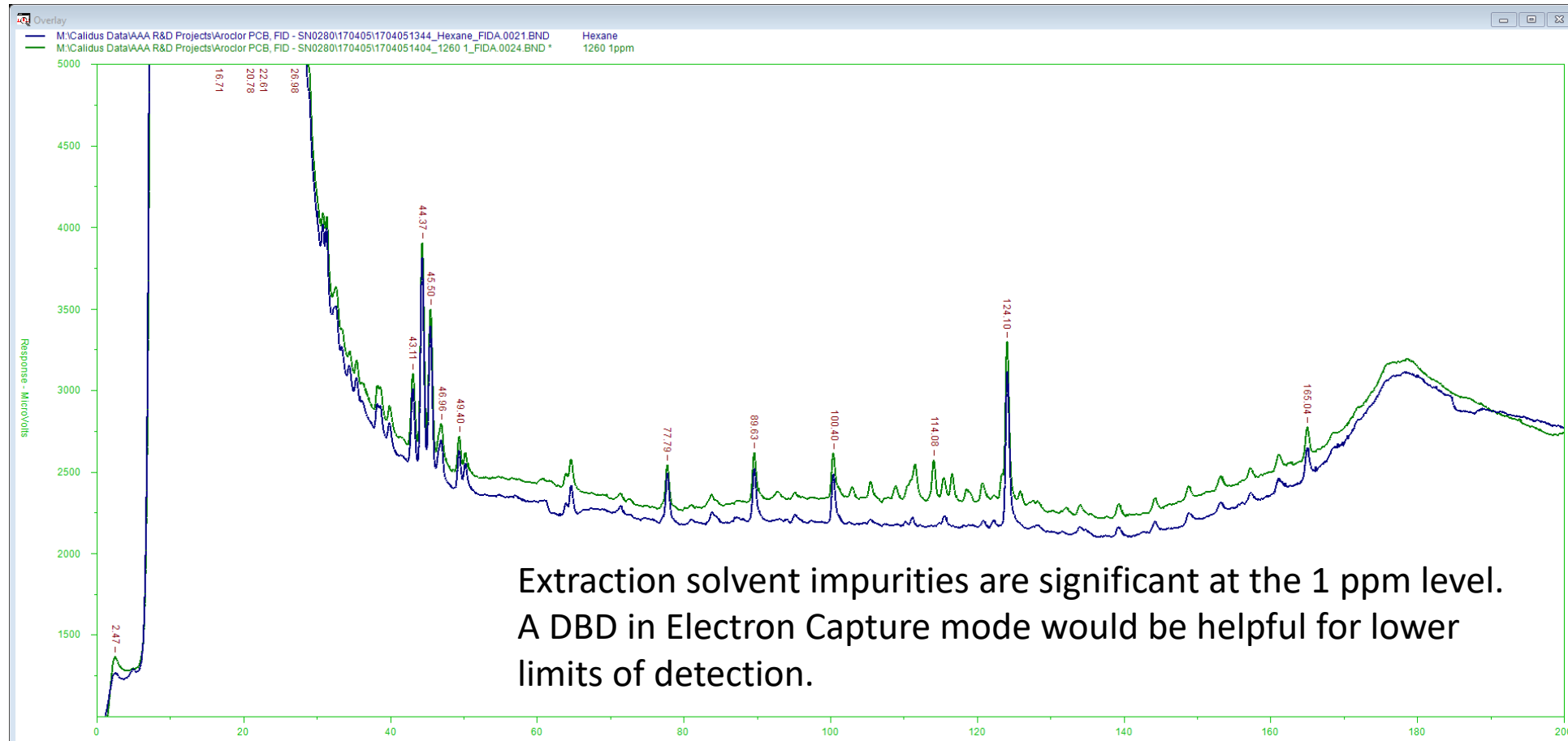
Full scale at 30,000 microvolts



**FAST  
&  
Sensitive**

# Aroclor PCBs – 1 ppm Overlaid Hexane

Near the limit of quantification, full scale at 5000 microvolts  
At this level some baseline subtraction could be beneficial if done with care.



**FAST  
&  
Sensitive**

Extraction solvent impurities are significant at the 1 ppm level.  
A DBD in Electron Capture mode would be helpful for lower limits of detection.





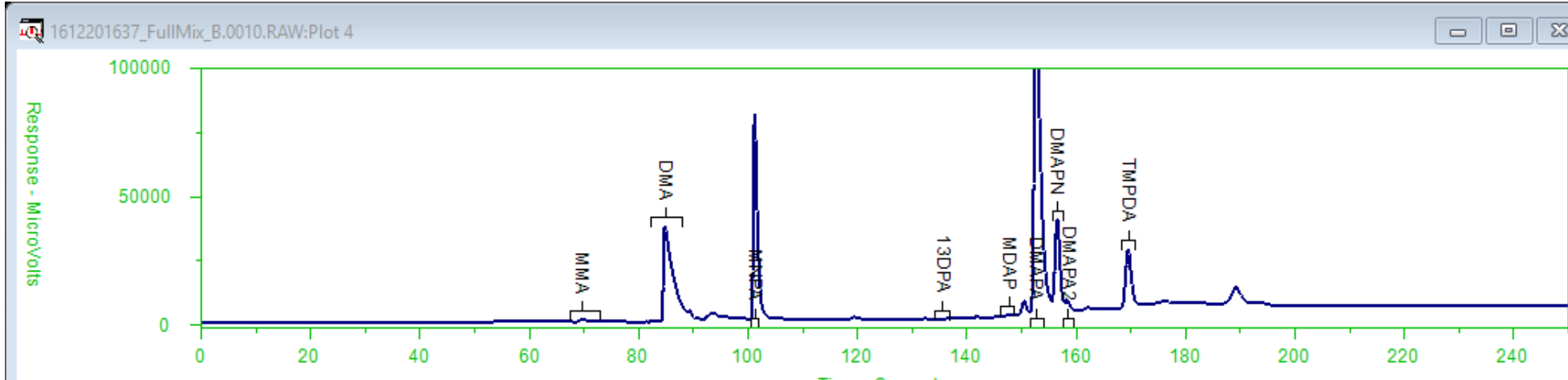
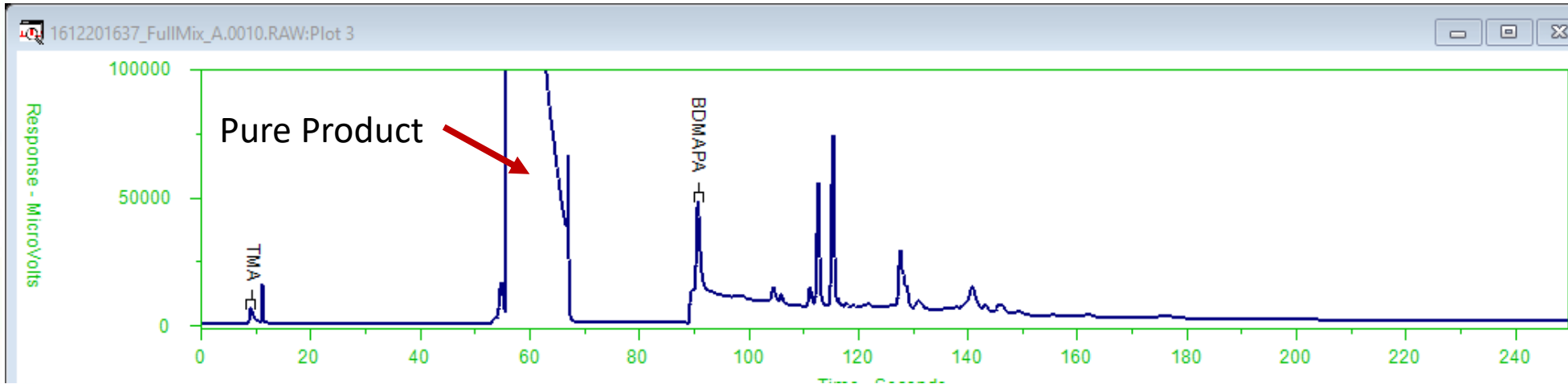
## • Impurities in Pure Product

- 2 Column modules, MXT-WAX & MXT-Qbond
- Heartcut operated twice to get the separation
- 2 FID modules to get all the components @ ~800 ppm



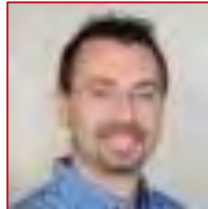
FAST, Selective  
and Sensitive

Parts per million level  
impurity measurements



Sensitive

Parts per trillion for tracer component

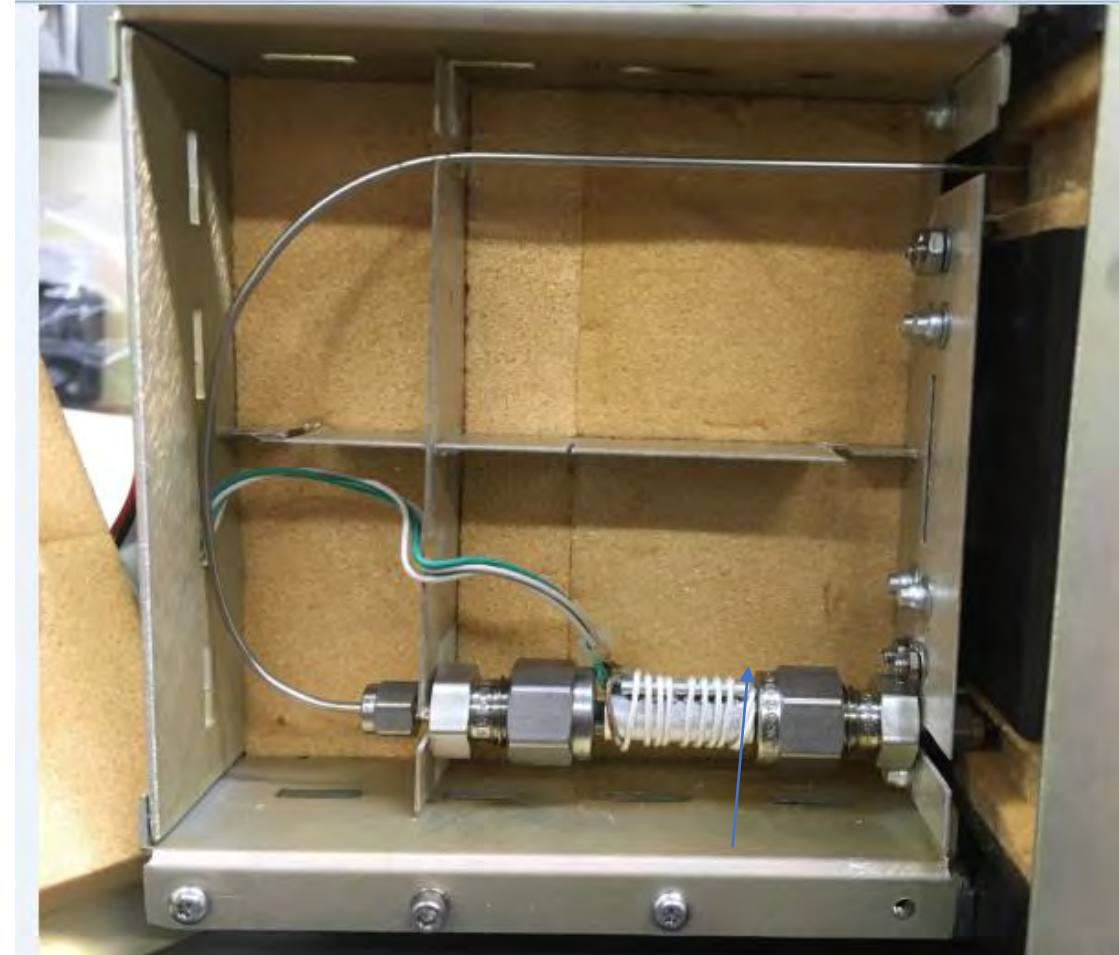


- Chemical Tracer Detection
  - Highly halogenated semivolatile aromatic hydrocarbon
  - Selective response using DBD in the Electron Capture mode is very high
- Project Objectives
  - Demonstrate adequate separation from air background components
    - Automotive exhaust
    - City environment hydrocarbon emissions
    - System background
  - Demonstrate limit of detection
    - Lowest possible using CALIDUS
    - 50 parts per quadrillion ultimately required
  - Transportability required



# Packed Trap Module

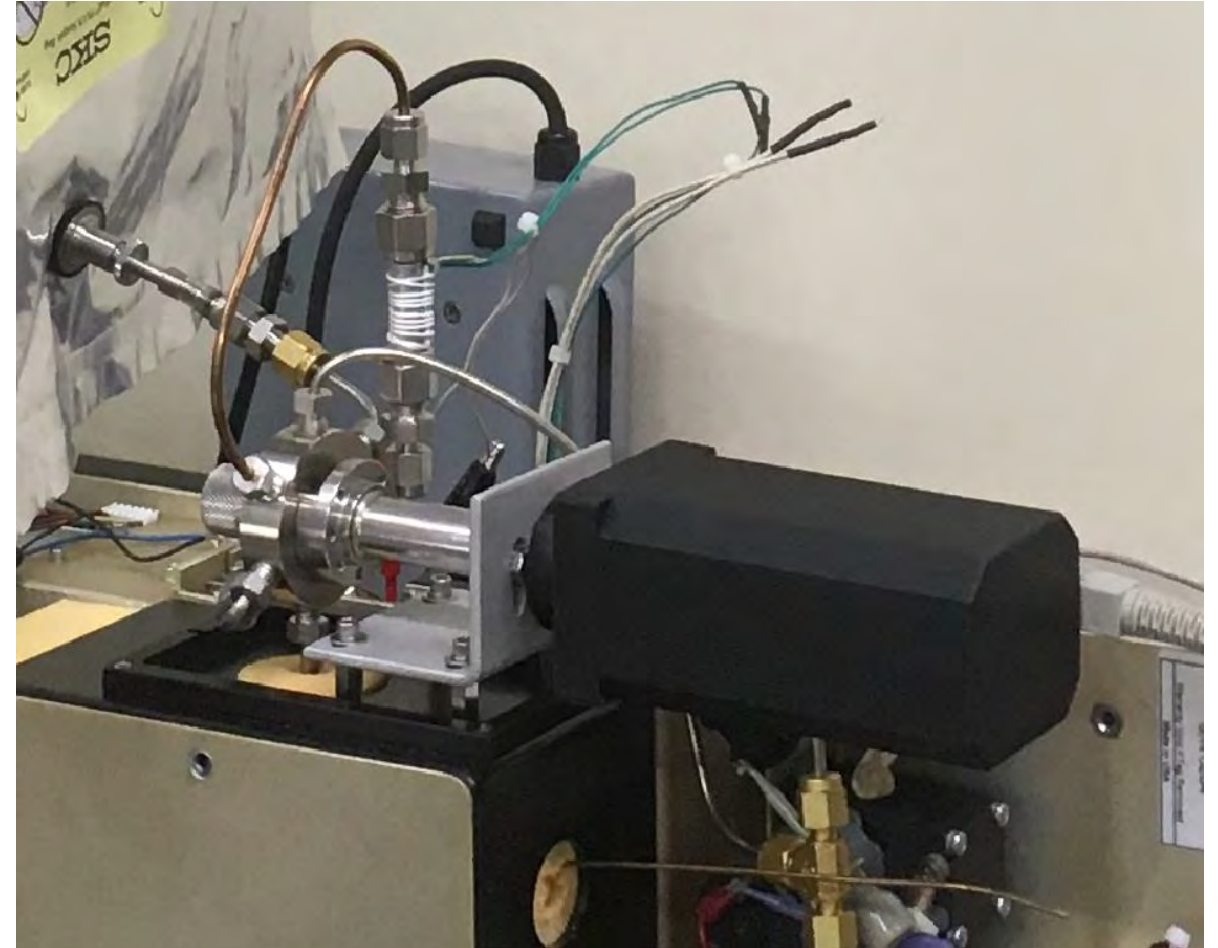
- Mass flow controller loaded trap
- ~0.5" long trap bed
- High velocity gas passing through the isothermal SPU affected the adsorption of analyte on the trap material
- Tenax TA showed poor adsorption for analyte
- Flow rates were too low
- System was re-plumbed with all 1/8" tubing and valves



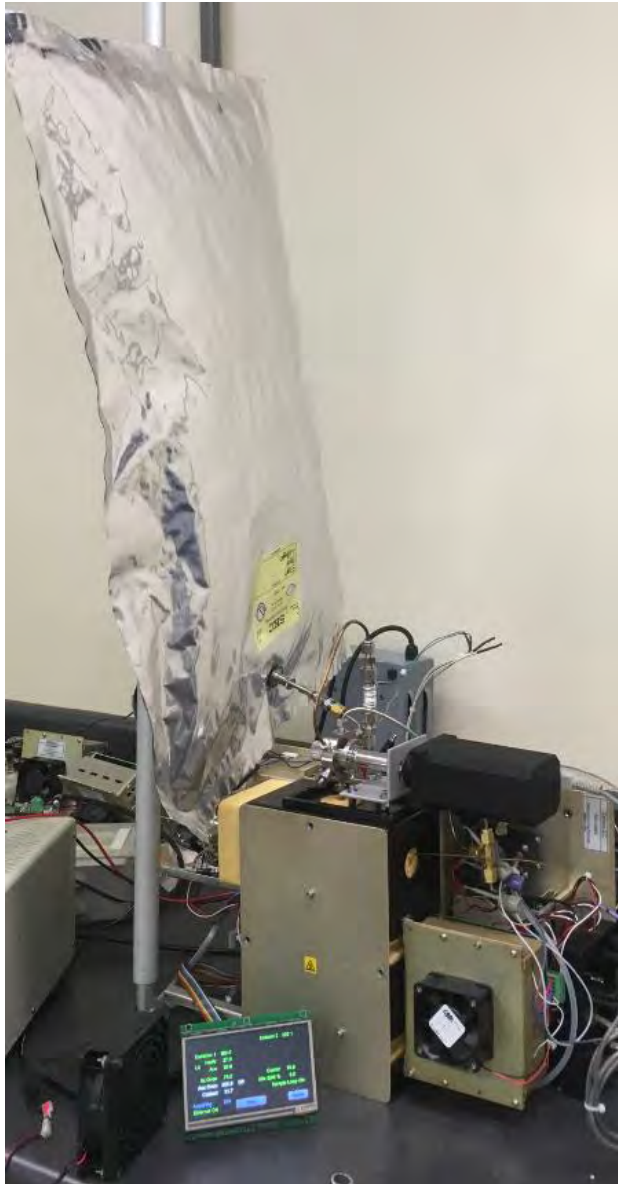
1/8" OD x 4mm ID glass tube

# Top Mounted Valve and Trap

- The 1/8" valve required external placement due to size and actuator requirements
- Prevents the incoming sample from preheating and affecting the adsorption of analyte on the trap as well as the bulk of the 1/8" tubing.
- In this configuration the trap was directly desorbed into the Carbolblack C column.



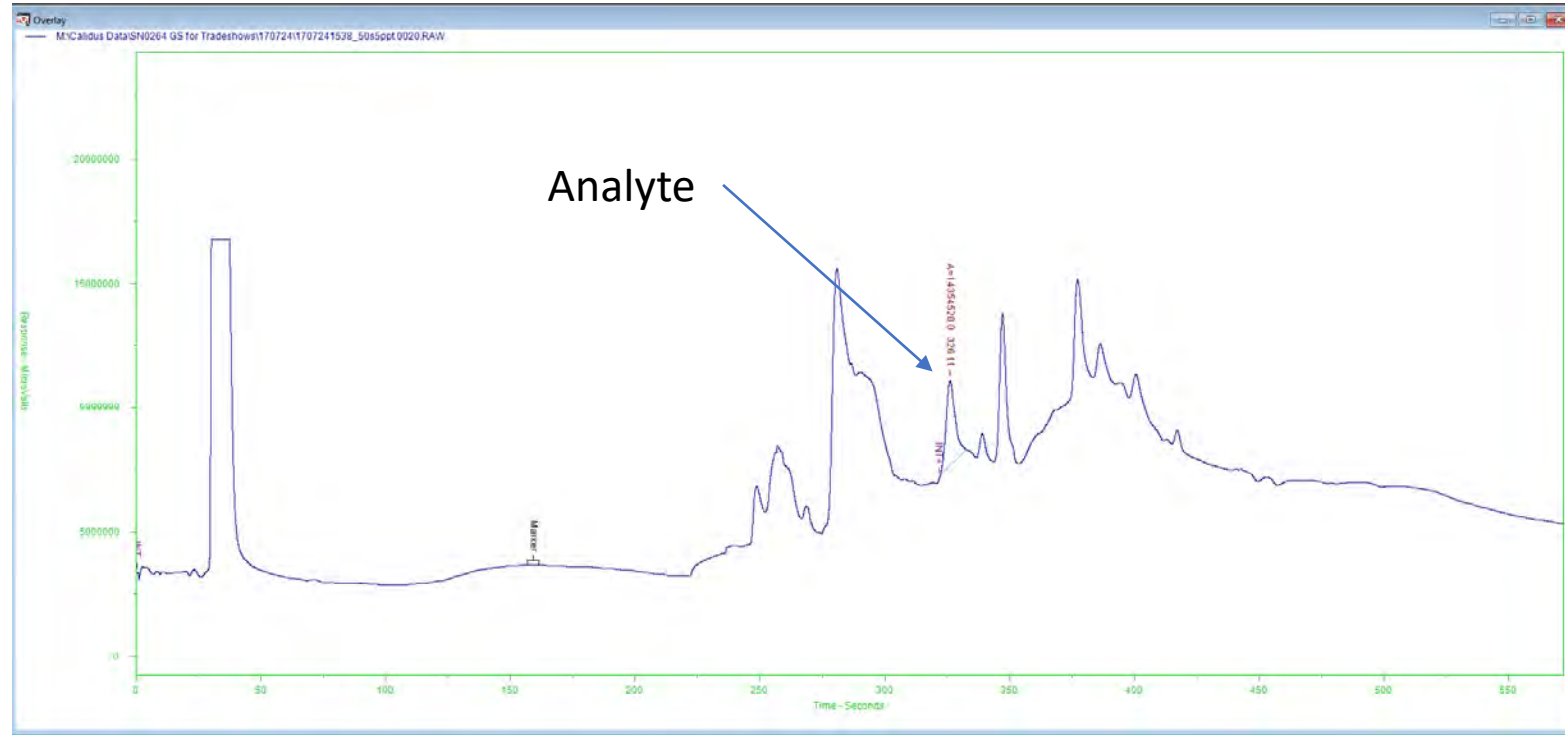
# 25L Aluminized Sample Bags....



- Sampling was tricky
- Preparing quantitative calibration blends was tricky
- Every point for absorption had to be eliminated
- Huge volumes required for successive dilution to the concentration levels desired
- Parts per trillion was achieved... but this was 3 orders of magnitude too high for the client

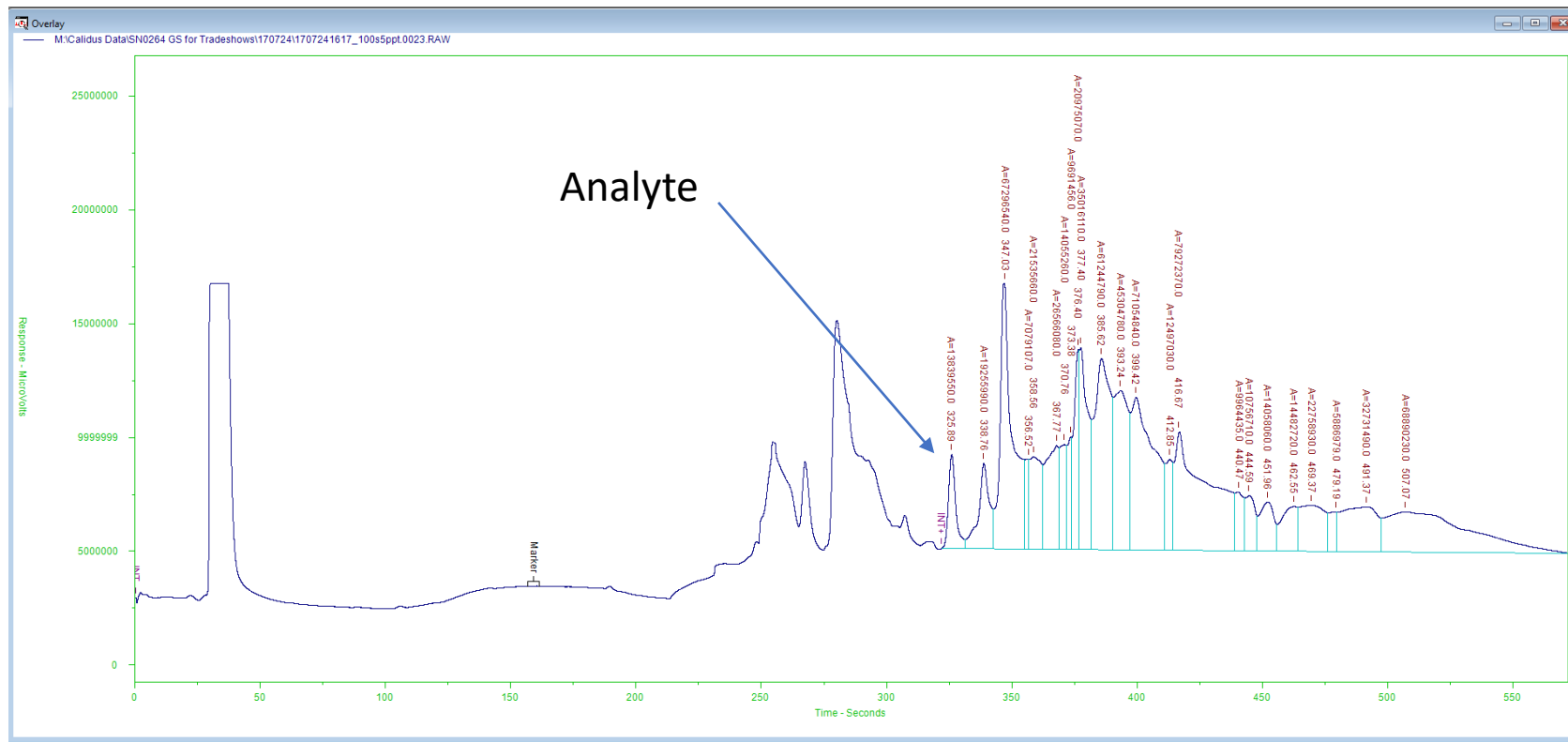
# Results: Carboxen 1000

1.08L, 5ppt analyte in N2



# Results: Carboxen 1000

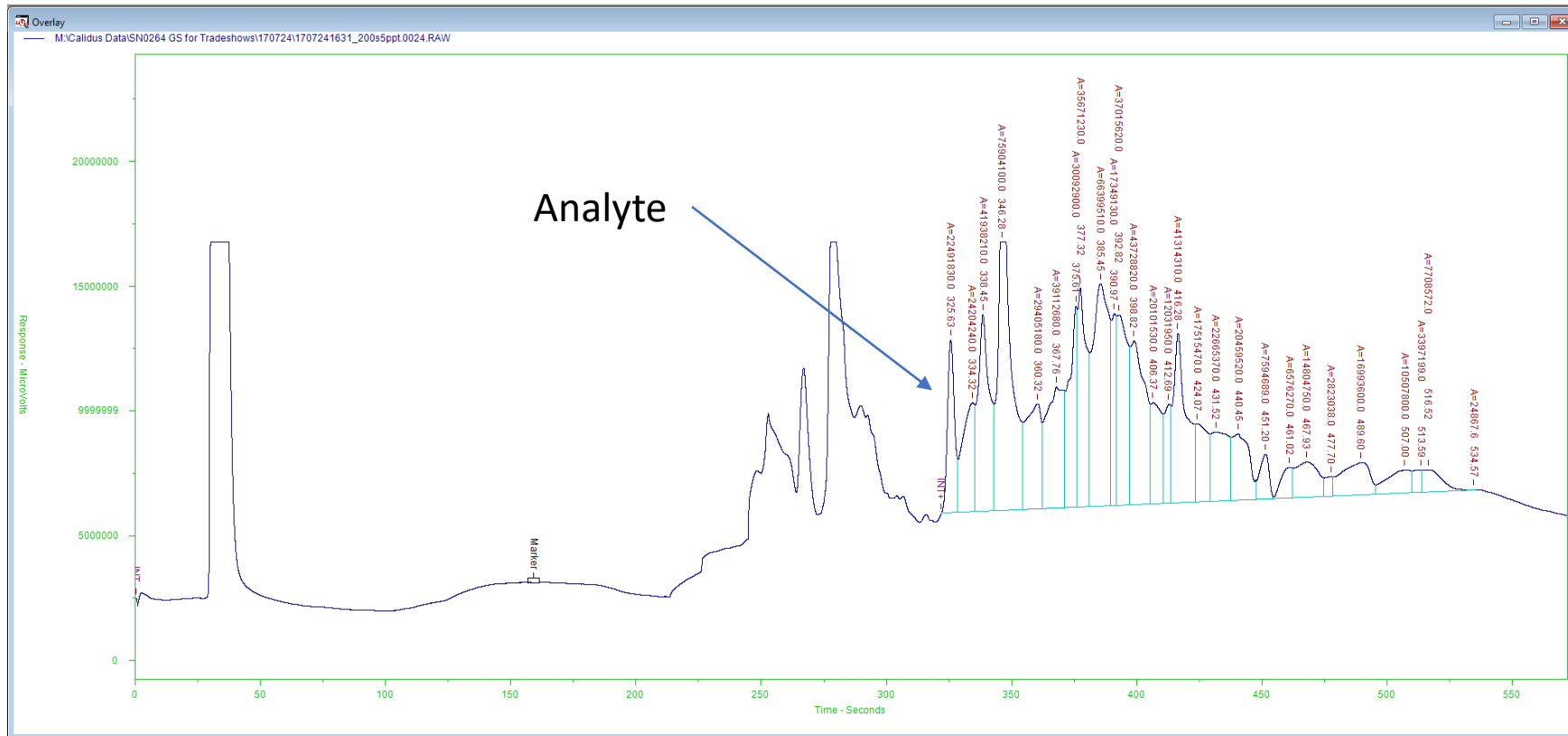
## 2.17L, 5ppt analyte in N2



# Results: Carboxen 1000



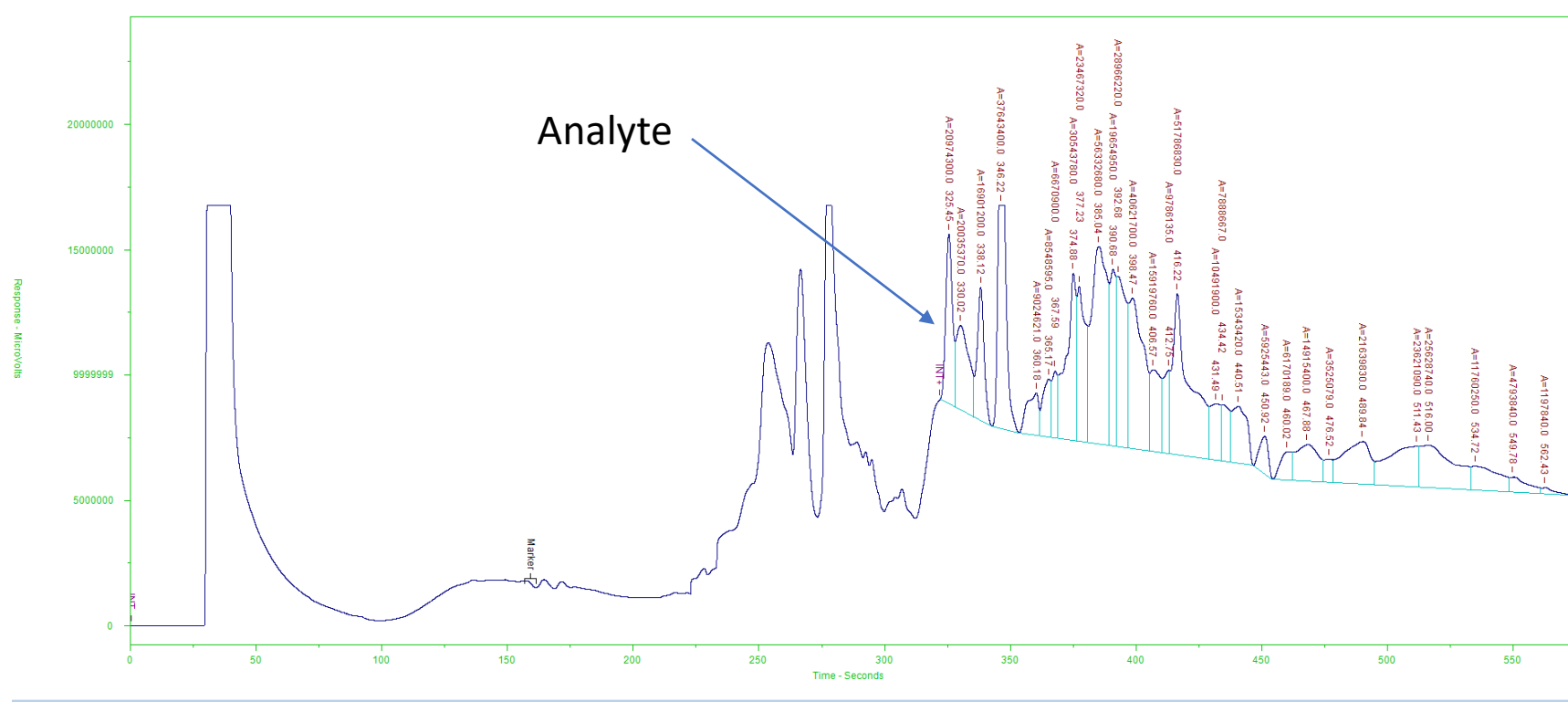
4.33L, 5ppt analyte in N2



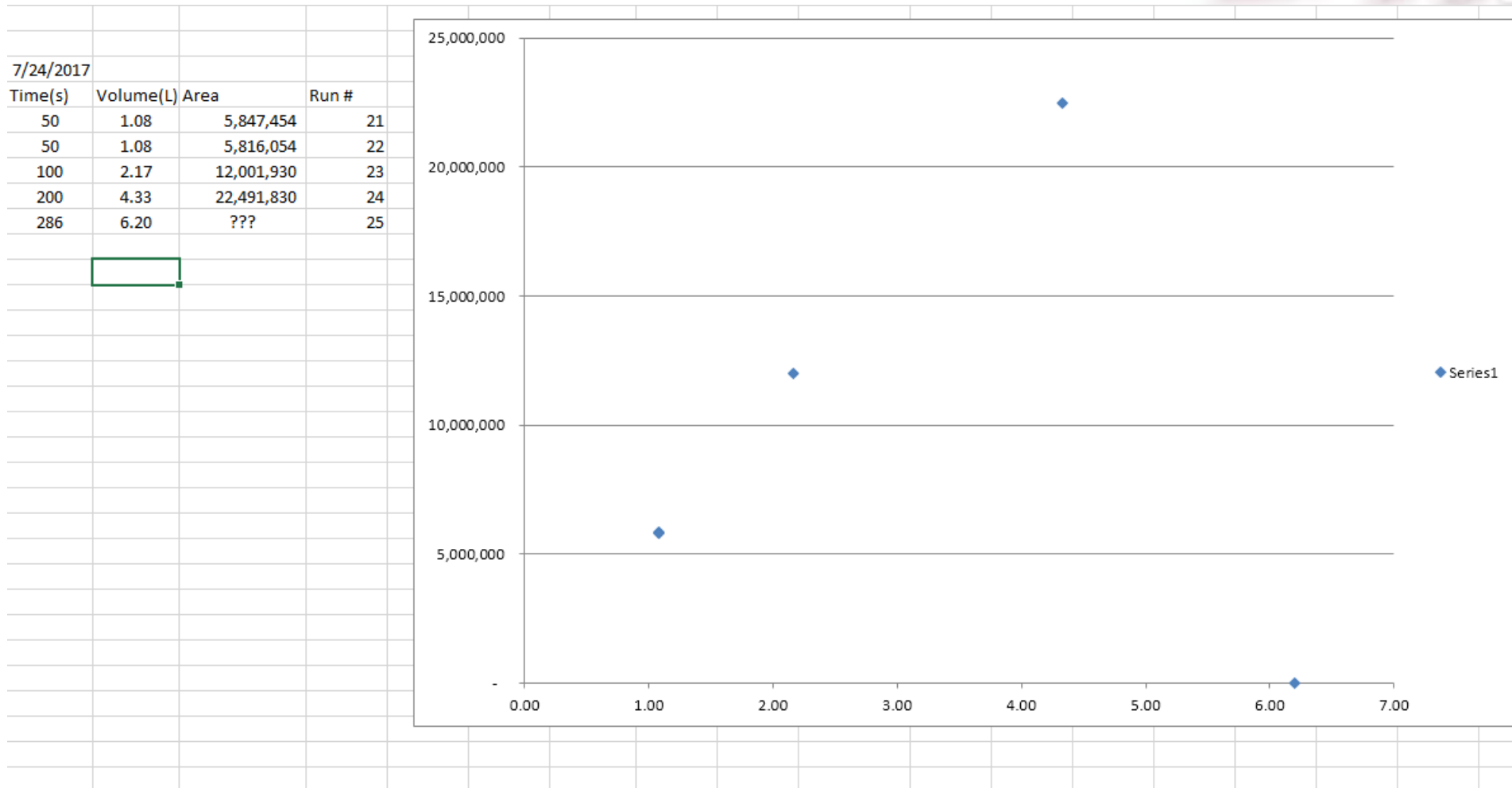


# Results: Carboxen 1000

6.2L, 5ppt analyte in N2



# Results: Carboxen 1000





## Result?

- Reasonable and linear results down to the 5 parts per trillion level
  - Obtaining 50 parts per quadrillion with this trap and detector is not possible
  - However, a real ECD would probably achieve the needed level
- Transportability could probably have been achieved
- Certainly demonstrated ambient air capability easily for parts per billion and in some applications, parts per trillion



**FALCON**

ANALYTICAL SYSTEMS & TECHNOLOGY



Mico & Fast  
GC using  
CALIDUS

- FAST
- FAST & Sensitive
- FAST, Sensitive and Selective
- And can be extremely Sensitive...

**Questions?**

