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ANALYTICAL SYSTEMS & TECHNOLOGY



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ANALYTICAL SYSTEMS & TECHNOLOGY



Recent Advancements in Ultrafast Gas Chromatography from the Winery to the Refinery to the Wellhead

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ABSTRACT

IFPAC

February 11-14, 2018



Ultrafast gas chromatography continues to expand in application capability. Resistively heated stainless steel programmed temperature capillary column module development has advanced to the point where up to 16 meters of column can be deployed per column module for up to 32 meters using a single split/splitless injector and the complete set of available detector modules: TCD, FID, FPD and DBD. While analyses requiring such column lengths can hardly be called fast, they certainly are faster than the old “big box” air bath oven technology.

We will discuss recent applications in food, beverage and ingredients, pesticide residues on foodstuff, impurity analysis in 99.99%+ pure chemicals and specialty chemicals, refined products and even analysis of wellhead reservoir fluids at pressures up to 2000 psi from fixed gases to C35 and beyond with a single sample injection.

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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

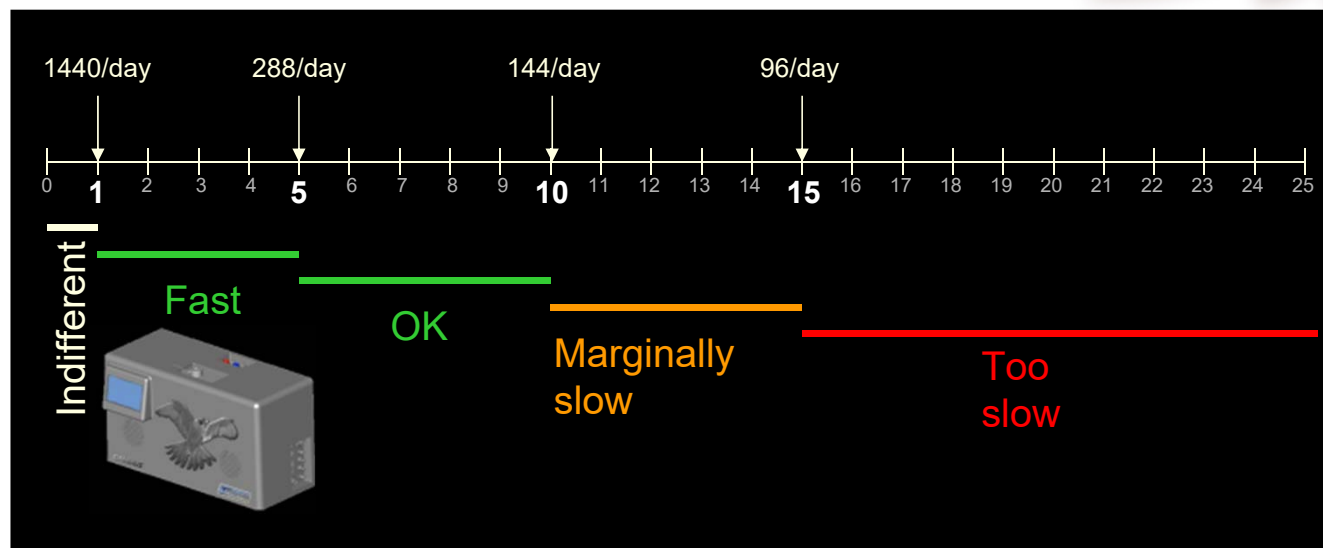
SPEED

Speed, Selectivity, Sensitivity



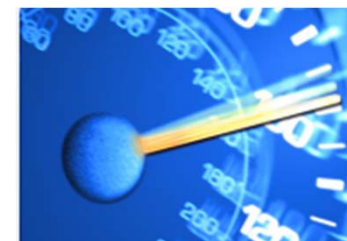
It is a balancing act.

*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





CALIDUS™
Intellectual
Property

2 Patents Issued

2 Patents Pending



Fast Micro Gas Chromatograph System
US Patent 8414832

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) **Inventors:** 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 689 days.

(21) **Appl. No.:** 12/555,783
(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

(58) **Field of Classification Search** 422/70; 422/89; 73/23.39; 23A; 61.53; 61.57; 61.58; 95/87; 96/102; 100; 210/198.2
See application file for complete search history.

(56) **References Cited**

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* cited by examiner

Primary Examiner—Jim Laddow
(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 in at least one electrically conductive element in contact 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 containing inlet, a hydrogen inlet, an analysis port and a flame region, oxygen delivery means for delivering oxygen through the oxygen inlet to the flame region, a hydrogen and analysis delivery system for delivering hydrogen and analysis to the flame region, and a detector arranged to detect flame extinction.

21 Claims, 8 Drawing Sheets



Trans-Configurable Modular Chromatographic Assembly
US Patent 8336366

US008336366B2

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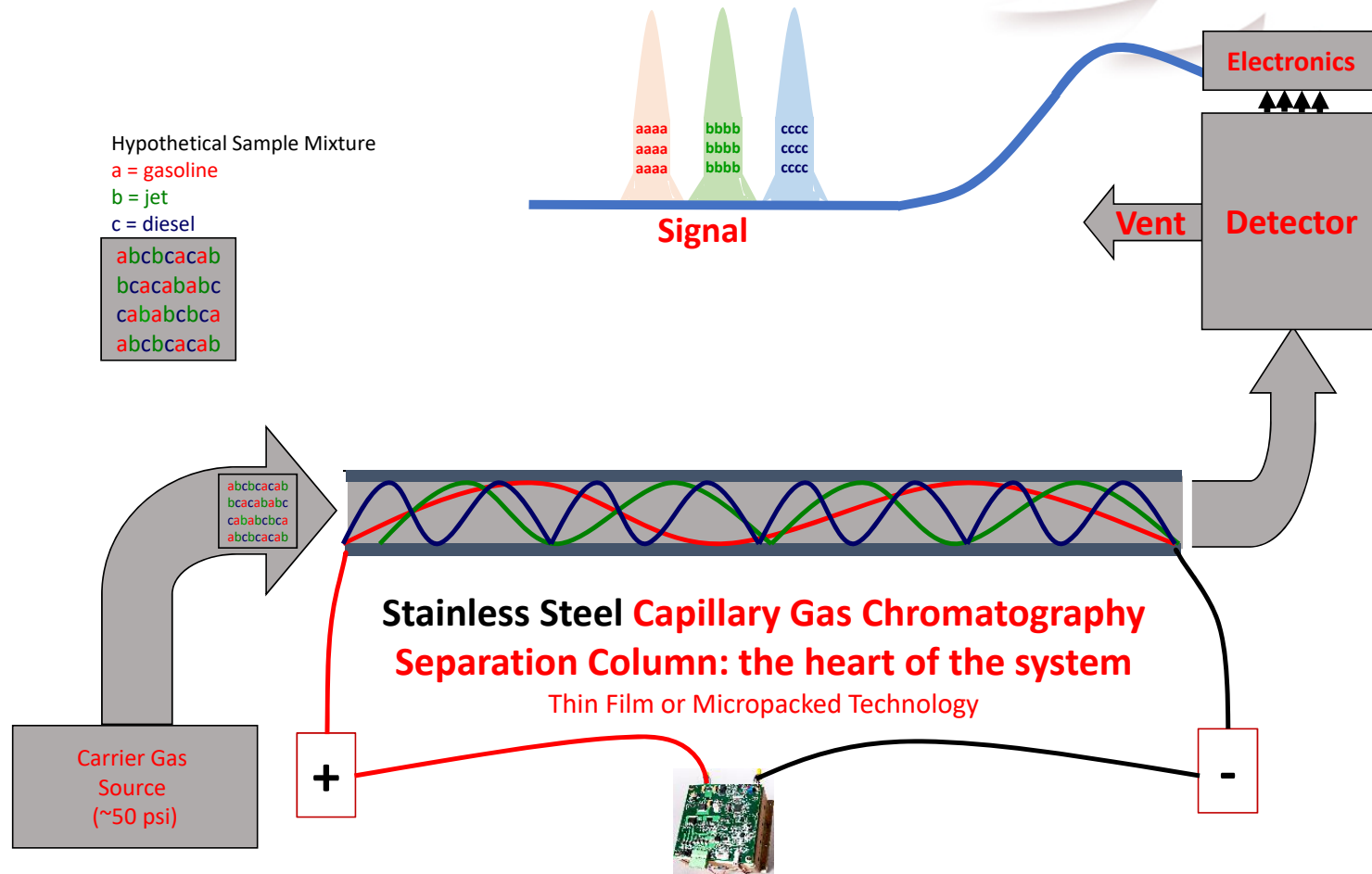
Primary Examiner—Hezron E Williams
Assistant Examiner—Rodney T Frank
(74) **Attorney, Agent, or Firm**—Sheldon H Parker, Esq.

(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

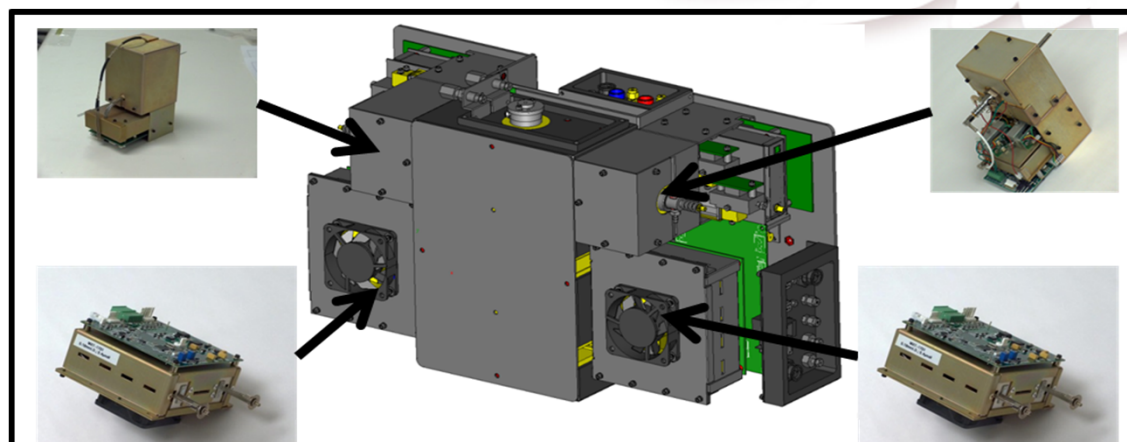
- Split/splitless injector
- Septum purge
- Inlet glass liner
- Column switching

- Column Modules

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

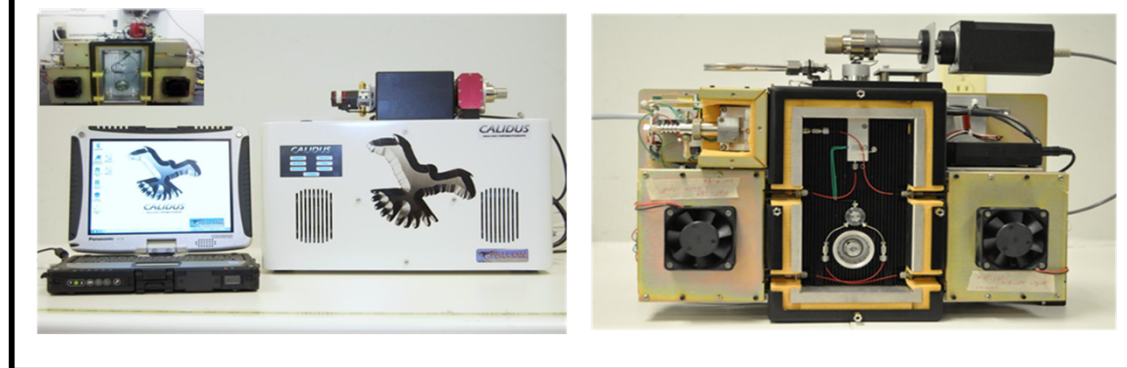
- Detectors

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



Swappable
Choice of
Detectors

Choice of
Columns



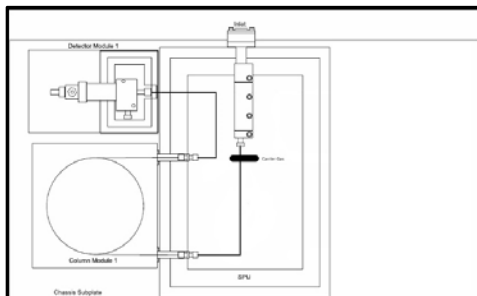
Flowing Gas
or Liquid
Sample GC
System



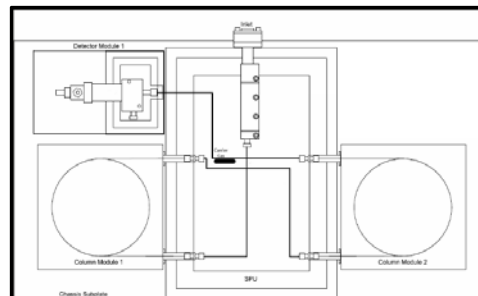
Modules Combined into Instrument **Models**

CALIDUS™
Modular,
Ultrafast GC
Systems

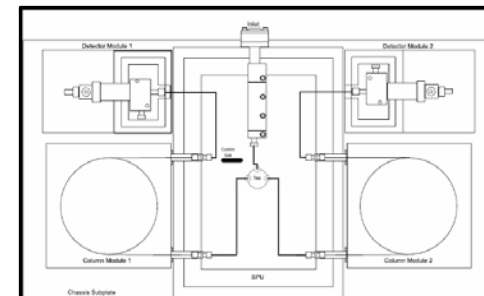
Single Split/Splitless
Injectors with
Septum Purge



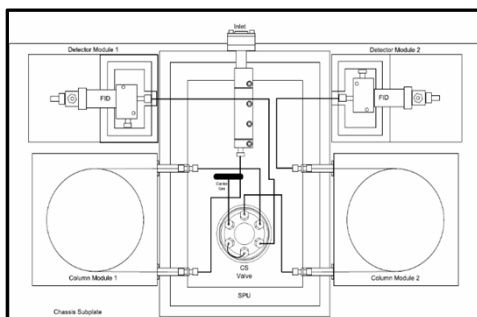
101 – single column 2m – 16m,
single detector



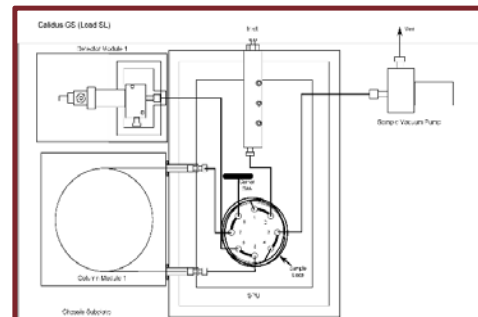
201 – single column 4m – 32m,
single detector in series



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

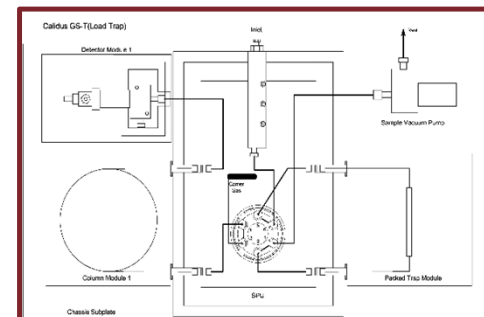


CS– dual column 2m – 16m, dual
detector with column switching
valve, up to 32 meters total



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

New



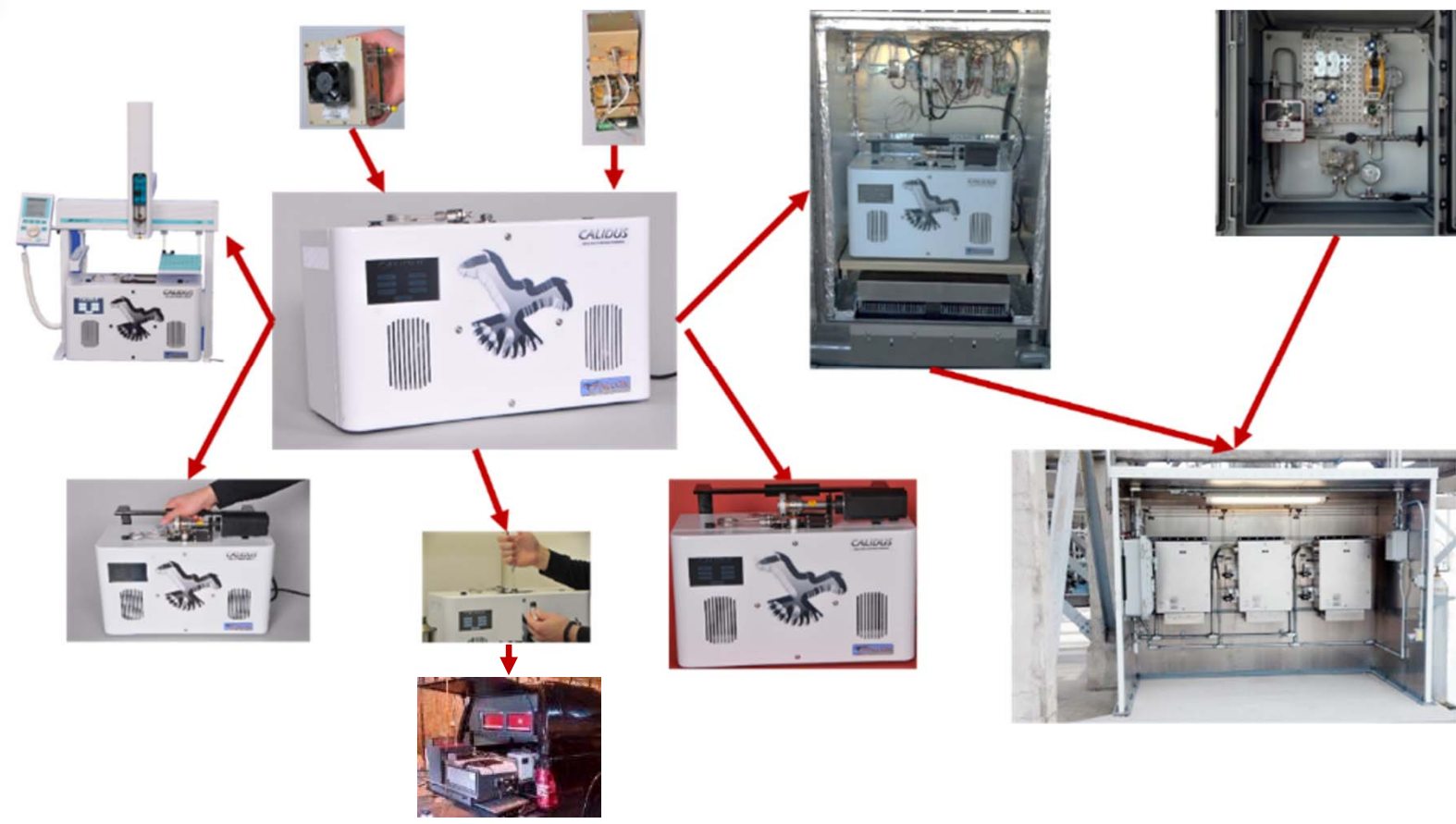
GS-T – single column 2m – 16m,
with preconcentration trap, single
detector with sample pump

New



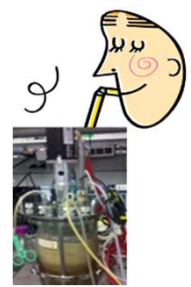
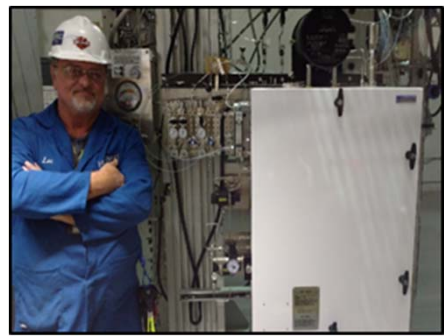
Modules Make
Instruments,
Instruments Make
Analyzers
Analyzers Make System
Solutions...

One Solution



Broad Based Deployment of CALIDUS

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



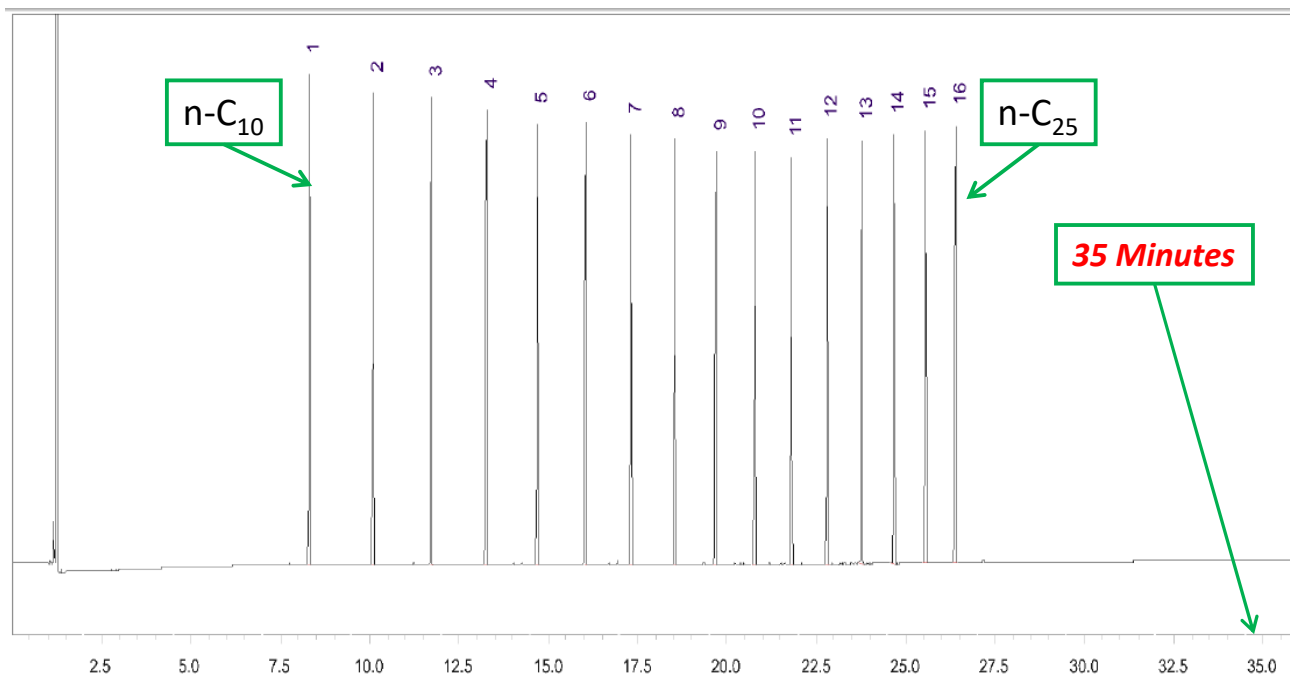
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Slow, Big Box GC



Chromatogram Shipped with n-C₁₀ to n-C₂₅ Alkanes Calibration Sample (Agilent GC)

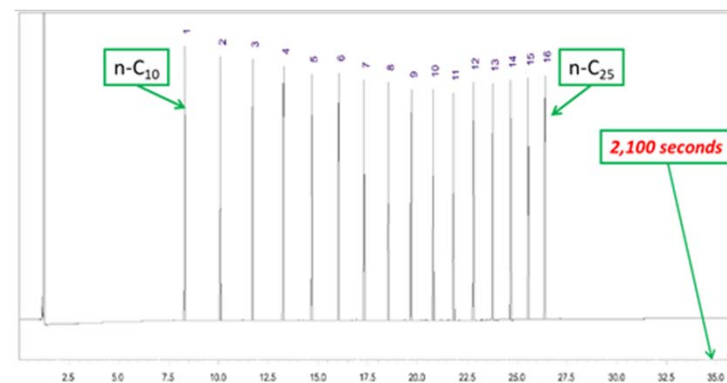
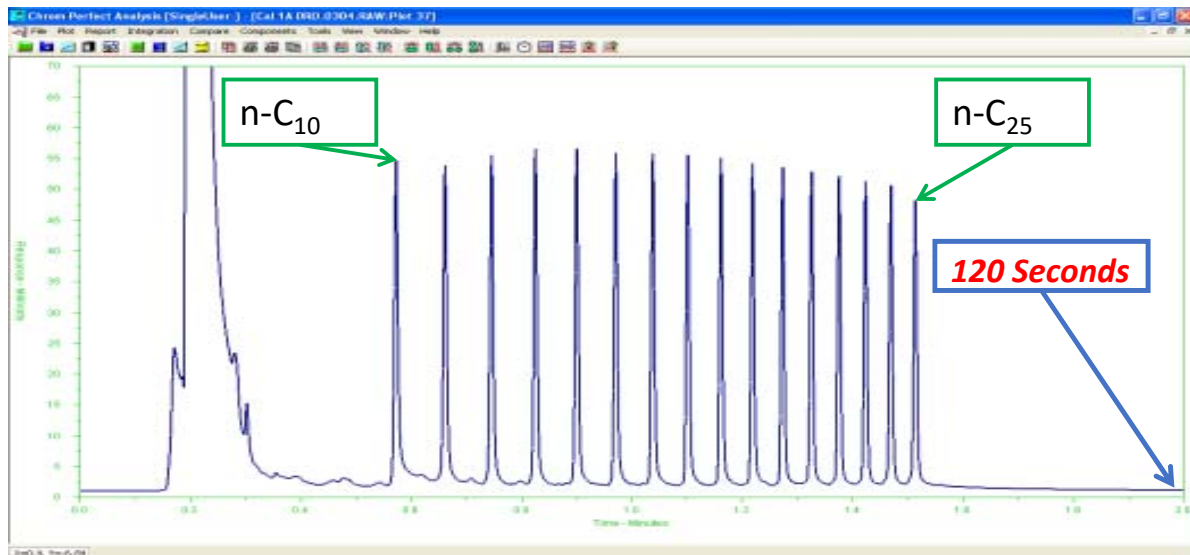


Retention Time in **Minutes**

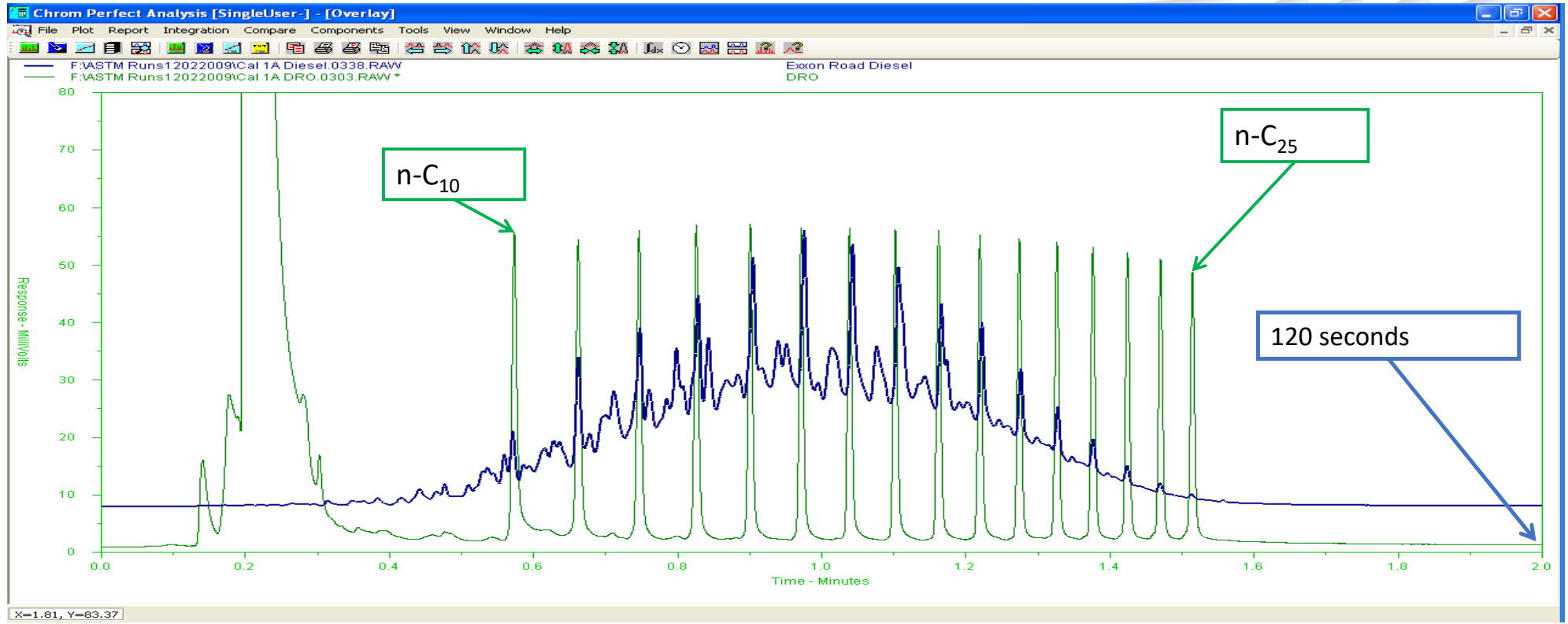
Ultrafast!



- Calibration standard for DRO method
- Small molecules (low boiling point) elute earlier (left), in this case starting with decane (n-C₁₀).
- Large molecules (high boiling point) elute later (right), here ending with pentadodecane (n-C₂₅)



ExxonMobil Road Diesel Overlaid n-C₁₀ to n-C₂₅ Alkanes

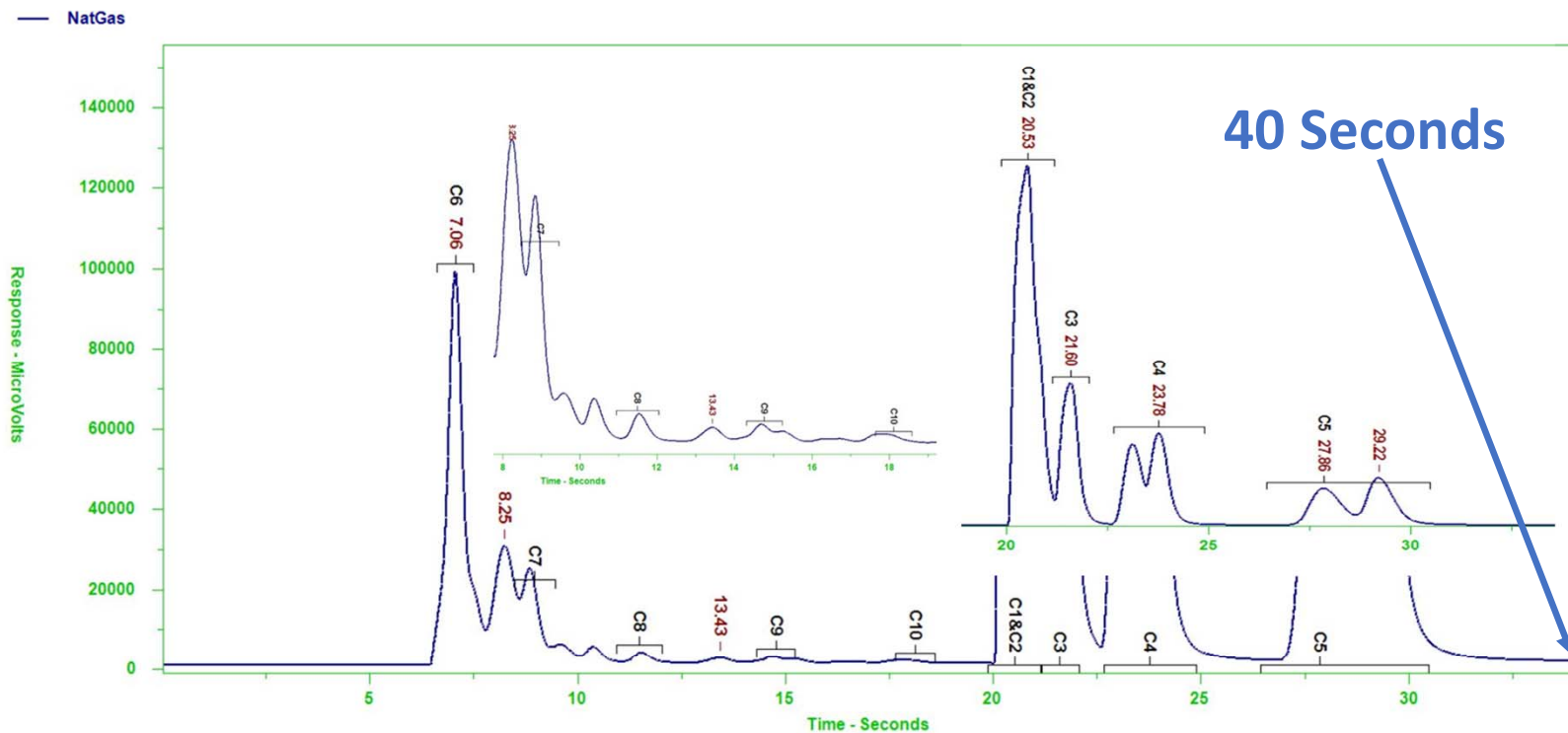




Hydrocarbons C₁ & C₂ to n-C₁₀



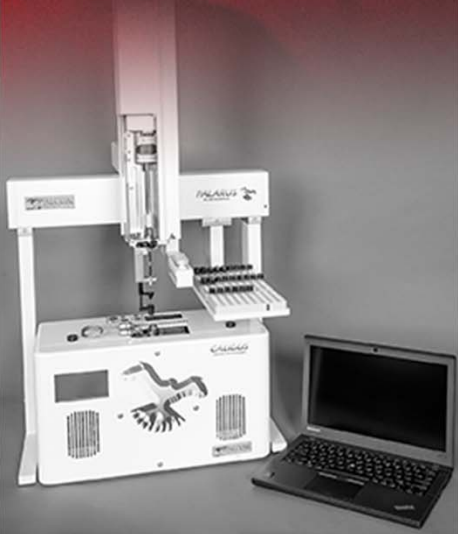
FAST





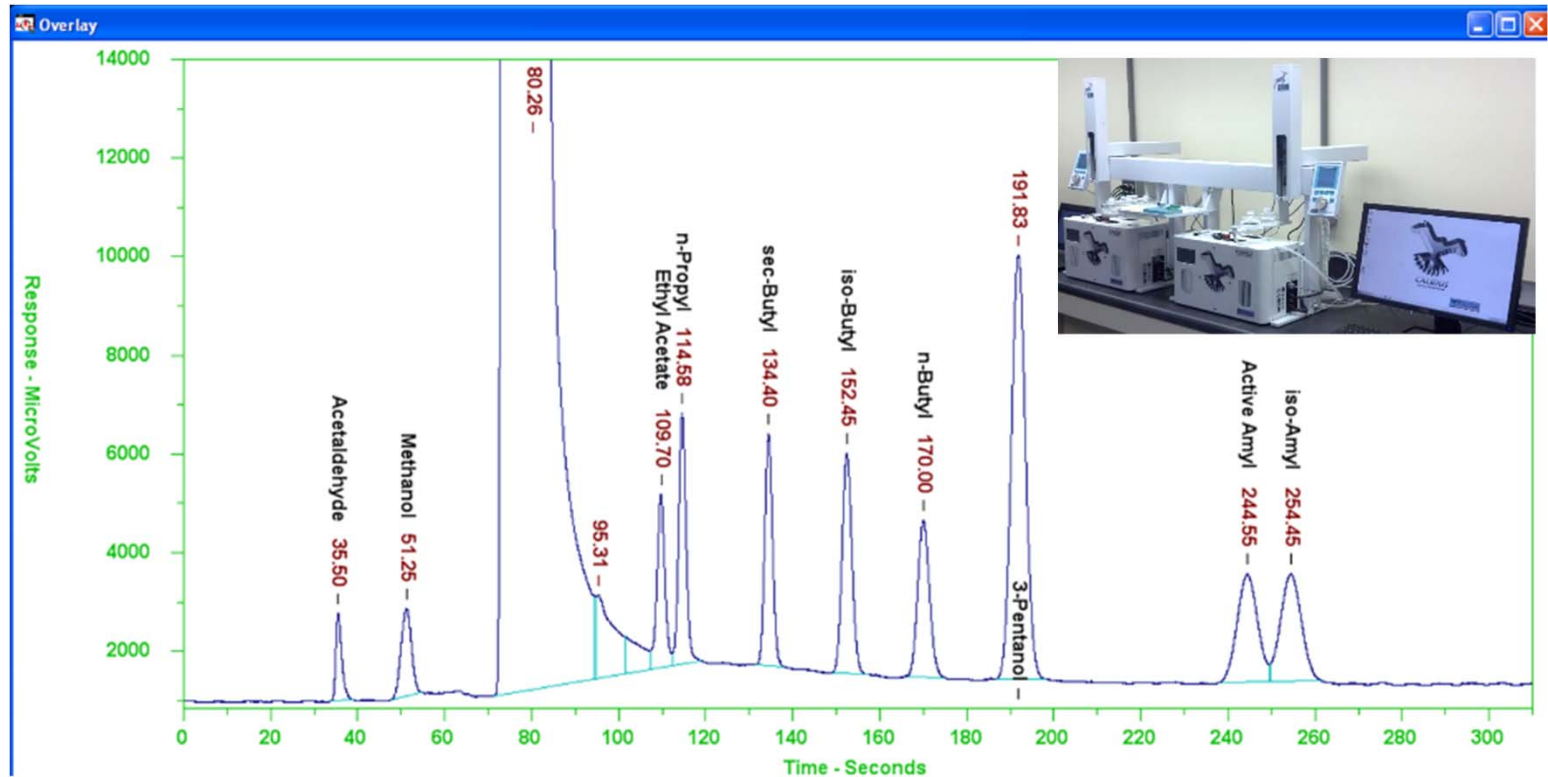
Adult Beverages, Food Ingredients & Contamination

Food & Beverage relating
to product quality,
authentication and
contamination



• Beverage

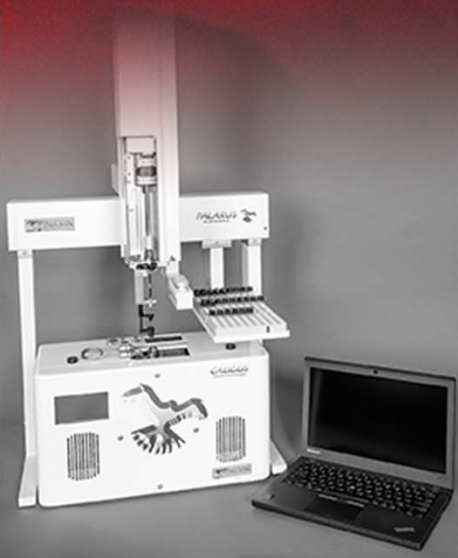
- Ethanol and fusel oils in wine and distilled spirits
- Validation that ethylene glycol is NOT present (Italy)
- Soon in Hungary, forensic authentication for wine & liquor



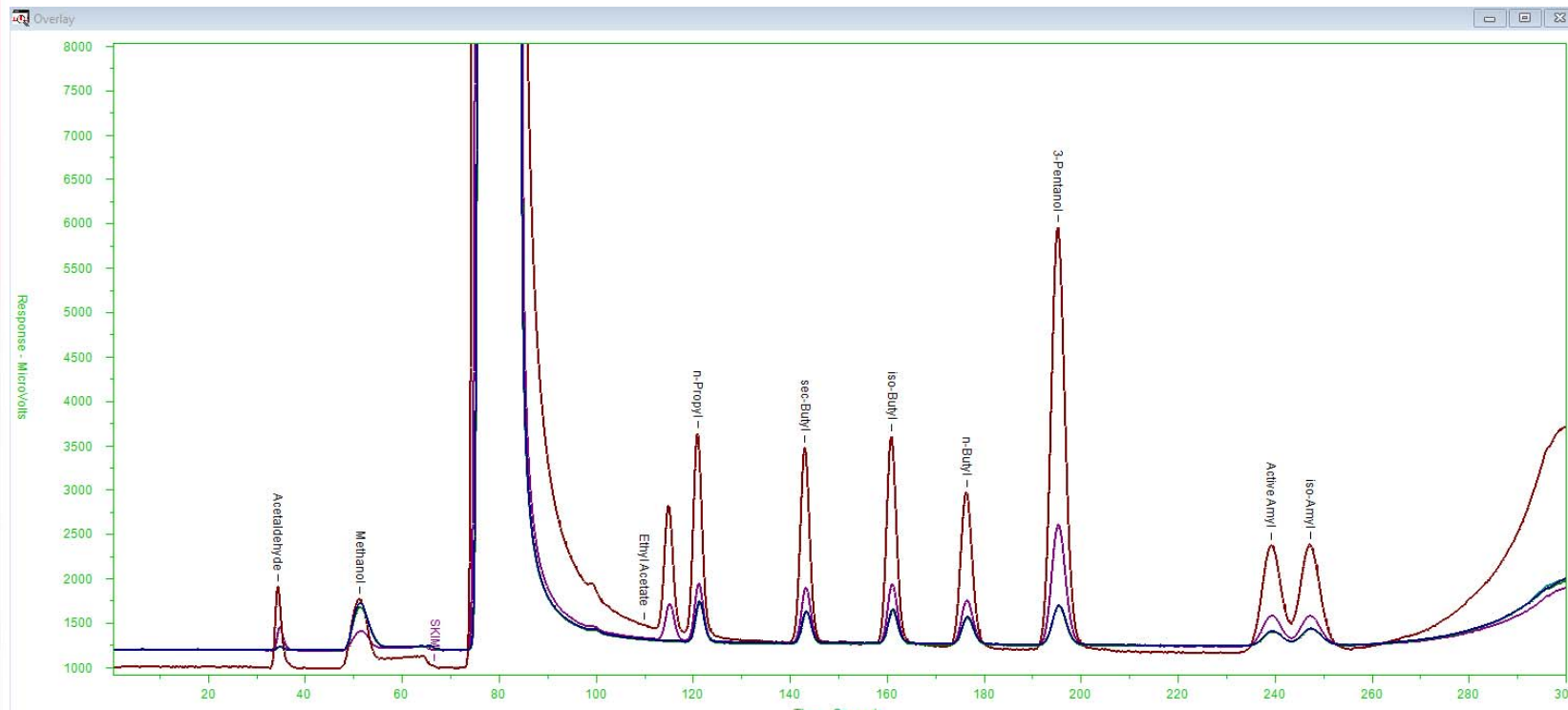


Various Distilled Spirits

Ethanol & fusel oils



- Ethanol & Fusel Oils in Distilled Spirits
Jose Cuervo, Grey Goose, Johnnie Walker
Black, & Crown Royal



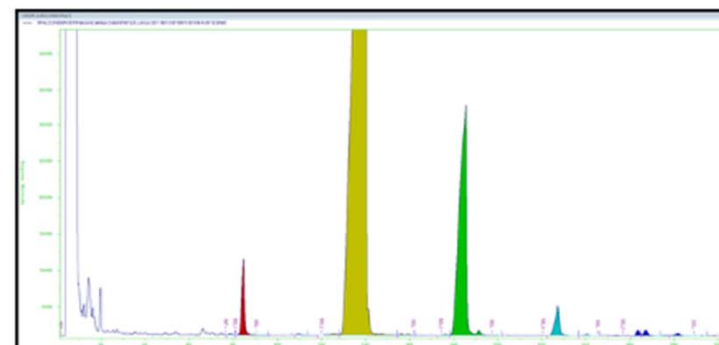
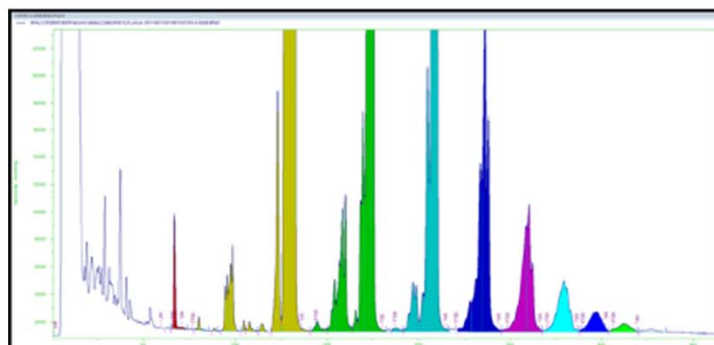
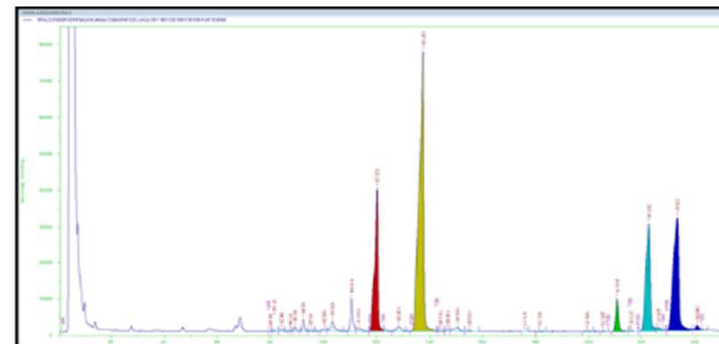
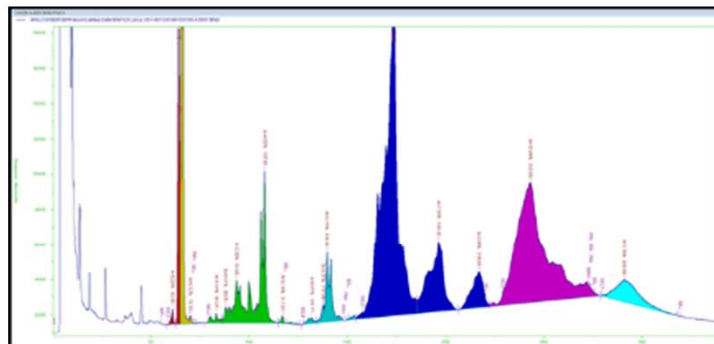


Food Grade Fatty Acids (batch endpoint determination)

Improved product quality,
neither over nor under
"cooked"



Short cycle times resulted in 4 batches per day up from 3 batches per day by simply using CALIDUS ultrafast GC ~700 second cycles vs previous 35 minutes

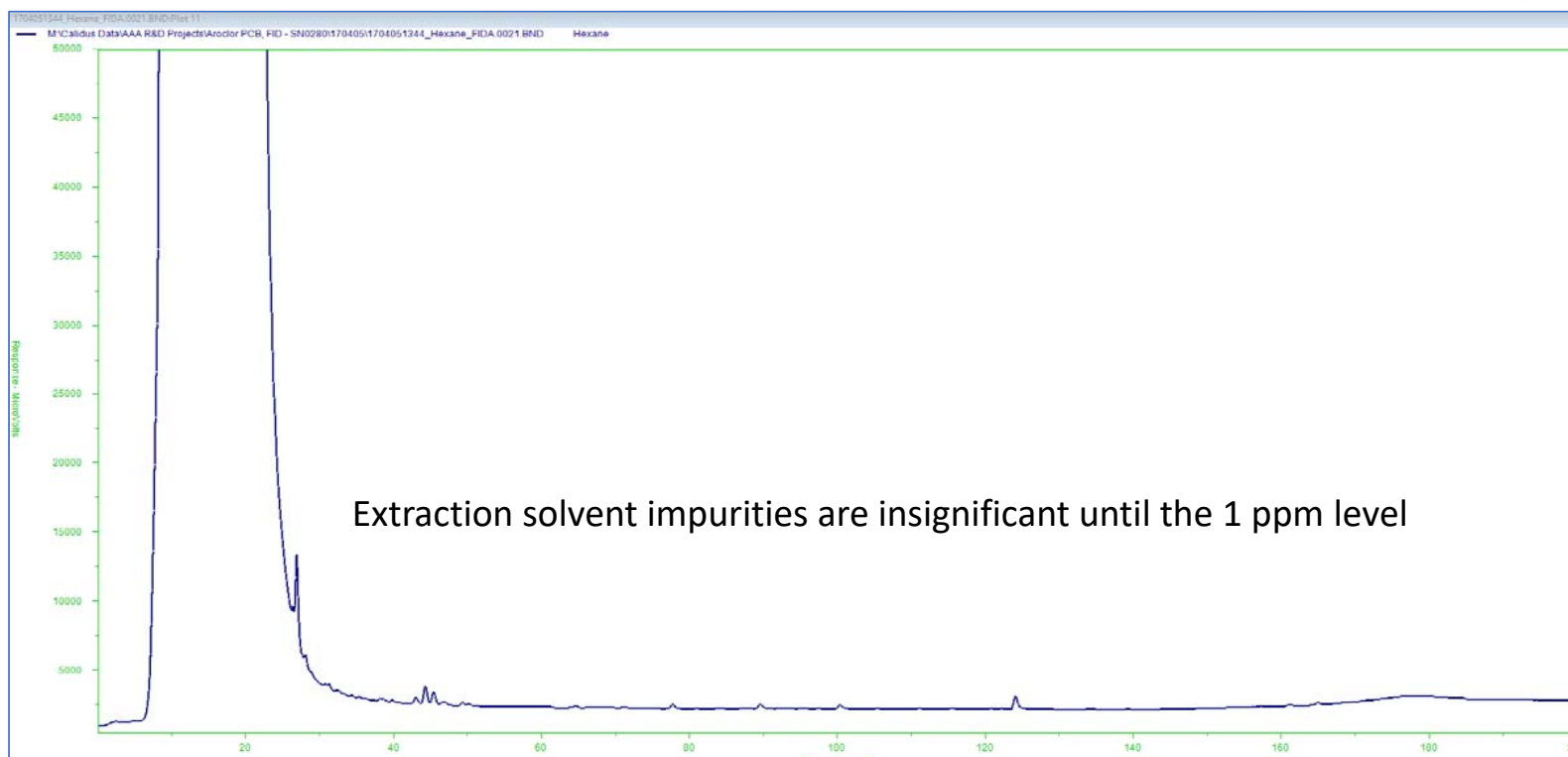


Hexane Extraction Solvent for Aroclor



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

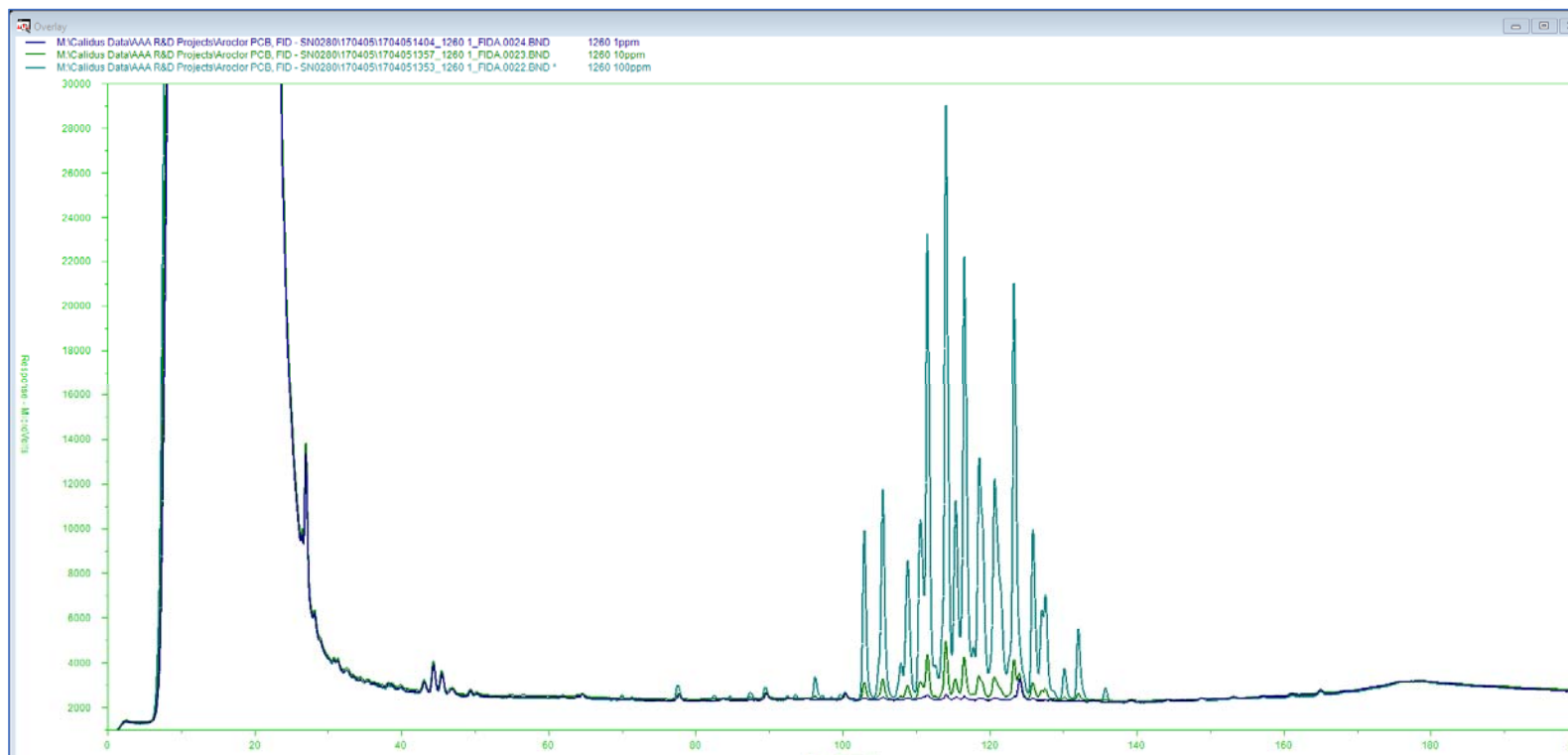
**FAST
&
Sensitive**



Aroclor PCBs – 1, 10 & 100 ppm



Full scale at 30,000 microvolts



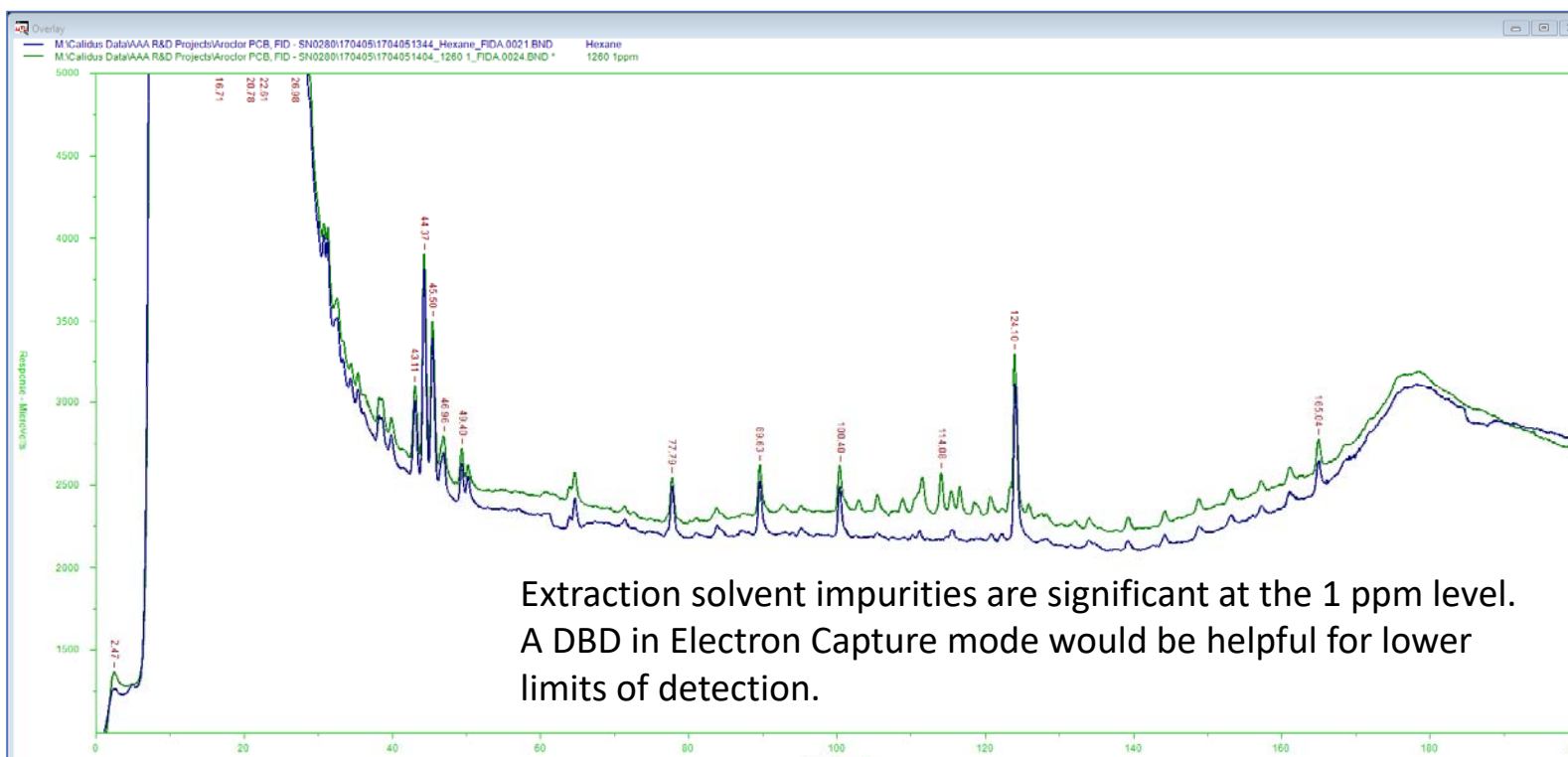
**FAST
&
Sensitive**

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**





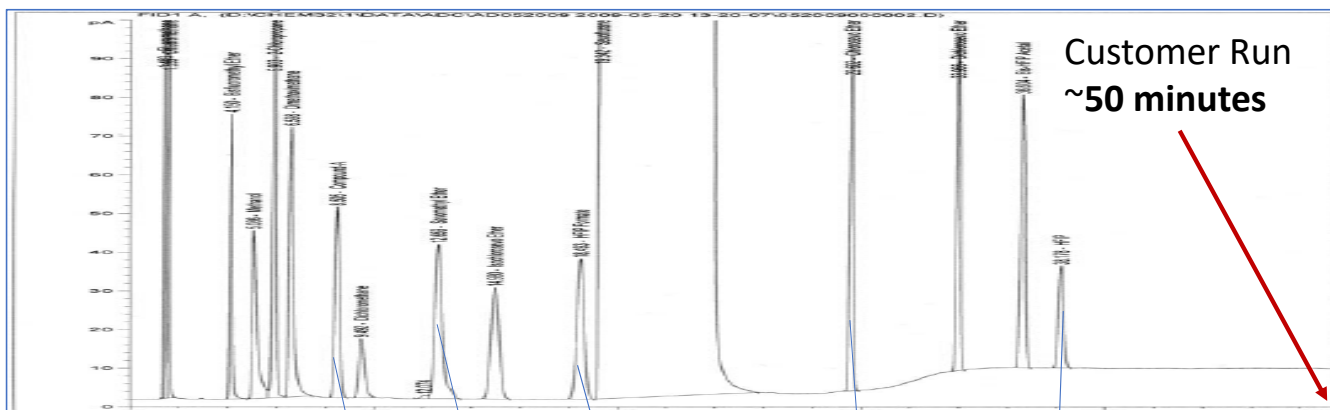
FAST

Pharmaceutical
Applications

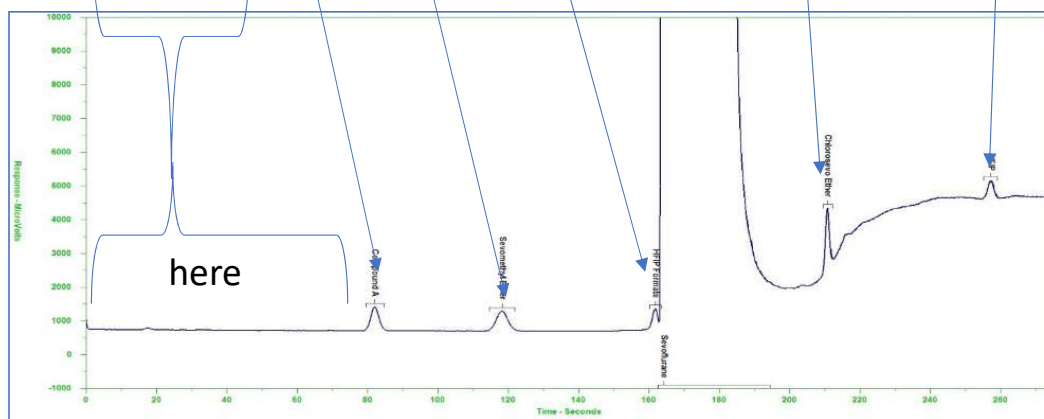
Anesthetics and residual
solvents



Anesthetic “non-quantitative impurity standard”



Plenty of
space for
these



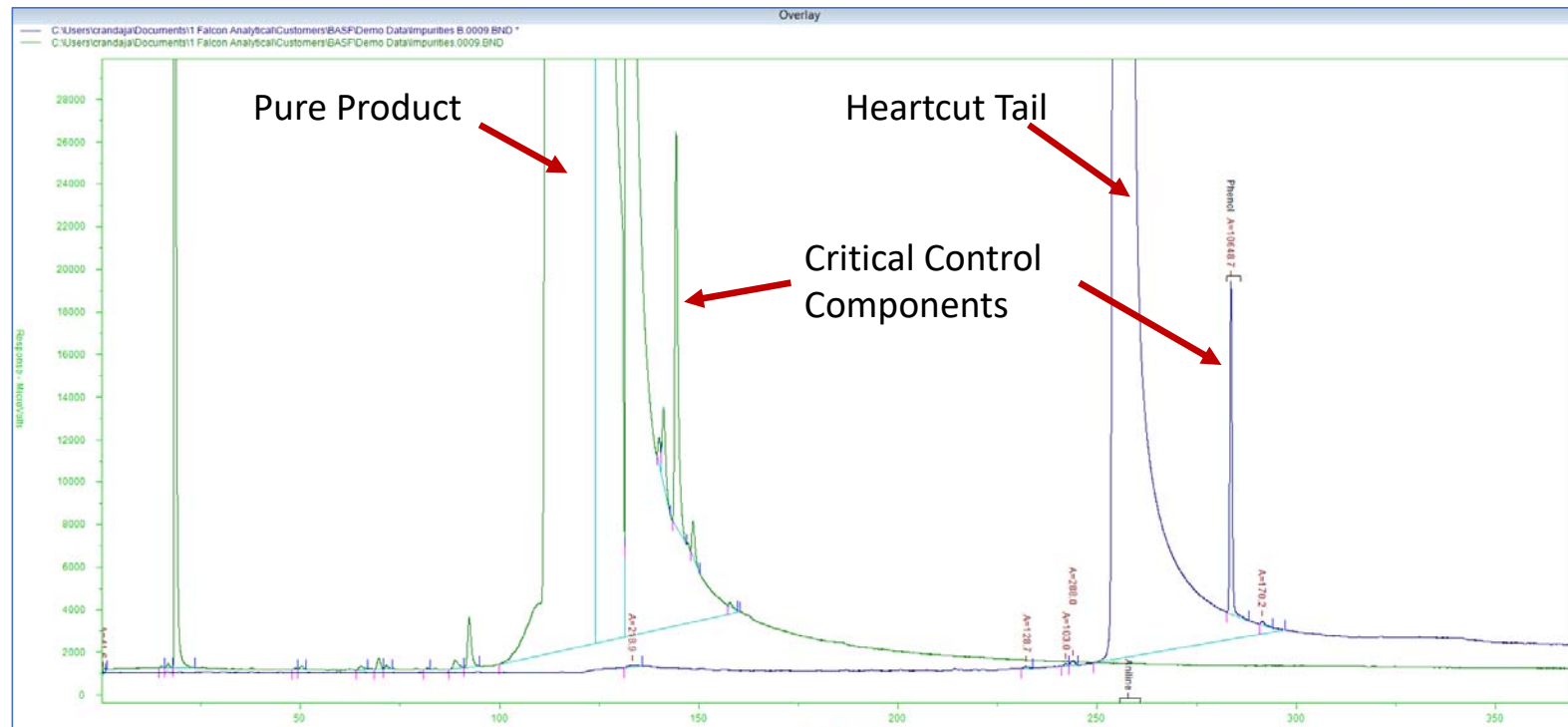


**FAST, Selective
and Sensitive**

Parts per million level
impurity measurements

- 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





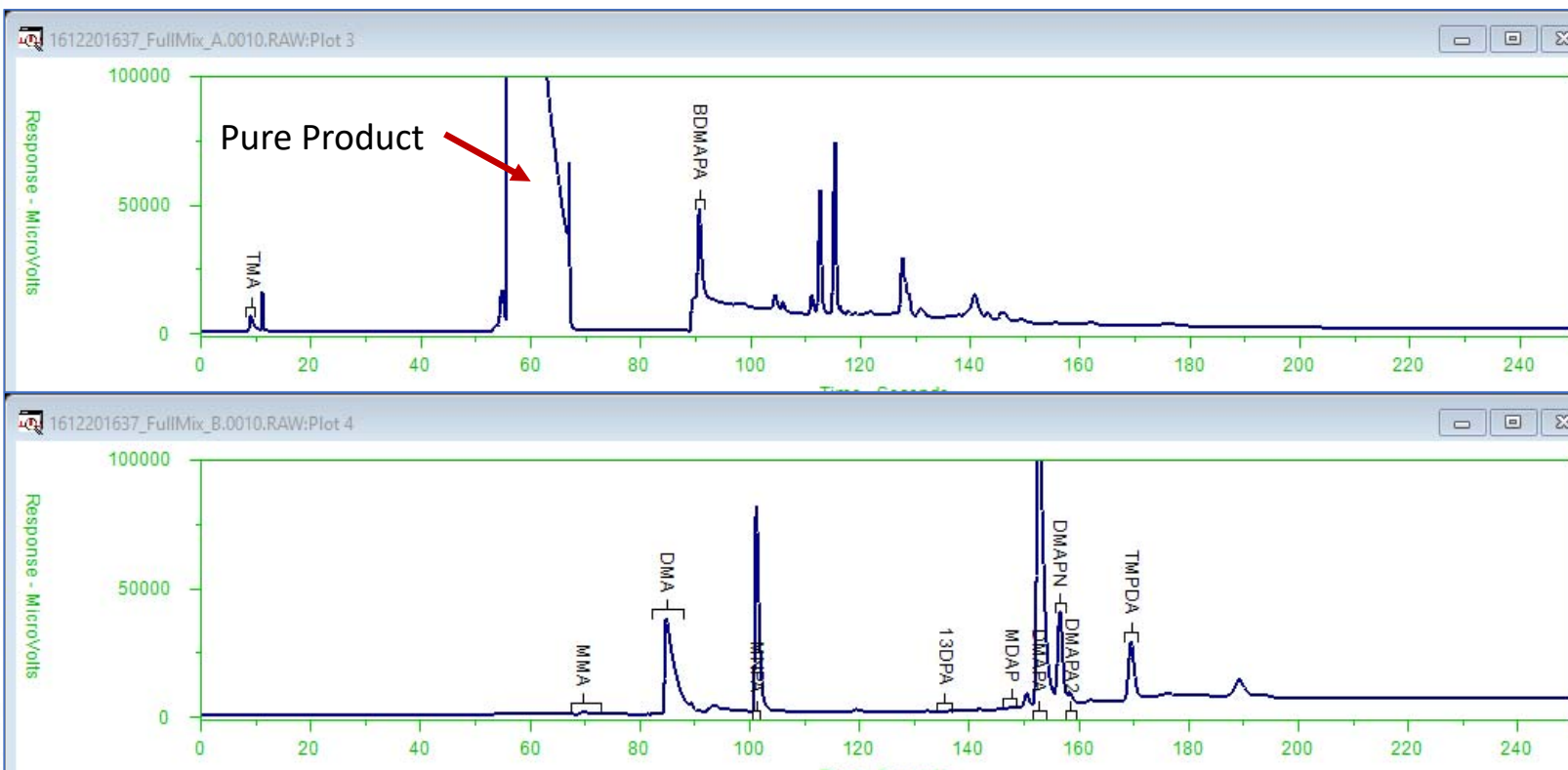
**FAST, Selective
and Sensitive**

Parts per million level
impurity measurements



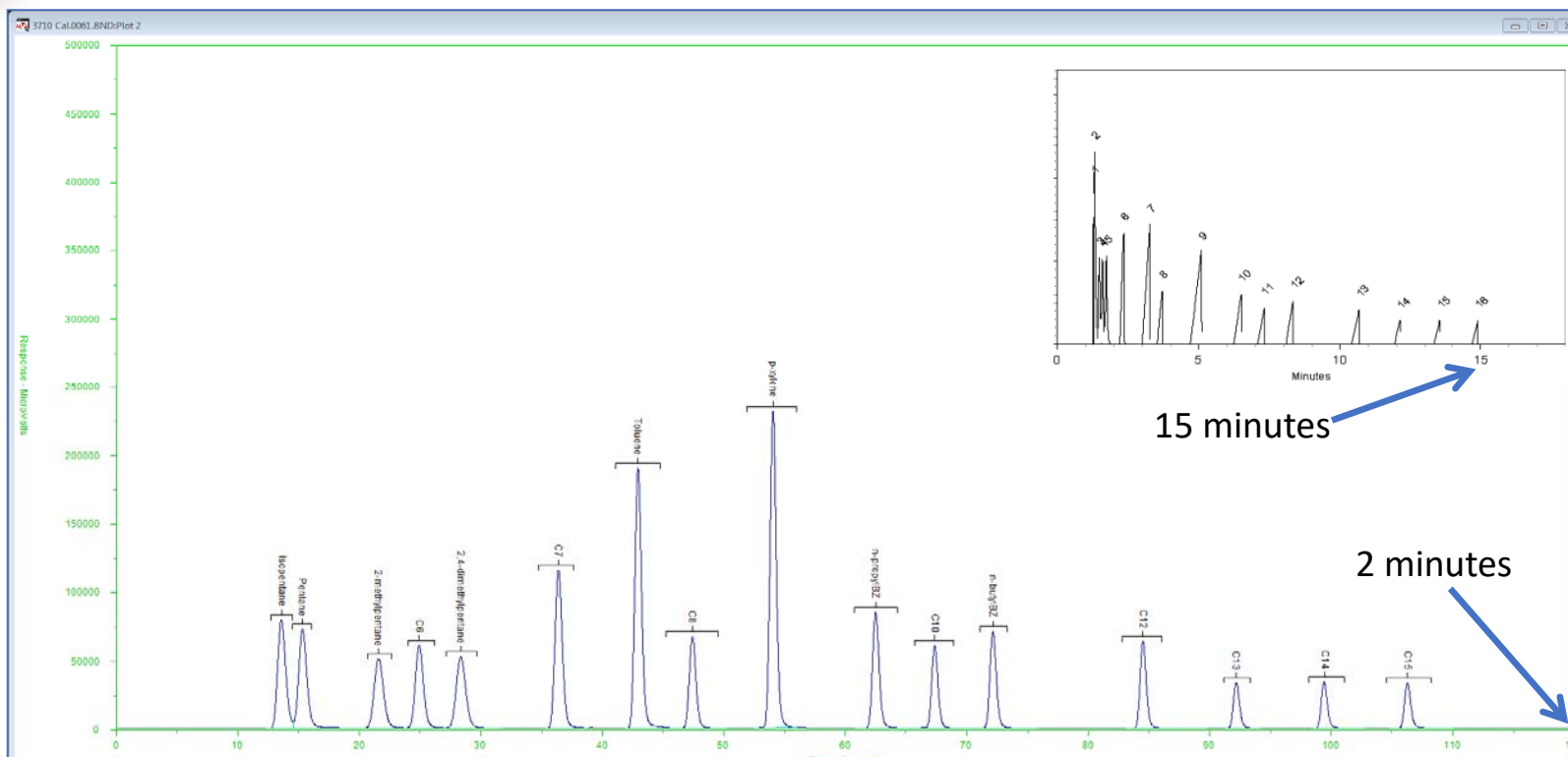
- Impurities in Pure Product

- 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
Gasoline
Simulated
Distillation

Restek ASTM D-3710-95 Standard

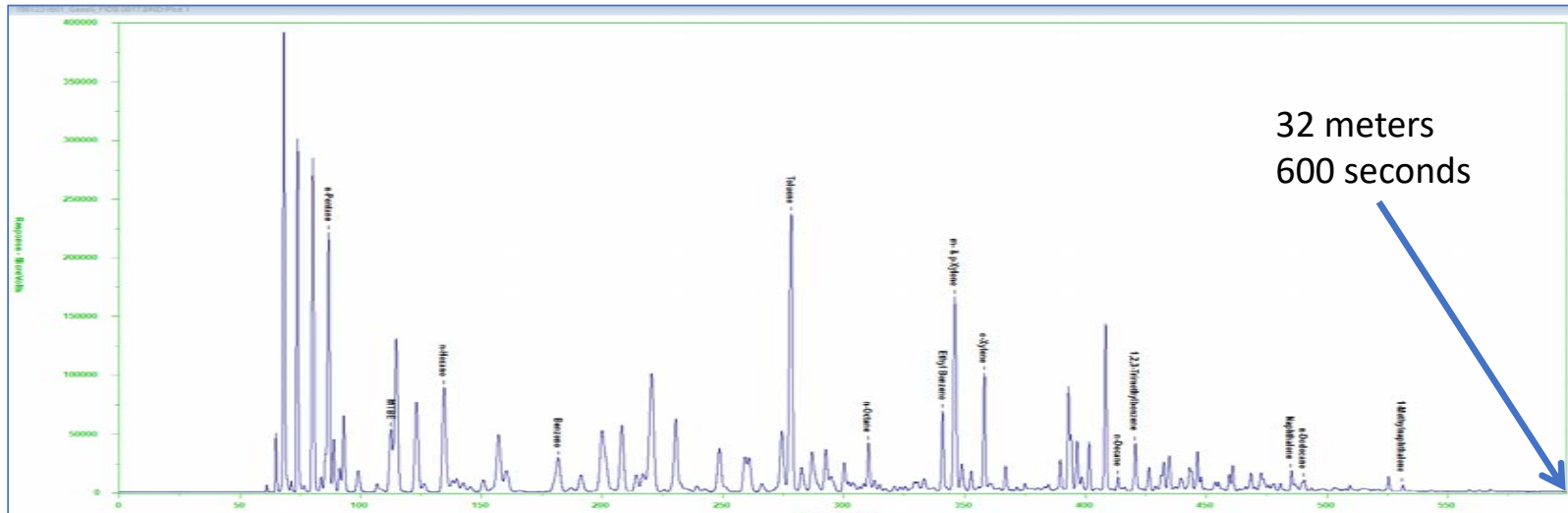
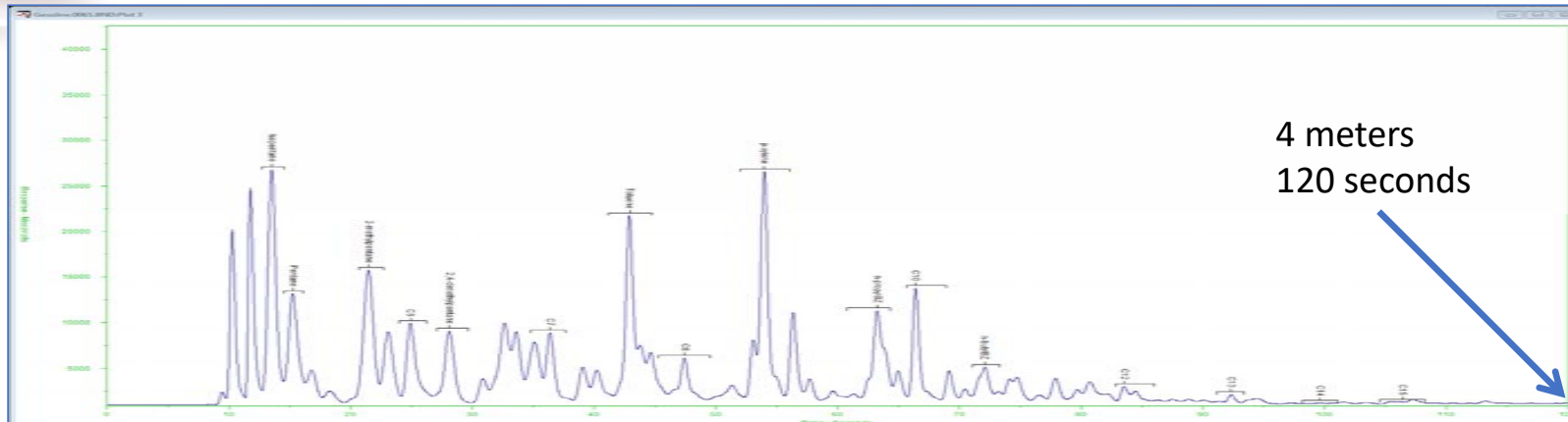




FAST
Gasoline
Simulated
Distillation



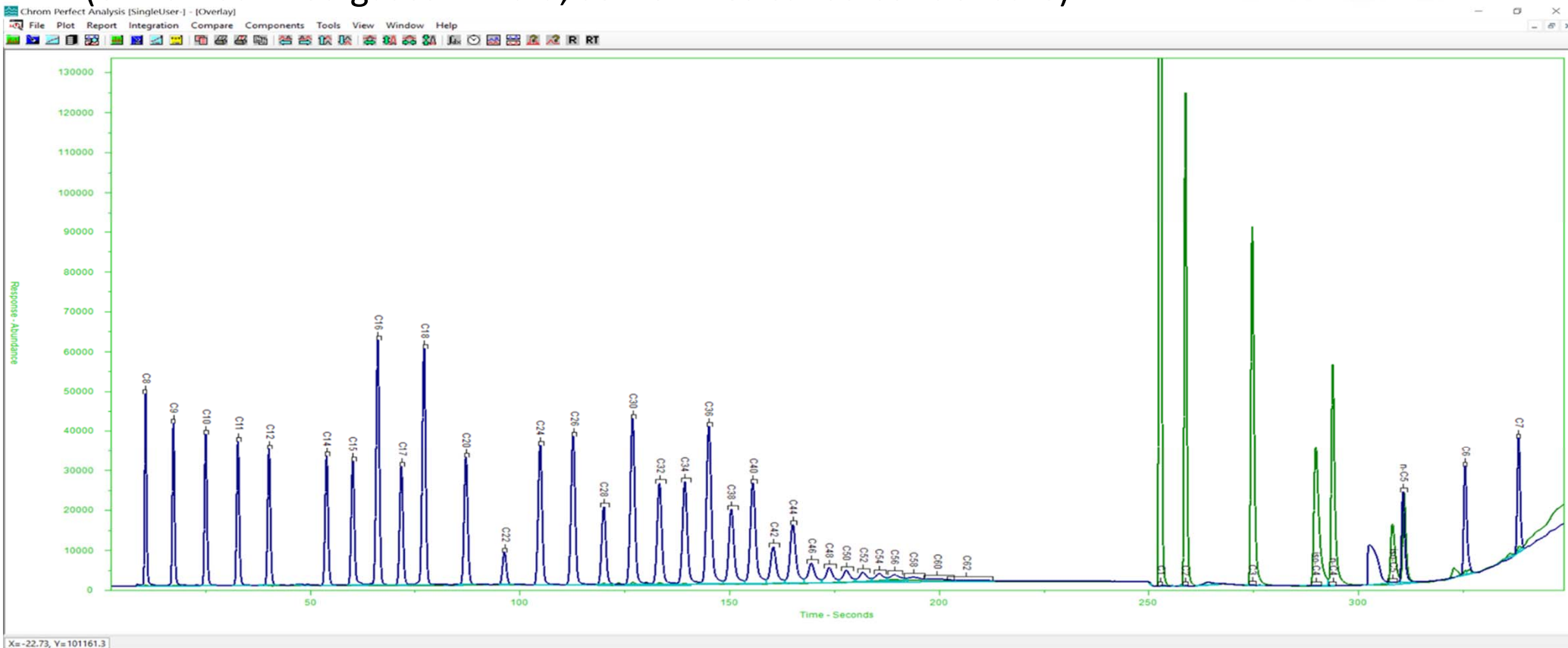
Premium Unleaded Gasoline



To the Wellhead



- Single injection up to 2000 psi drillstem fluid (entrained fixed gases in fluid, sometimes called condensate)

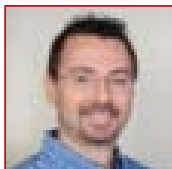


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Sensitive

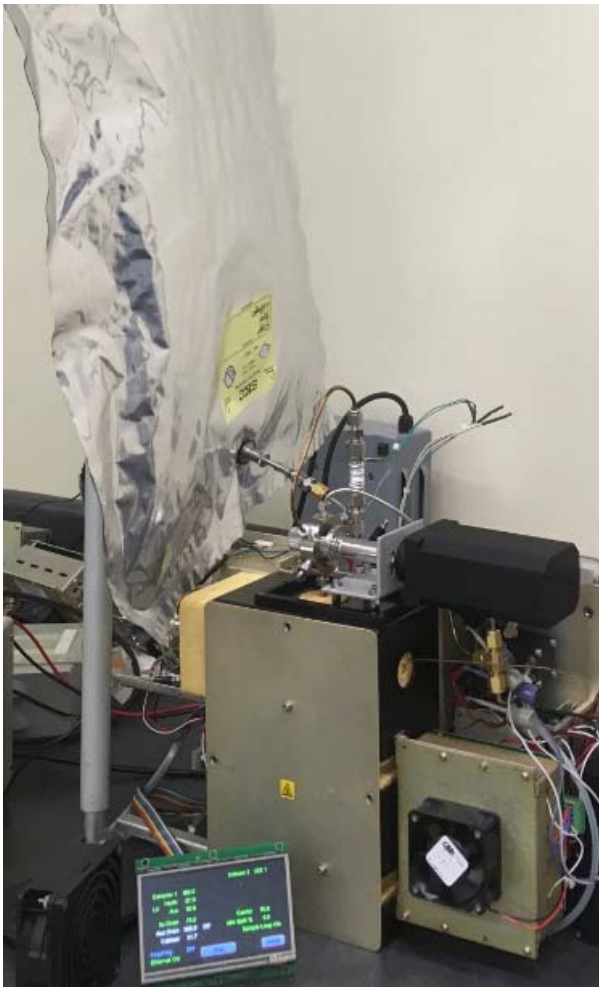
Parts per trillion for tracer component



- 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



25L Aluminized Sample Bags...

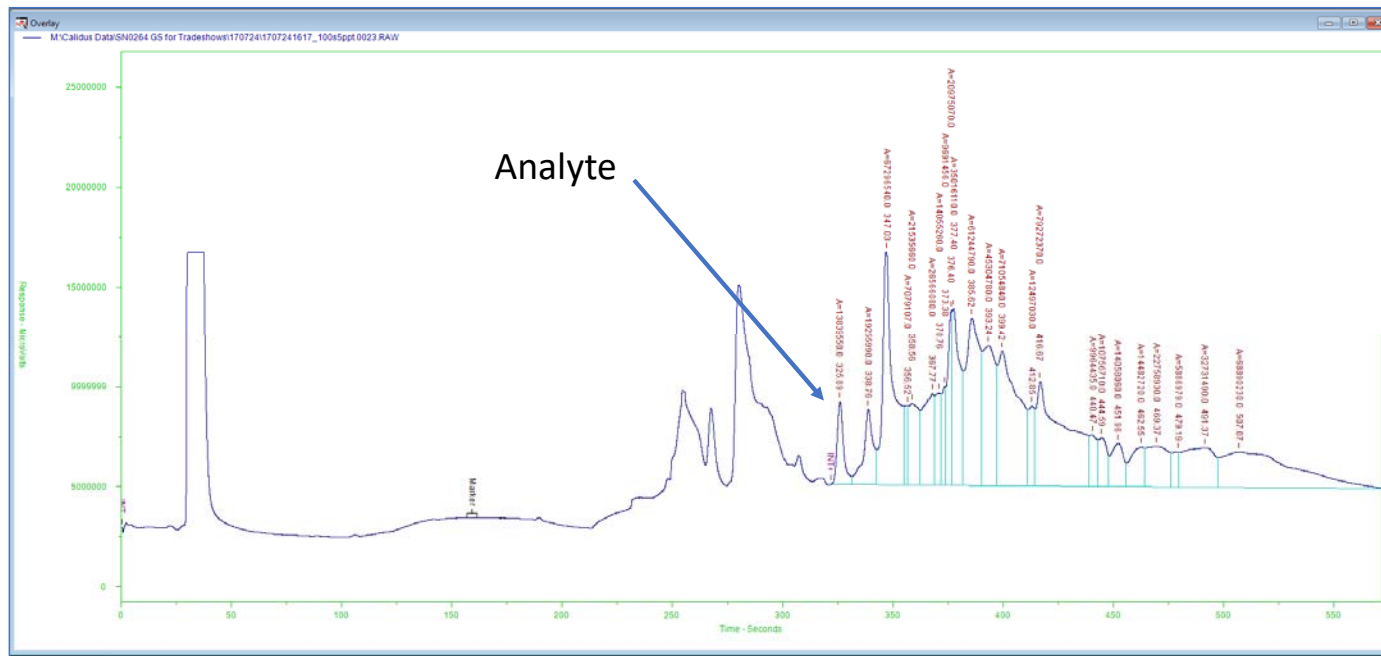


- Sampling was tricky
- Preparing quantitative calibration blends was tricky
- Every point for absorption had to be eliminated
- Huge volumes required for successive dilution to the concentration levels desired
- Parts per trillion was achieved... but this was 3 orders of magnitude too high for the client

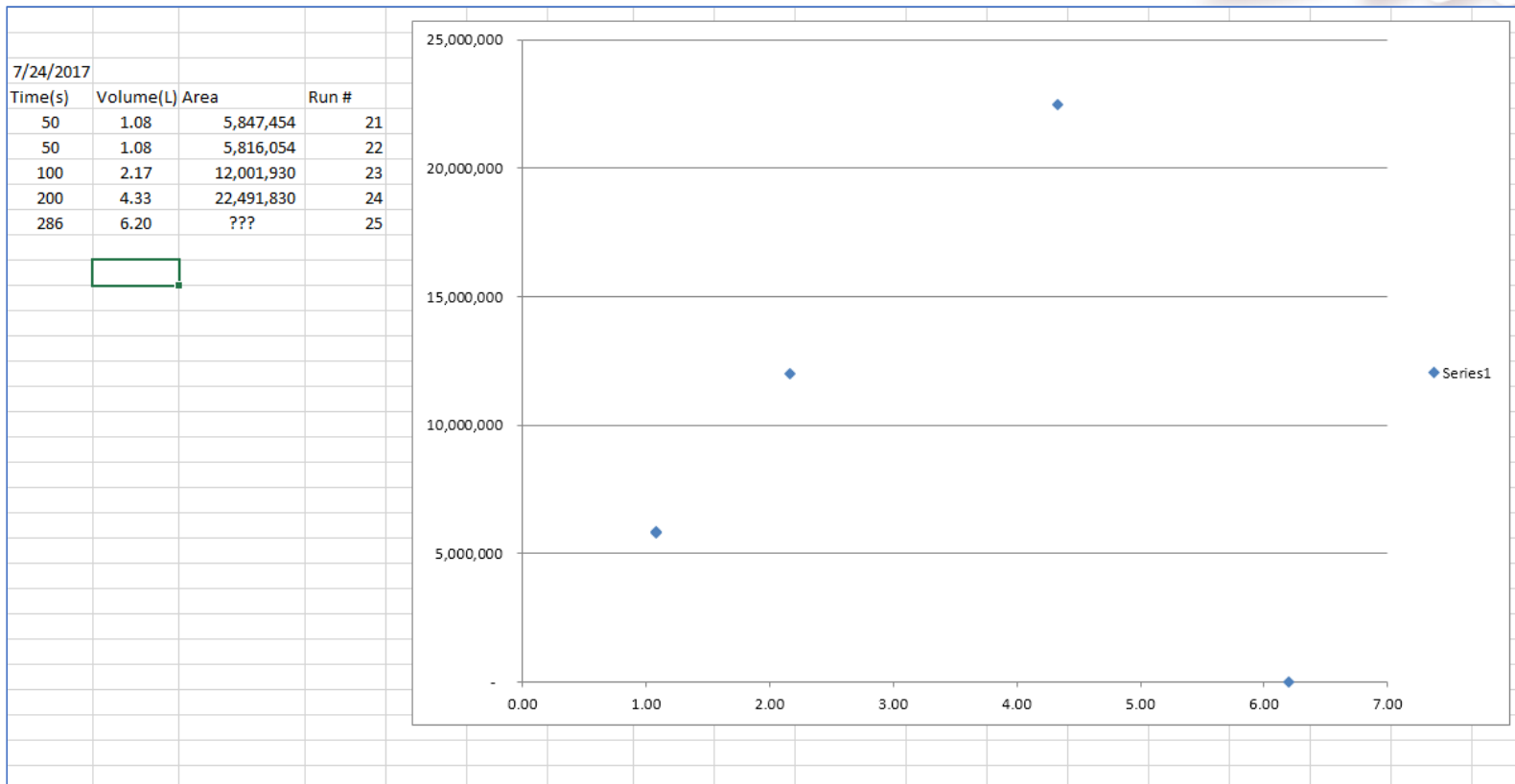
Results: Carboxen 1000



2.17L, 5ppt analyte in N2



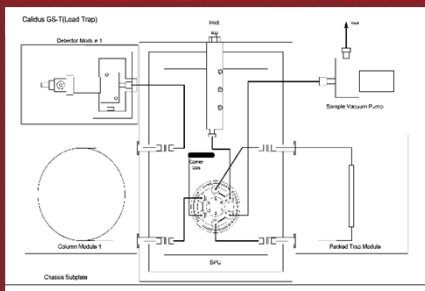
Results: Carboxen 1000



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CALIDUS GS-T



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 traditional 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

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Mico & Fast
GC using
CALIDUS

- FAST
- FAST & Sensitive
- FAST, Sensitive and Selective
- And can be extremely Sensitive...
- From the winery to the refinery to the wellhead

Questions?

