Mass Spectrometry Solutions from LECO

Life Science & Chemical Analysis Centre
St. Joseph, Michigan, USA

Outline

- Brief History of LECO
- Overview of Time-of-Flight mass spectrometry
  - – Comparison to scanning instruments
  - – LECO's TOF MS Instruments
    - Spectral reproducibility
    - Fast spectral acquisition rates
    - Increased linear dynamic range
    - Deconvolution Overview
- Experimental Studies for:
  - – Sampling Rate
  - – Deconvolution Capability
  - – Usage as a High-Speed GC and GCxGC detector
- GCxGC Overview
  - – GCxGC Theory
  - – Experimental Examples

LECO Corporation

- Privately owned, 3rd generation U.S. Company
- Introduced first rapid carbon determinator to steel industry in **1936**
- Headquartered in Saint Joseph, MI
- Completely vertically integrated
- 25 global subsidiaries serving 100 countries

LECO Background

- A broad base of technological expertise
  - Mass Spectrometry (TOF)
  - Organic and Inorganic Elemental Analysis
  - Materials Characterization
  - Microscopy and Image analysis

Brief History of LECO in TOF-MS

- LECO has always been about "Delivering the Right Results", since establishment nearly **75** years ago
- Circa 1991 began collaboration with Indiana University on ICP-TOF.
- Circa 1995 licensed Michigan State University DAS (ITR) and data processing patents.
- Pegasus GC-TOF and GC x GC TOF systems 500 sps
  - Pegasus 1996
  - Pegasus II 1997
  - Pegasus III 2000
  - Pegasus 4D 2002
  - Pegasus HT 2005
- TruTOF HT benchtop GC-TOF 2007 80 sps
- Citius High Res TOF (LC-HRT) 2011 200 sps
- Pegasus High Res TOF (GC-HRT) 2011 200 sps

LECO Separation Sciences

Delivering the Right Results

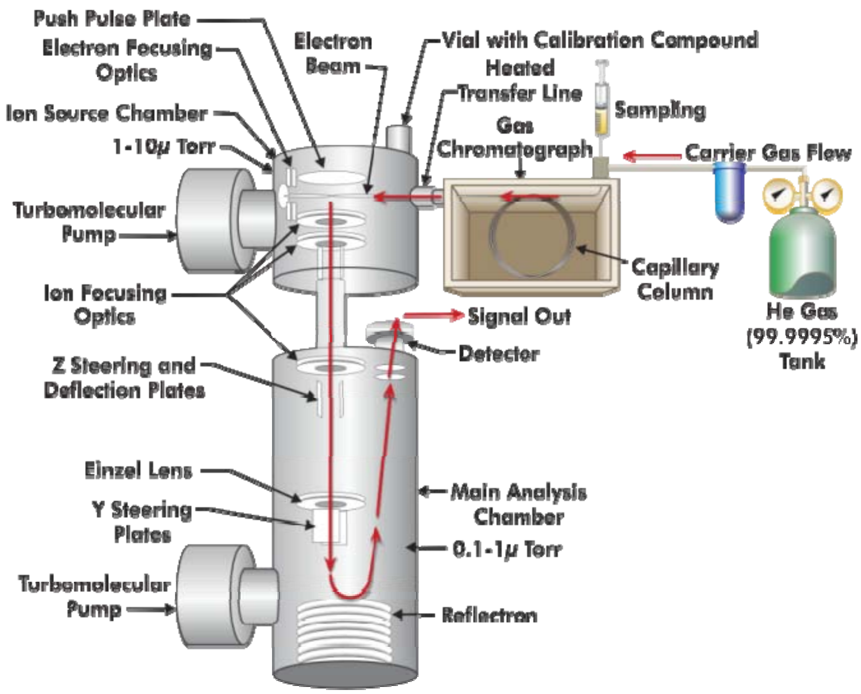
2011 Pittcon Editor's Gold Award

Citius LC-HRT
Pegasus GC-HRT

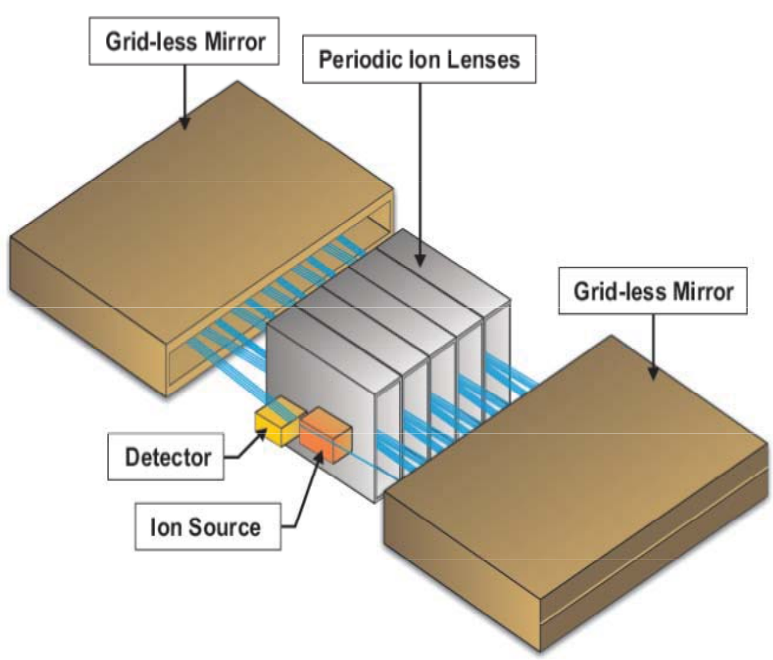
Pegasus 4D and HT

TruTOF HT

Time-of-Flight Mass Analyzers

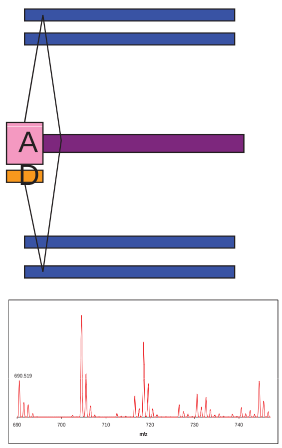


Time-of-Flight Mass Analyzers

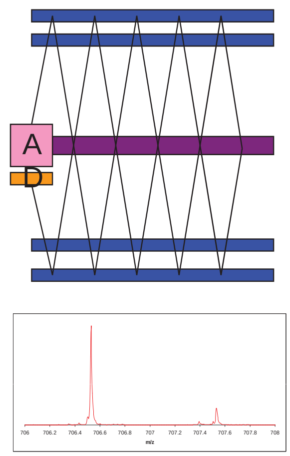


Modes of Analyzer Operation

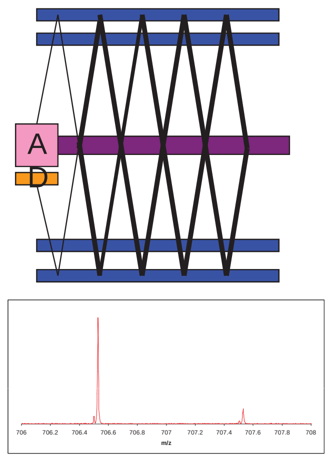
Nominal Mode	High Resolution Mode	Ultra-High Resolution Mode



R=2,500
m/z = 50-2500

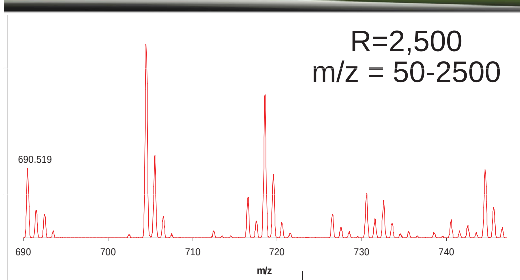


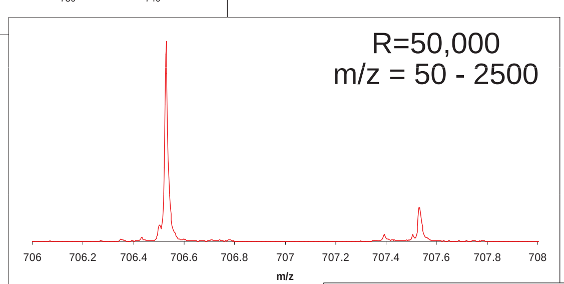
R=50,000
m/z = 50 - 2500

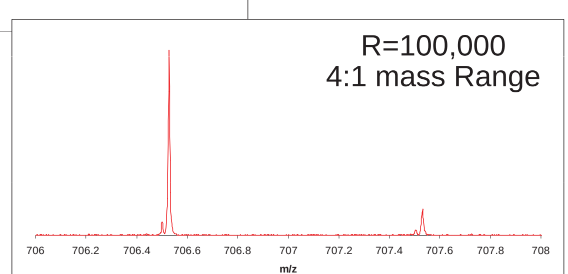


R=100,000
4:1 mass Range

Modes of Analyzer Operation







Benefits of Quads and TOFs

- Quadrupole
  - Inexpensive
  - Robust
  - Good for Qualitative and Quantitative work
  - Enhanced Detection Limits when operating in SIM
- Time-of-Flight
  - Excellent Qualitative and Quantitative results in single run
  - No Spectral Bias (skewing)
  - Excellent Detection Limits
  - Very Fast acquisition rates (up to 500 spectra/s)

Sampling Rate

- Quadrupoles
  - Scanning Instrument at 10,000 u/sec (~20 Hz)
    - Duty Cycle Time
  - Increase Scan Rate by Limiting Mass Range
    - (40 – 200 amu)
- Time-of-Flight
  - Non-Scanning Instrument
    - Full Mass Range Acquisition
    - All Masses are Collected
    - Acquisition Rates up to 500 spectra/s (500 Hz)

Sampling Rate is important for properly defined peaks and deconvolution

Proper Sampling Rates

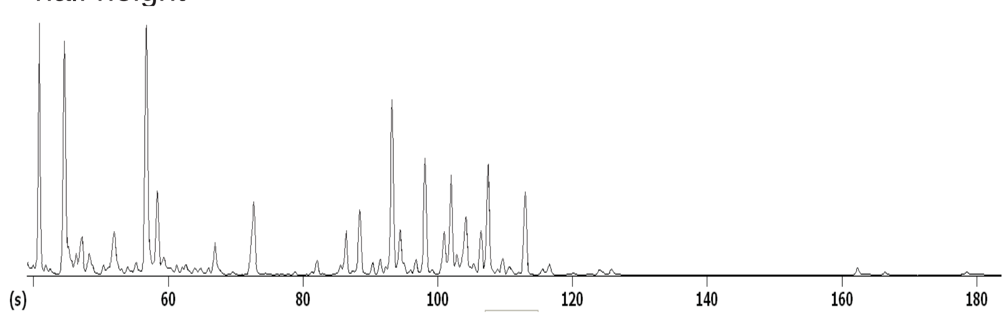
- Literature defines the proper sampling rate of a chromatographic detector to have an acquisition speed capable of delivering at least 10 points across a fully resolved peak to deliver accurate quantitative data

- For a 0.2s wide peak, what acquisition rate would you choose?
  A) 10Hz
  B) 20Hz
  C) 50Hz
  D) 100Hz
  E) 200Hz

Proper Sampling Rates

- Most samples are complex and do not contain fully resolved chromatographic peaks – therefore some method of deconvolution is needed.

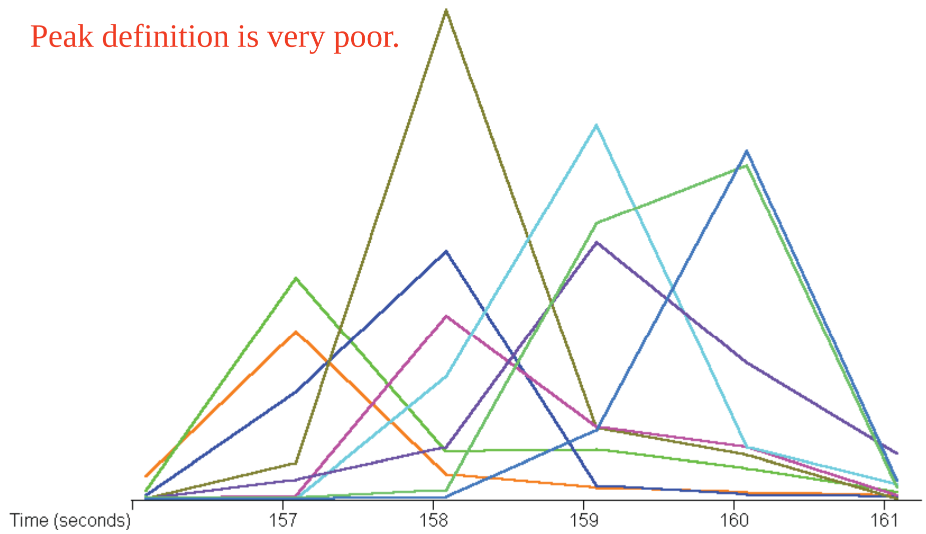
- LECO has published results showing that the statistical power of deconvolution is optimal with 12 data points across peak width at half height



Spectral Acquisition Rate

1 Spectra/sec

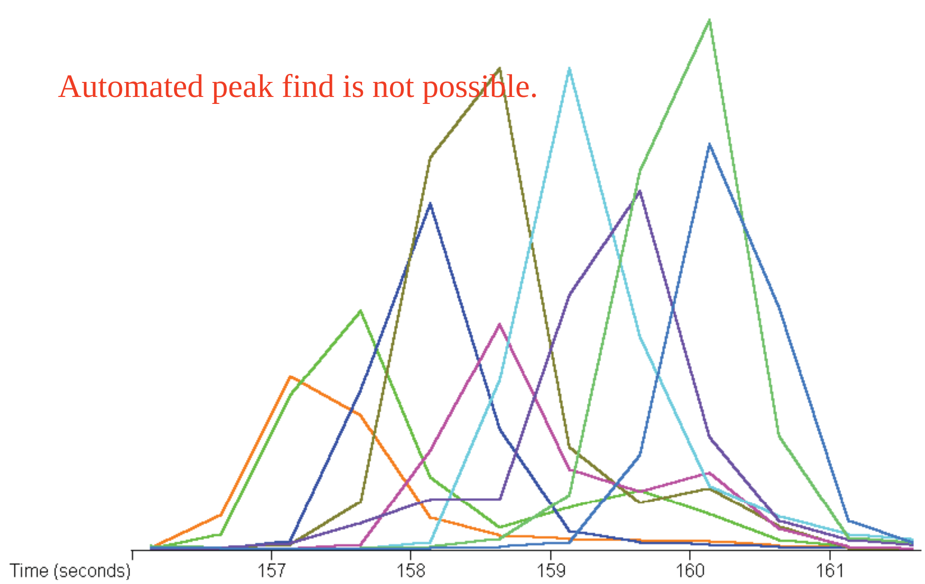
Peak definition is very poor.



Spectral Acquisition Rate

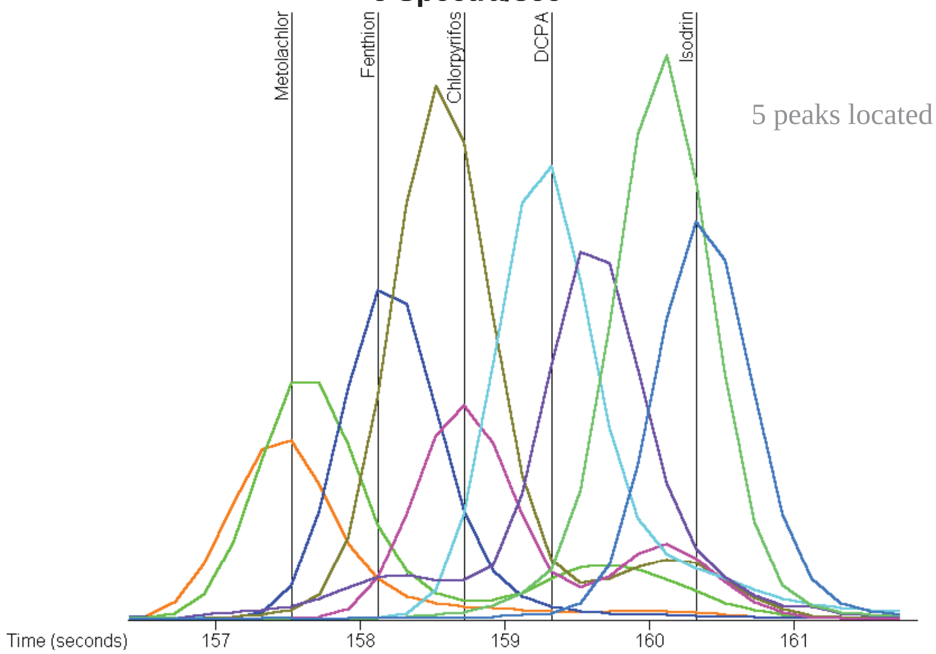
2 Spectra/sec

Automated peak find is not possible.



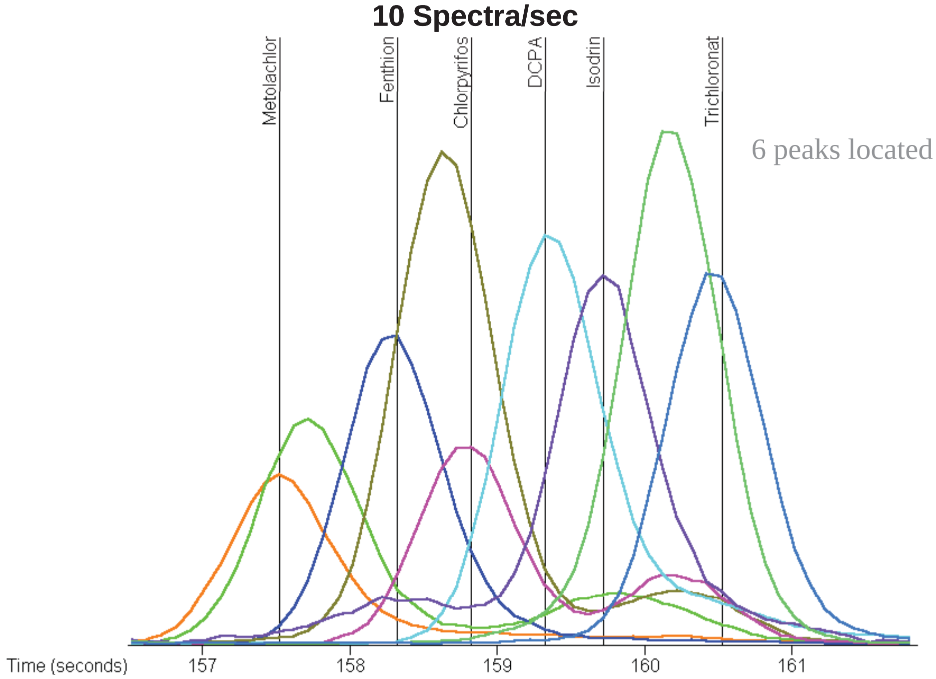
Spectral Acquisition Rate

5 Spectra/sec



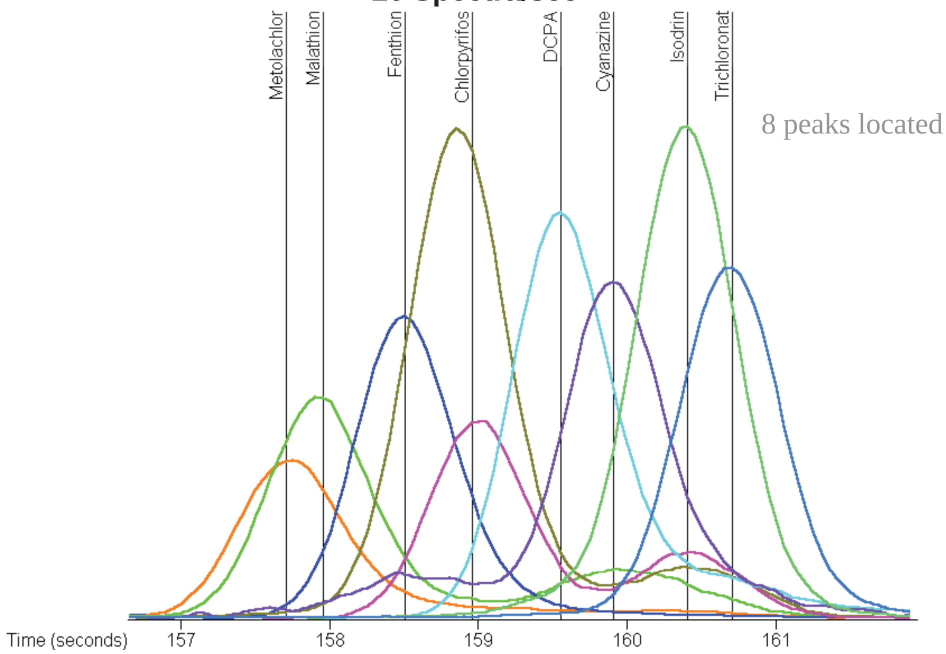
Spectral Acquisition Rate

10 Spectra/sec



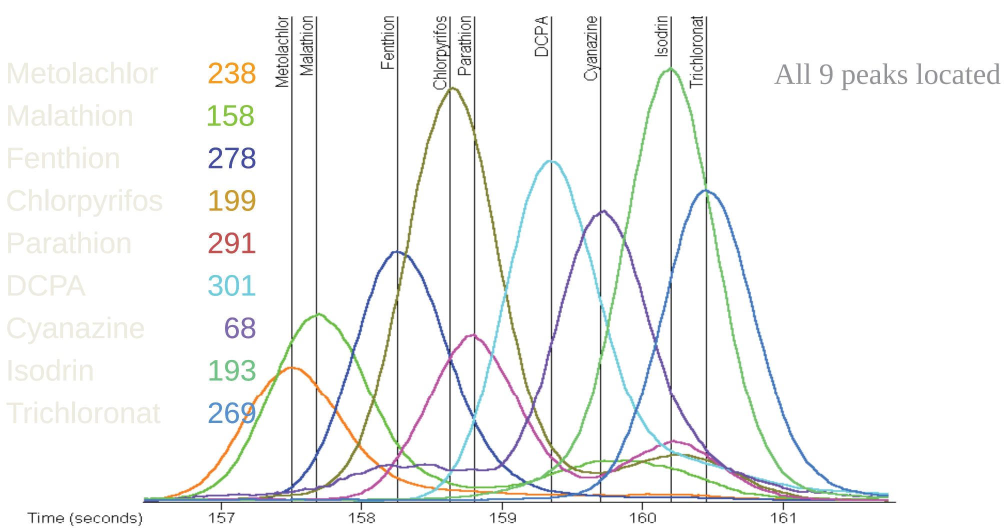
Spectral Acquisition Rate

20 Spectra/sec



Spectral Acquisition Rate

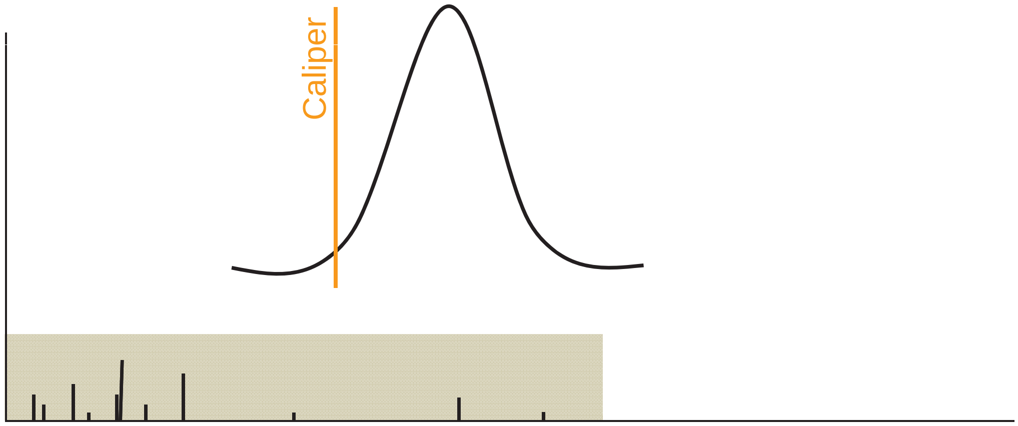
40 Spectra/sec



True Signal Deconvolution

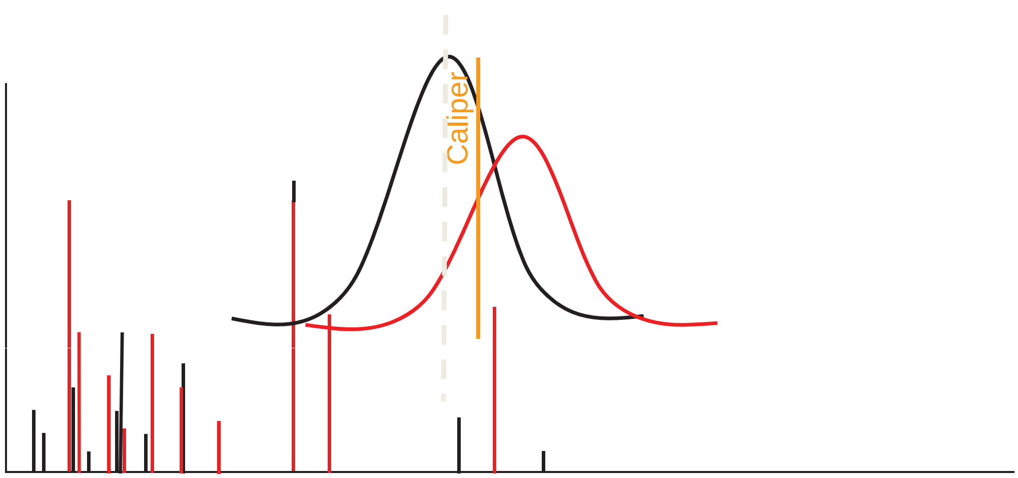
EI Spectra

A correlated set of ions
reaches the detector

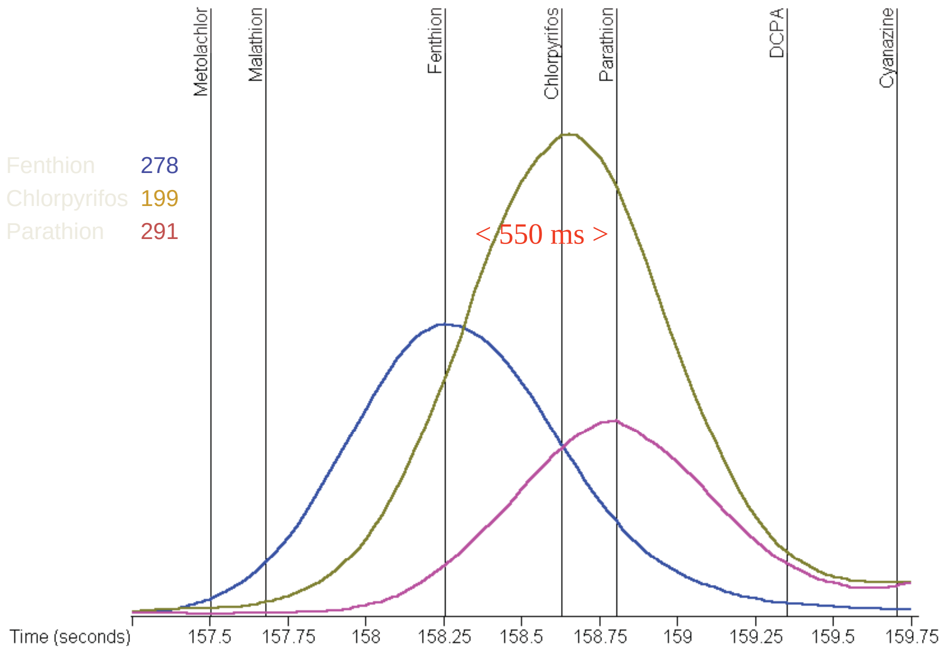


True Signal Deconvolution

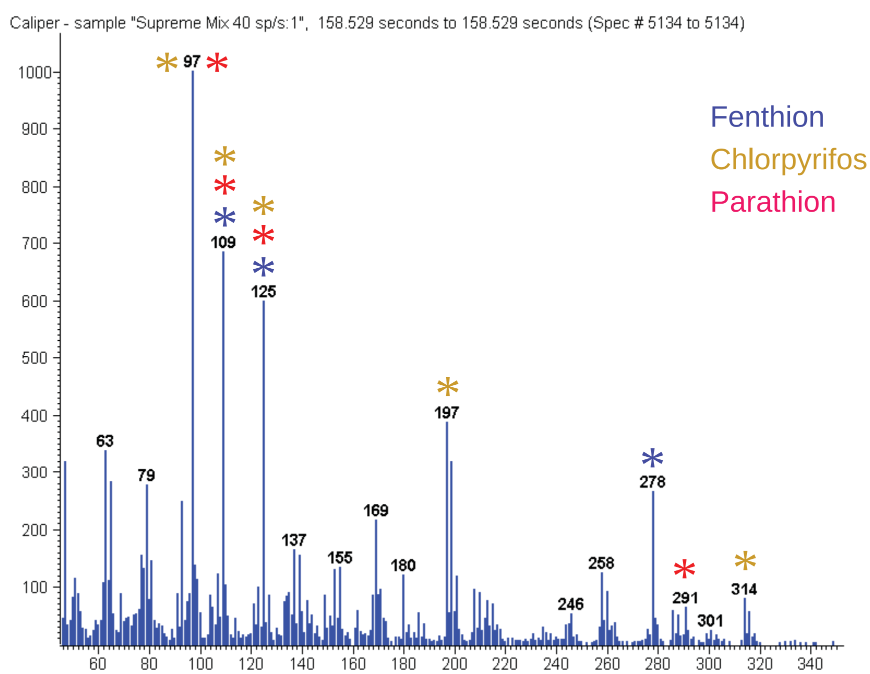
EI Spectra



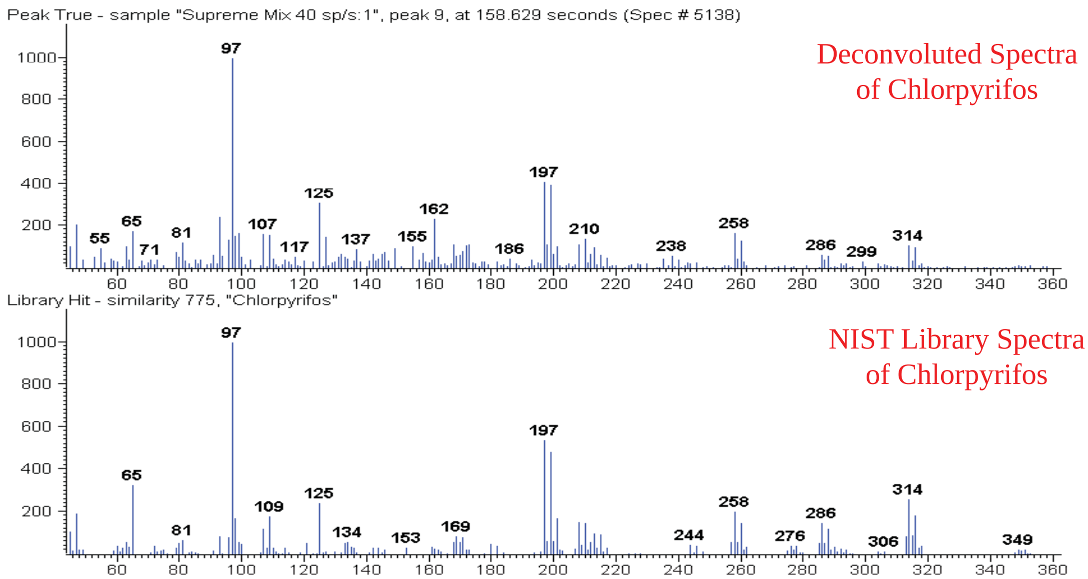
Coelution of 3 Pesticides



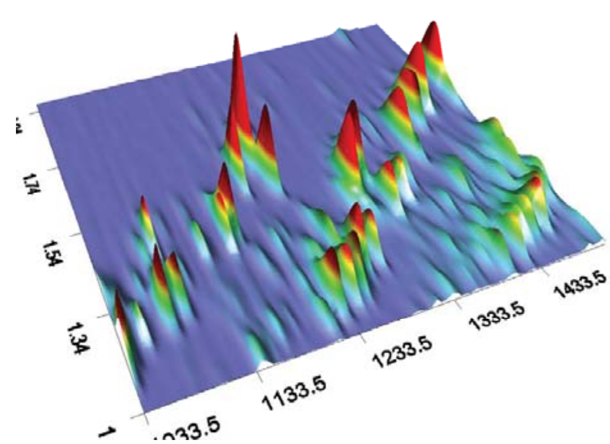
Spectral Coelution of Pesticides



Spectral Deconvolution of Pesticides



GCxGC: Theory, Practice and Optimization



Presentation Outline

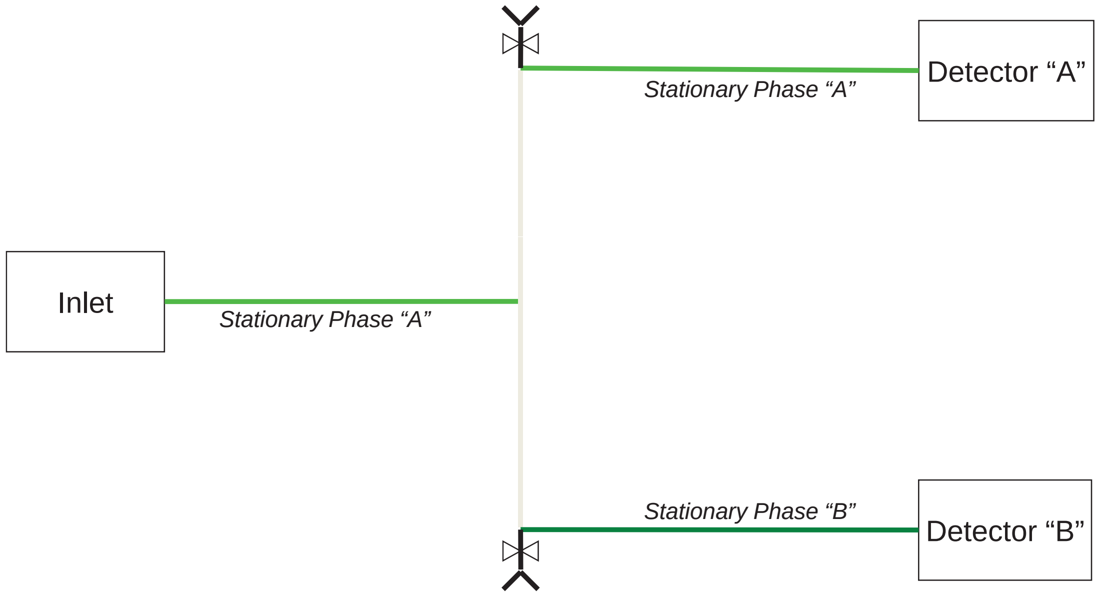
- An Introduction to GCxGC
  - What is GCxGC?
  - GCxGC Hardware
  - Interpreting GCxGC Chromatograms
- Applications
  - Environmental
  - Metabolomics
  - Petroleum
    - Advanced Data Processing
    - Classifications
    - Scripting

What is GCxGC?

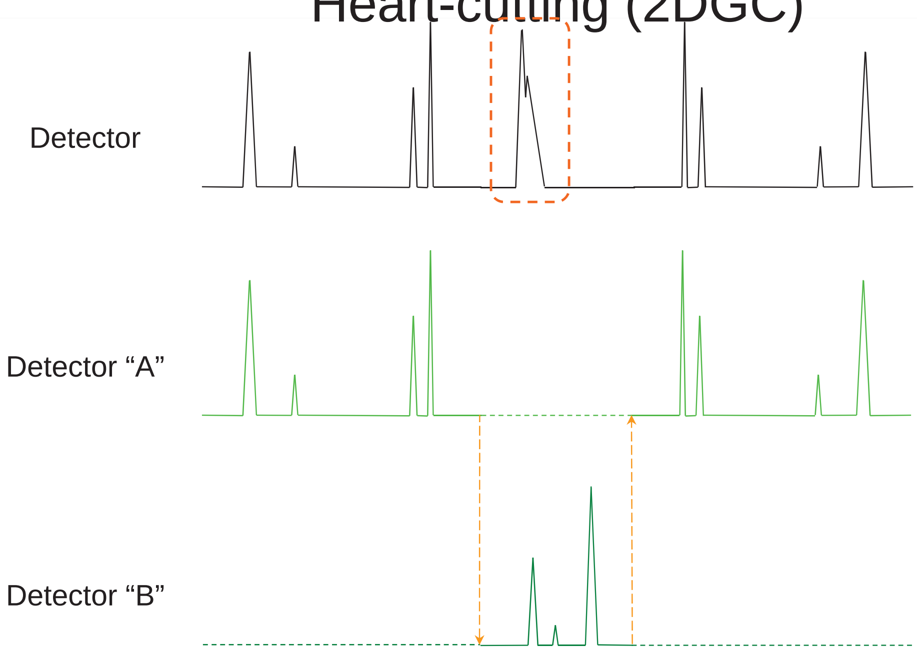
Multi-Dimensional Gas Chromatography

- 2DGC vs. GCxGC
  - 2DGC
    - Heart-Cutting
      - » Diverting a portion of effluent from a column onto a column of a different stationary phase
    - Multiple Columns
      - » Splitting the effluent from a column onto multiple columns of differing stationary phases
  - GCxGC (Comprehensive Two-dimensional Gas Chromatography)
    - Comprehensive
      - » All material that enters the 1st dimension column passes through the 2nd dimension column to the same detector
    - Uses a “Modulator” to partition 1st column effluent as discrete plugs onto the 2nd dimension column

Heart-cutting (2DGC)



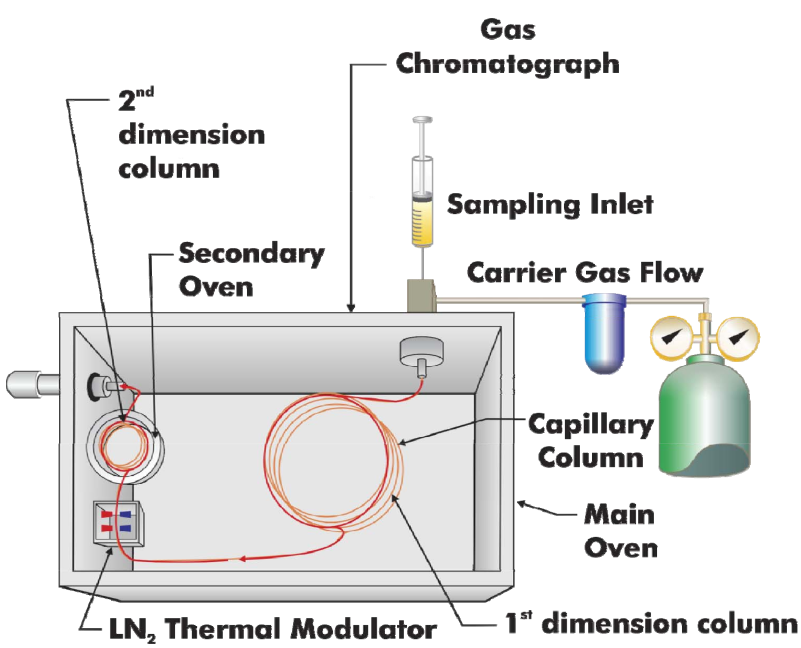
Heart-cutting (2DGC)



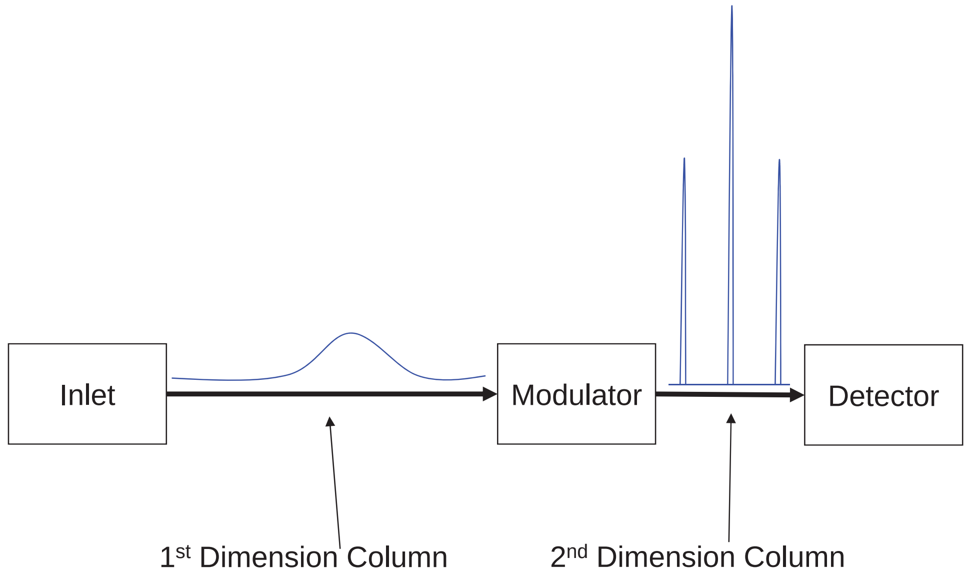
Heart-Cut 2DGC

- Each column requires an independent detector
- Each Heart-Cut must be targeted at a specific coelution
- Two data files

Thermally Modulated GCxGC Schematic



Simplified GCxGC Flow



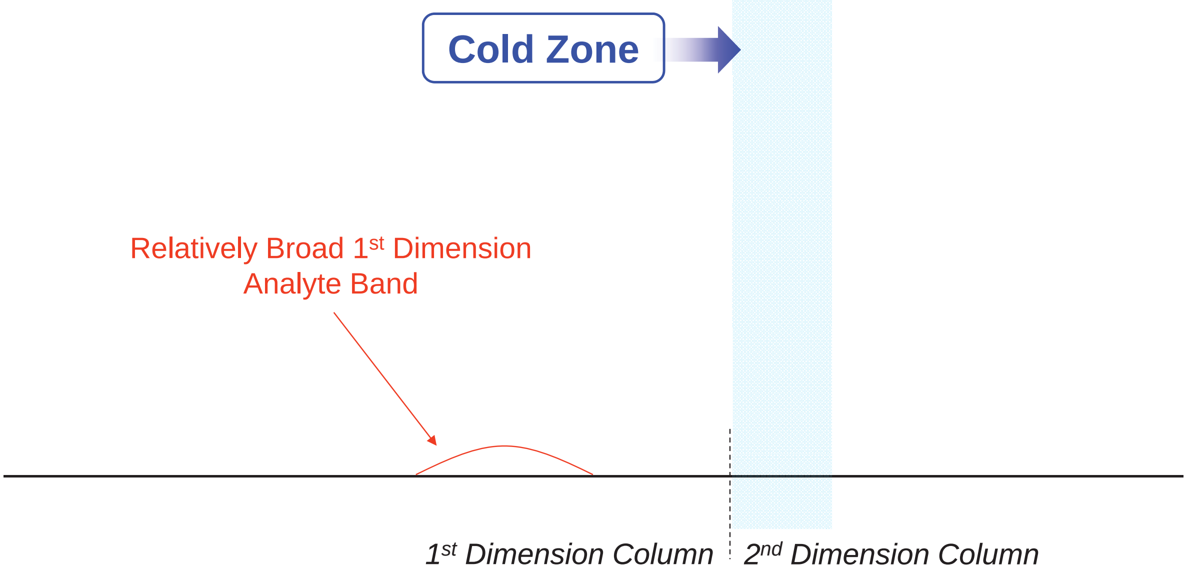
Modulation

- Modulator has two functions in GCxGC:

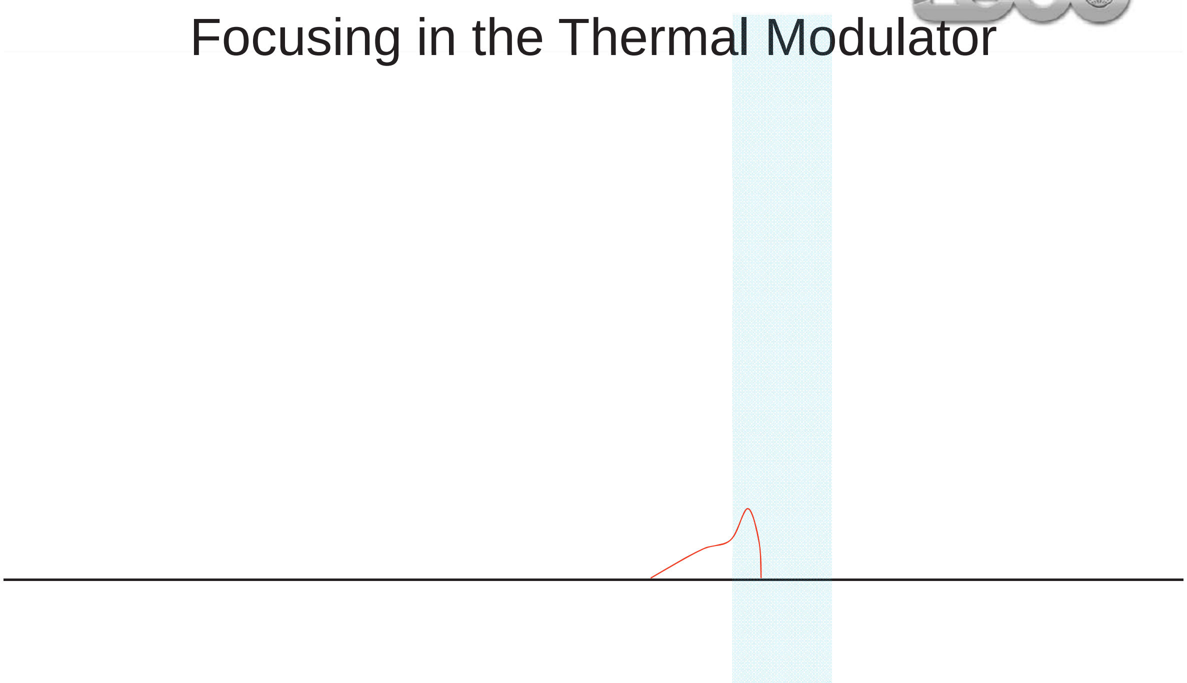
  1) Collect and focus segments of effluent from the primary column

  2) Act as the injector for the secondary column

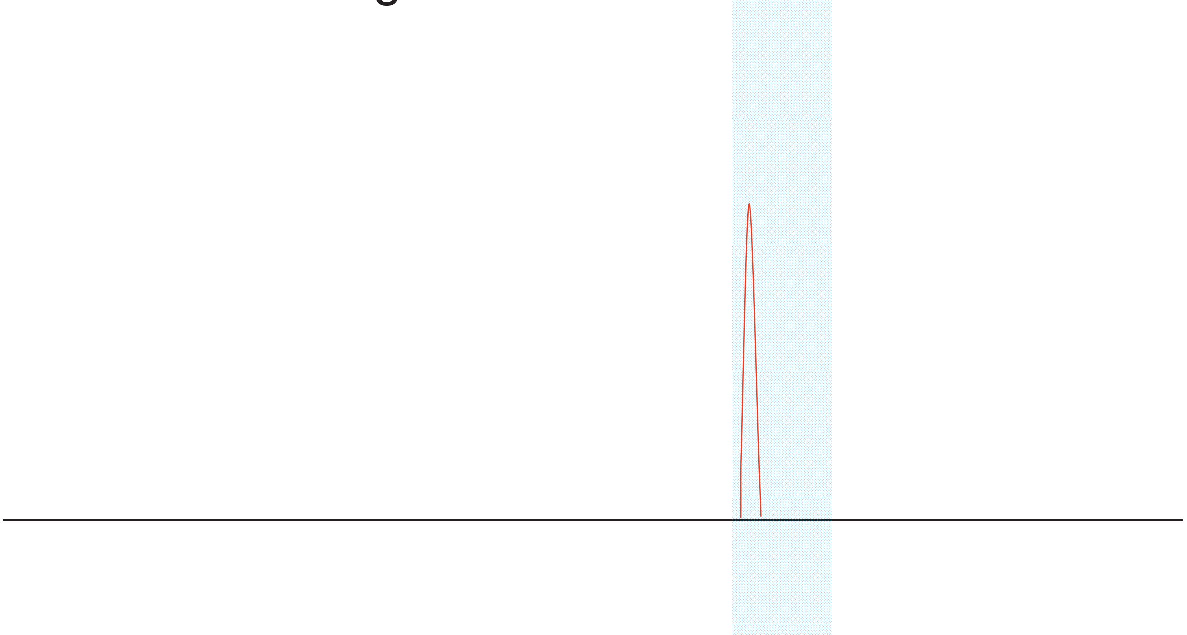
Focusing in the Thermal Modulator



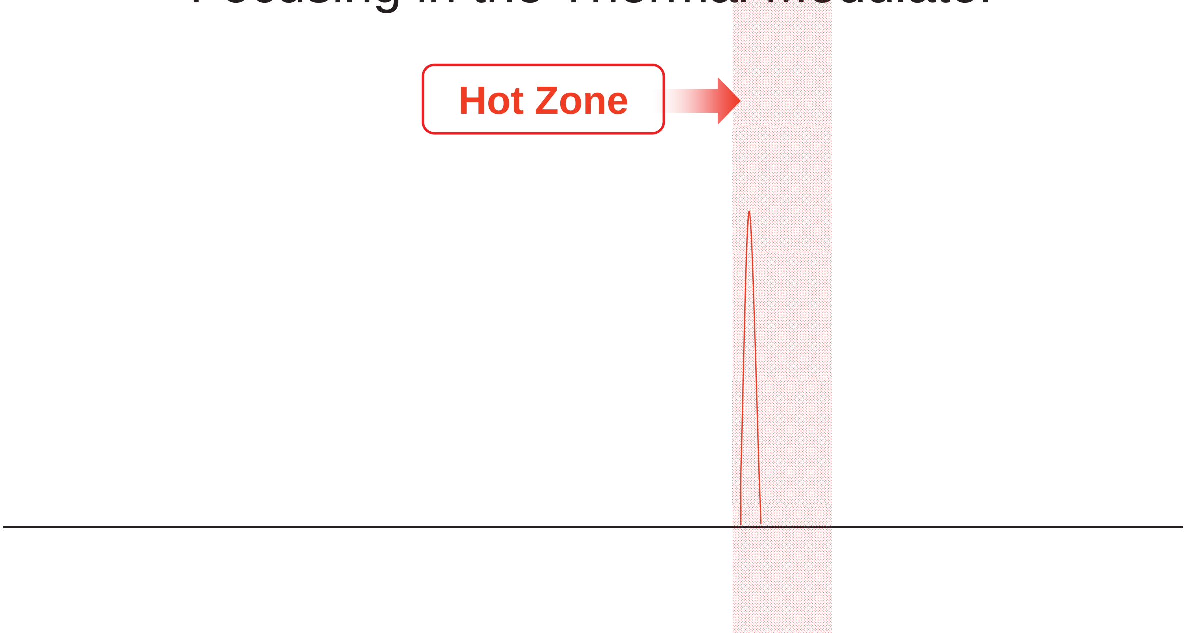
Focusing in the Thermal Modulator



Focusing in the Thermal Modulator

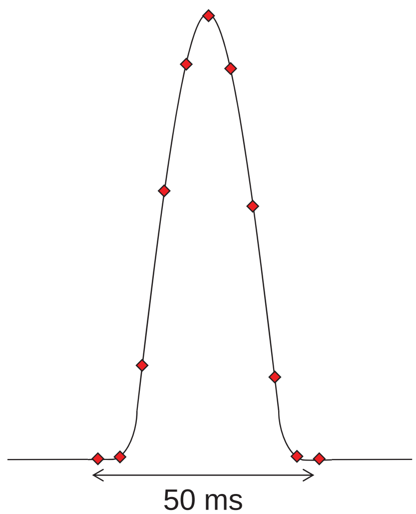


Focusing in the Thermal Modulator



Detector Requirements for GCxGC

Quantitation requires a minimum of 10 data points across a peak in order to define it



50 ms peak width at base

Need 10 data points / peak

5 ms between data points

Minimum Required Sampling Rate:

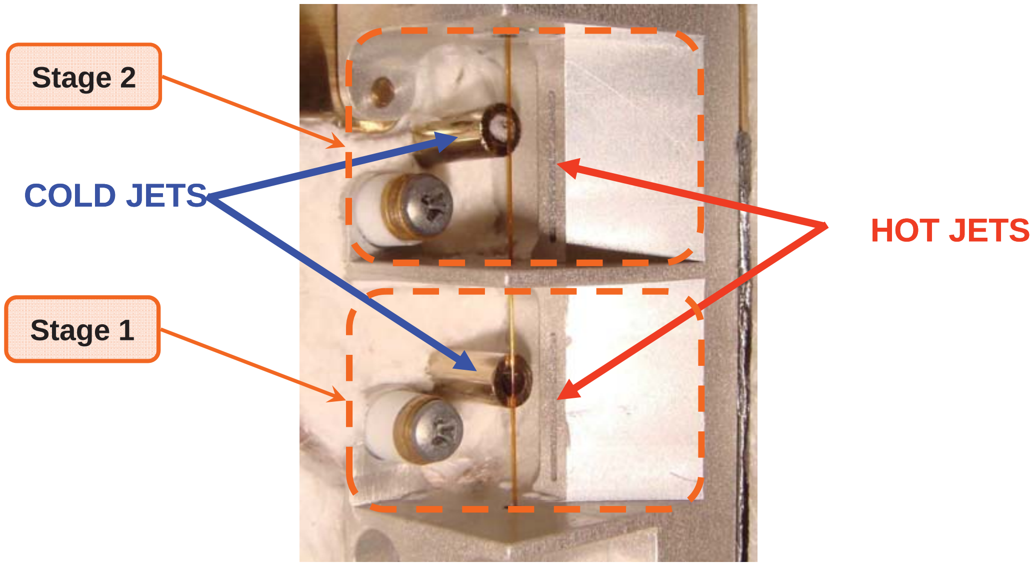
200 Hz for a 50 ms wide peak

GCxGC Hardware

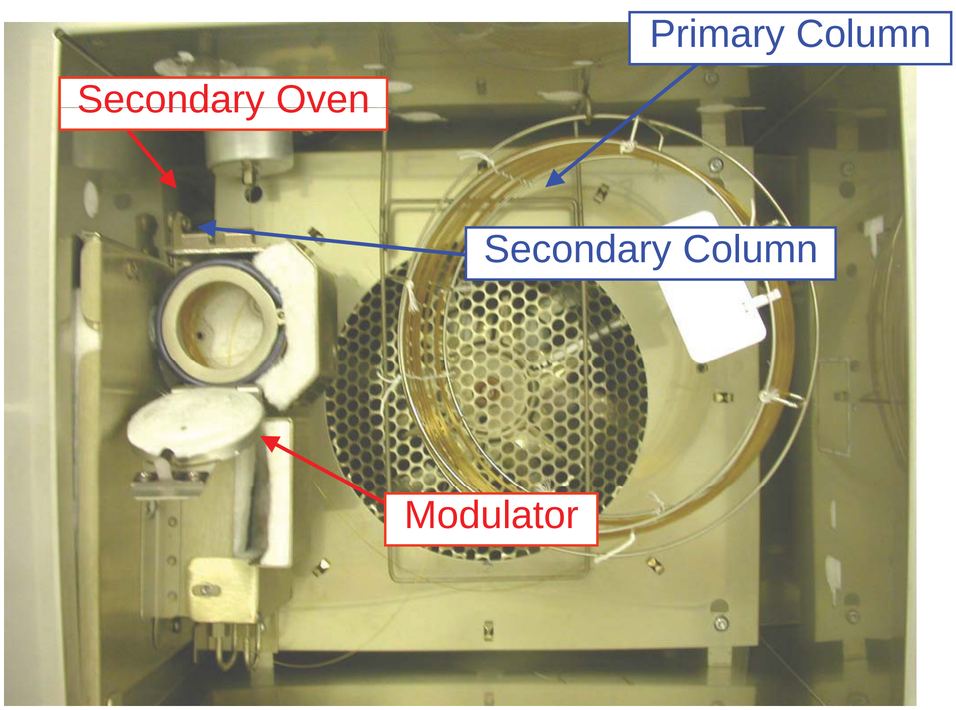
Dual-Stage Quad-jet Thermal Modulator

- Utilizes LN_2 or a Closed-loop Chiller for Cooling
- Utilizes an Secondary Oven for Independent Temperature Control of the Individual Columns
- Modulation Occurs on the Beginning of the 2^{nd} Dimension Column

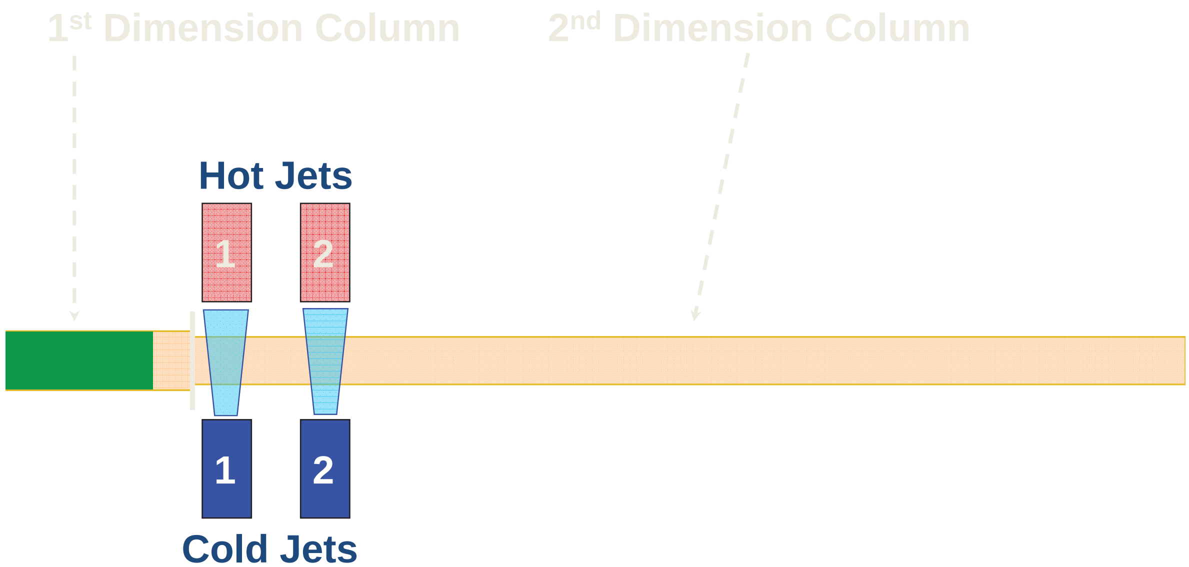
LECO's Dual-stage Quad Jet Thermal Modulator



LECO's GCxGC



GC×GC: Dual-stage Quad-jet Thermal Modulation



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GCxGC Overview

- GCxGC is accomplished through a series of rapid, independent 2nd dimension separations
- The modulator serves two functions: focusing sections of 1st dimension column effluent and acting as the injector for the 2nd dimension column
- GCxGC is comprehensive. All material that enters the 1st column passes through the modulator, the 2nd column and on to the detector

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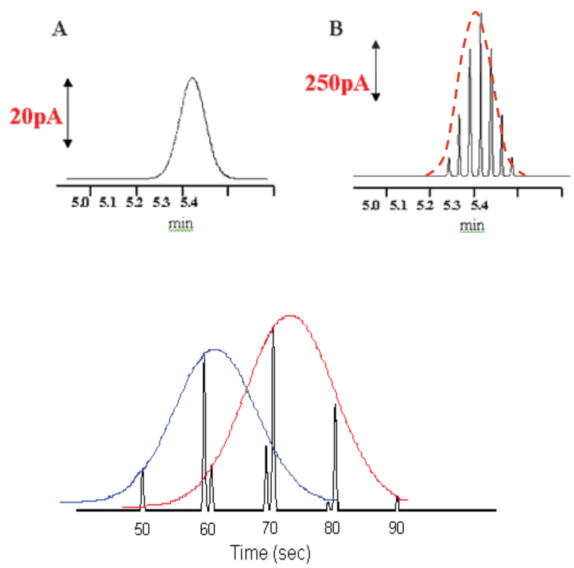
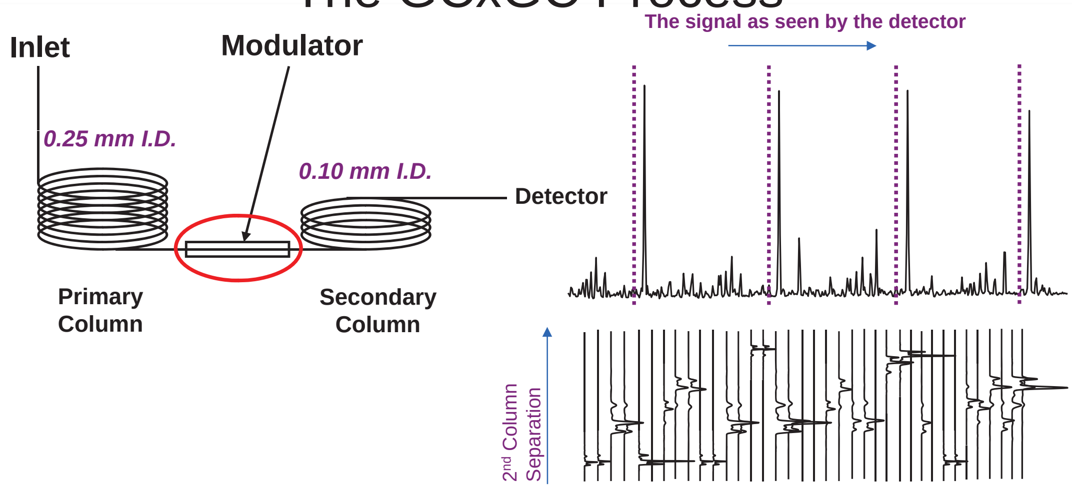
GCxGC Overview



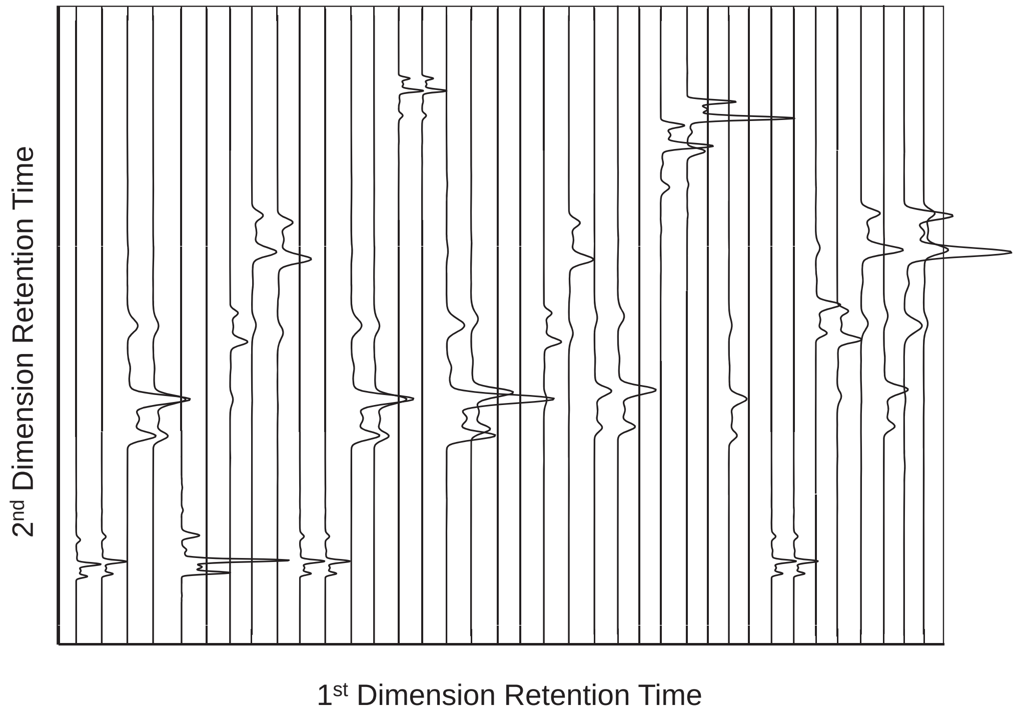
- **Primary column separates components based on volatility and also generates wide bands**
- **The modulator focuses and re-injects time-fractions of the primary column effluent onto the second column for a second separation**
  - 5+ modulations per peak
- **The second column performs a rapid separation of each injected sample from the modulator based on polarity**
  - t_m ~ 1.0 s for a 1.0m column

The GCxGC Process

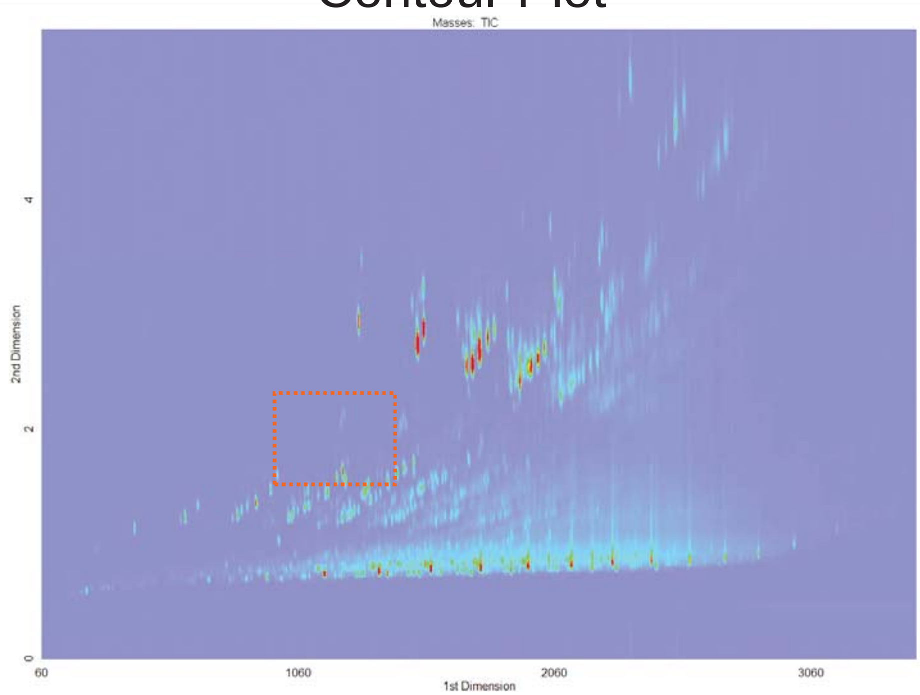


The effluent from the primary column is focused and segmented by the modulator into a discrete "plug". Each plug is then injected onto the secondary column by the modulator, where it is separated. The GCxGC process is a series of independent second column separations.

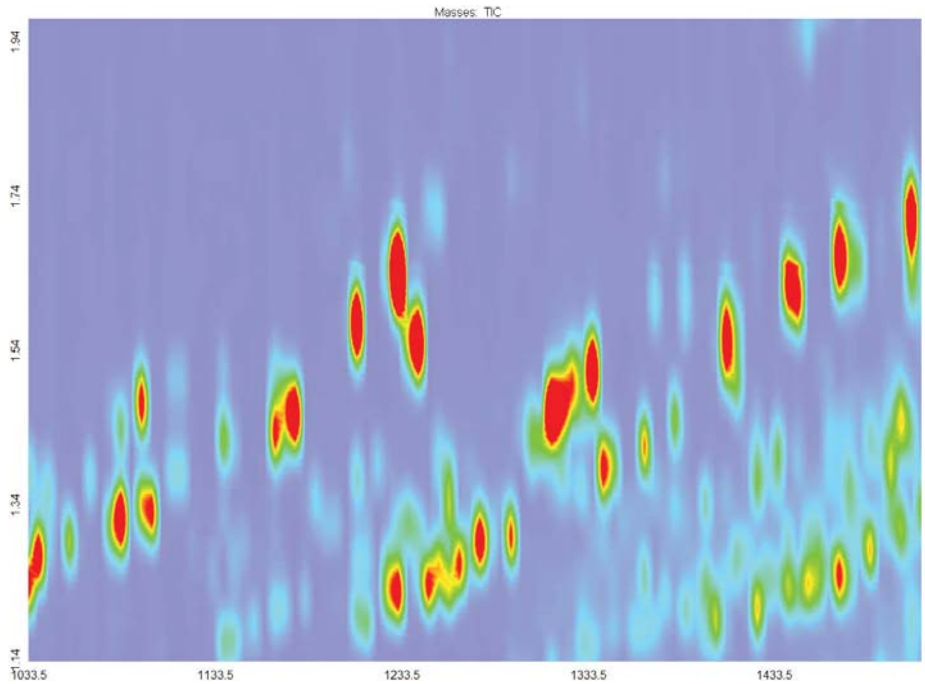
Retention Plane



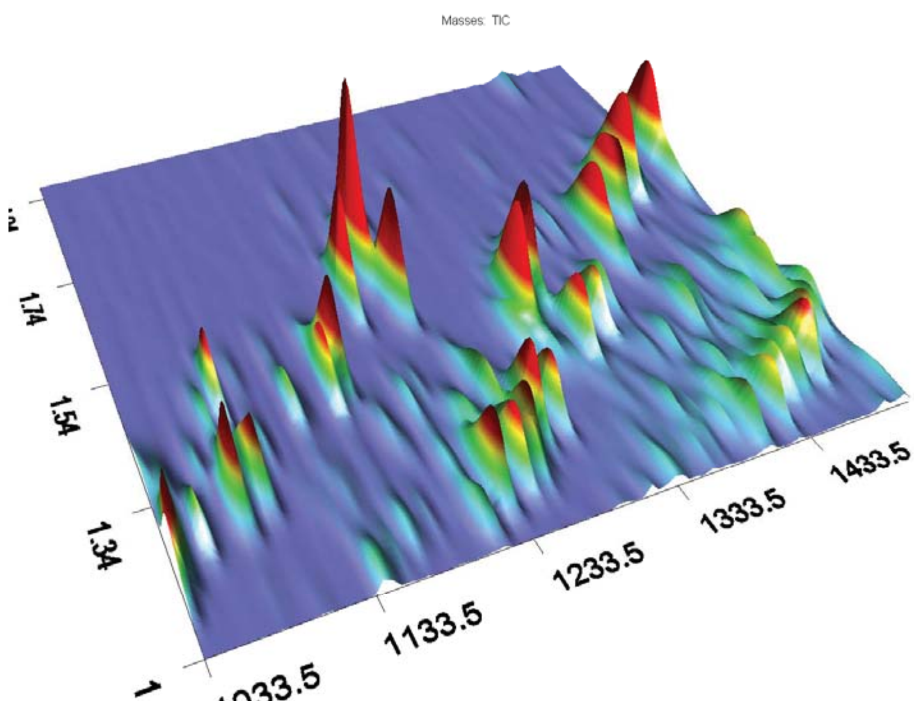
Contour Plot



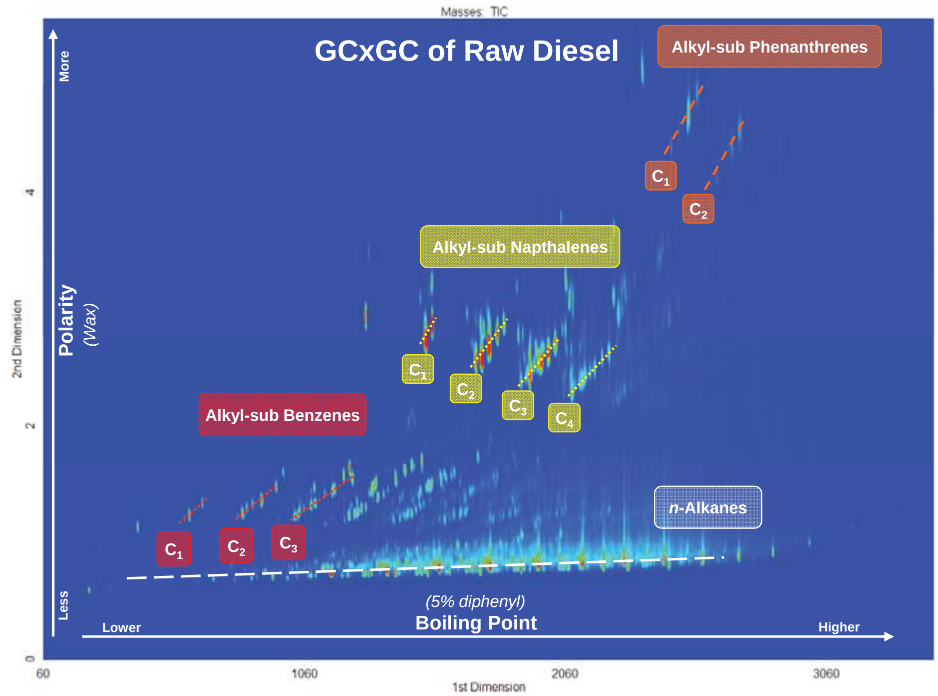
Contour Plot



Surface Plot



Features of a GCxGC Contour Plot



GCxGC Applications

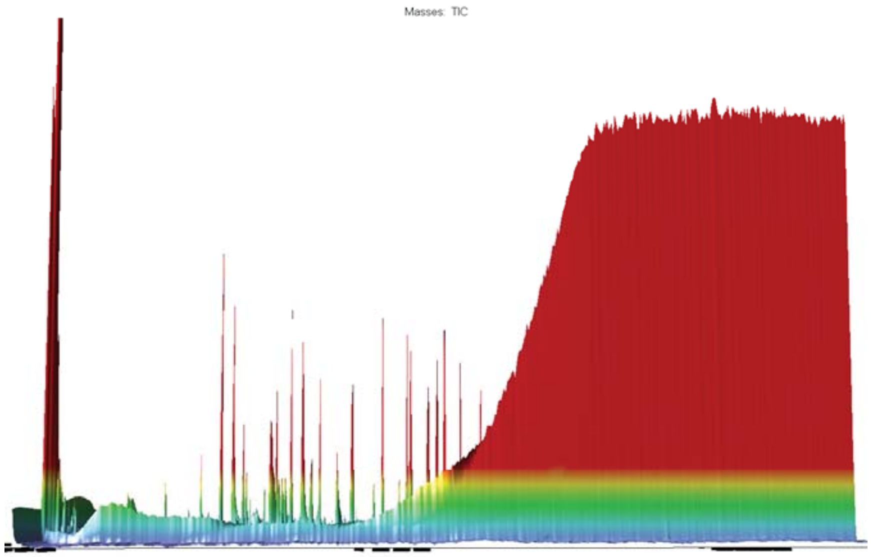
Environmental

Metabolomics

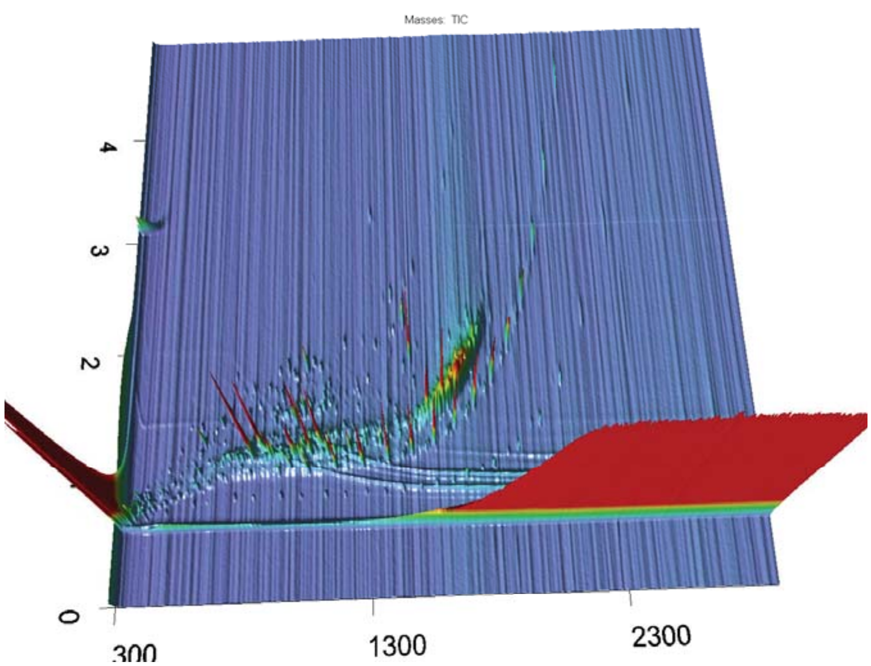
Petroleum

- Diesel
- Gulf Oil Spill

Environmental – PBDEs & PCBs in Fish



Environmental – PBDEs & PCBs in Fish



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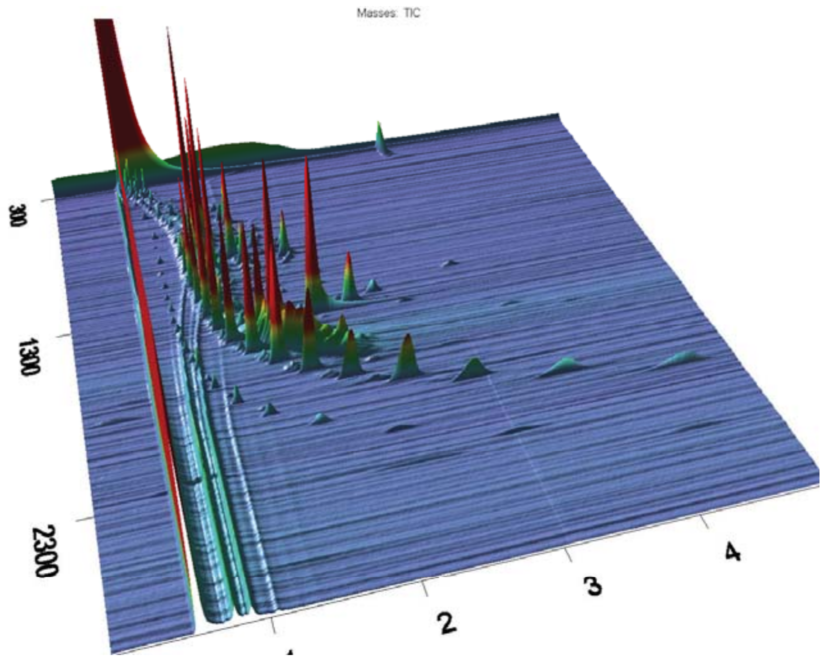

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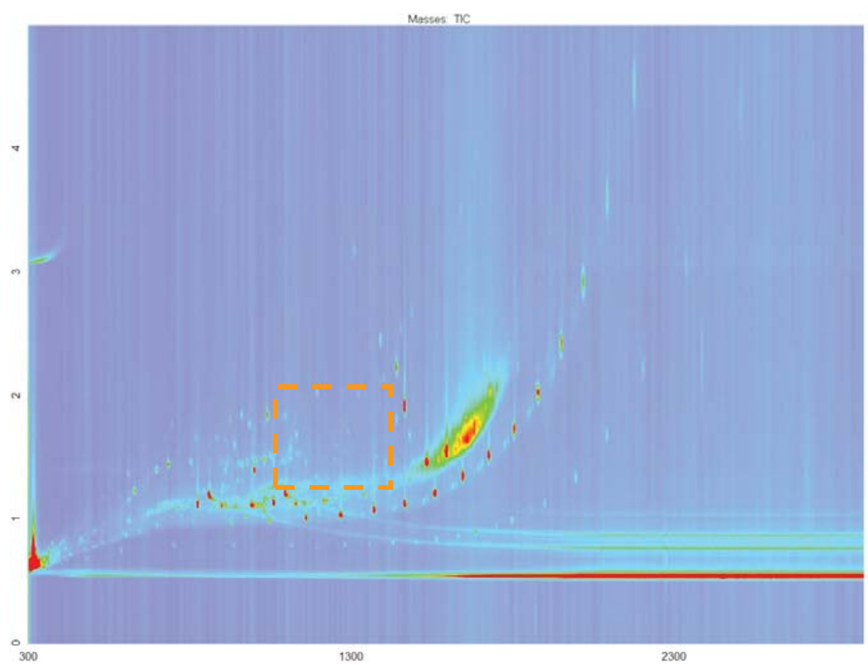
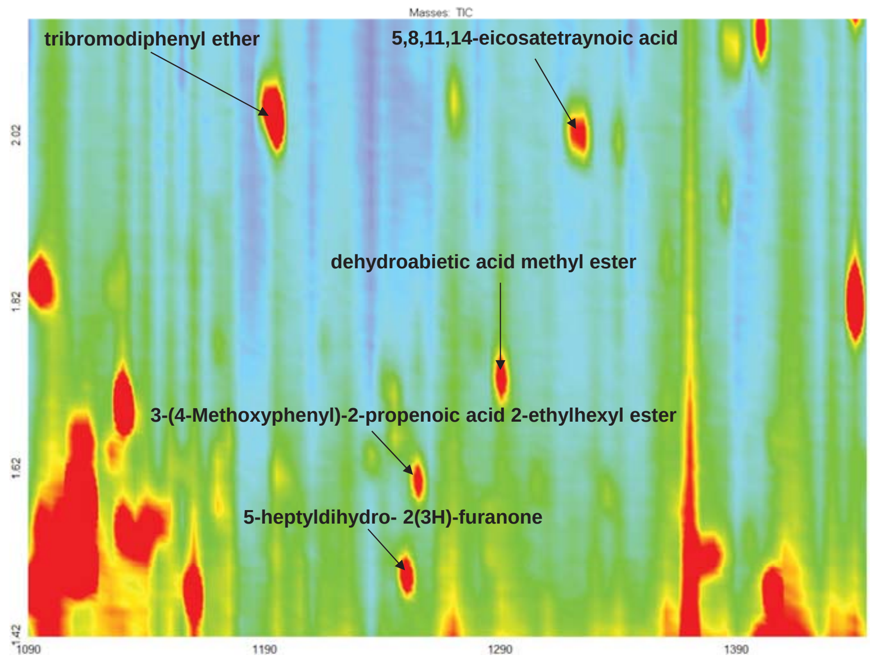


Environmental – PBDEs & PCBs in Fish



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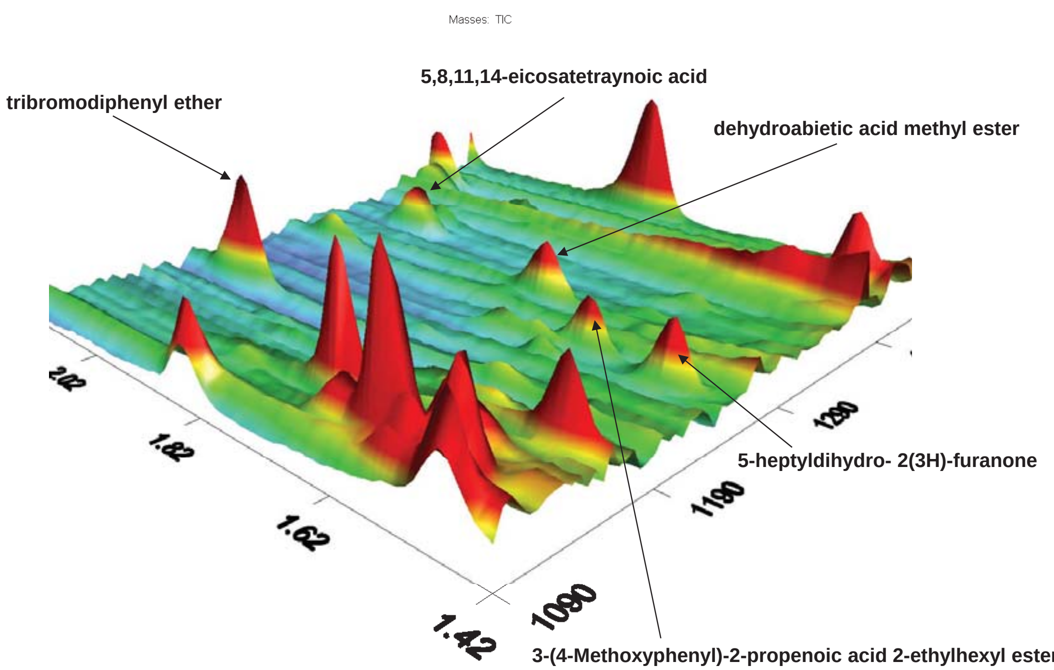
Environmental – PBDEs & PCBs in Fish



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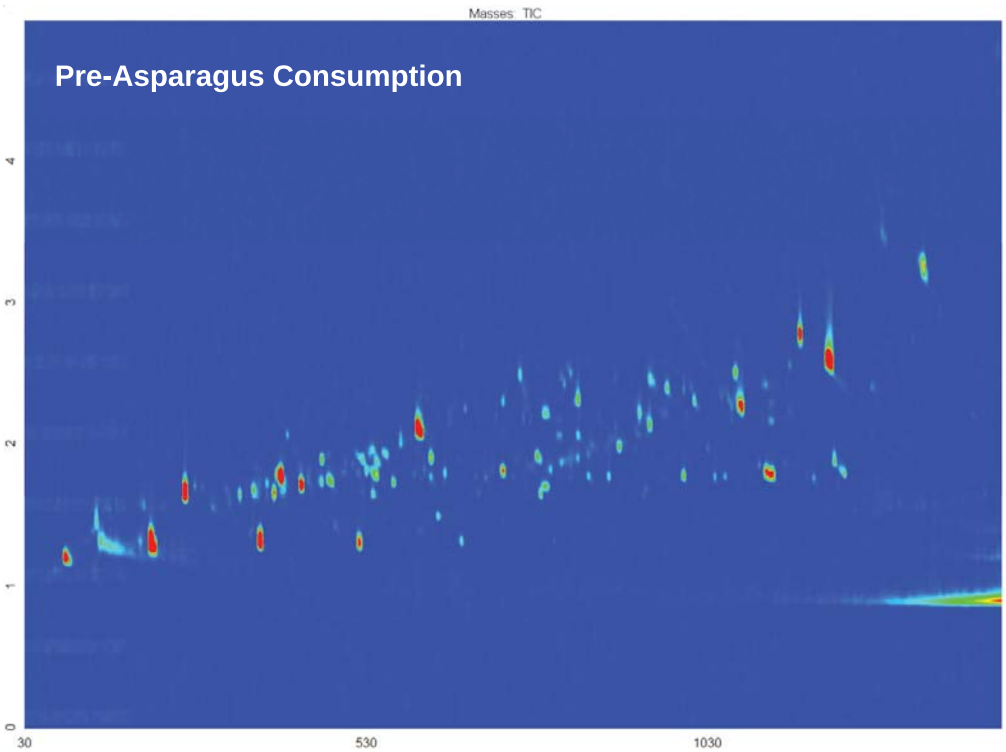
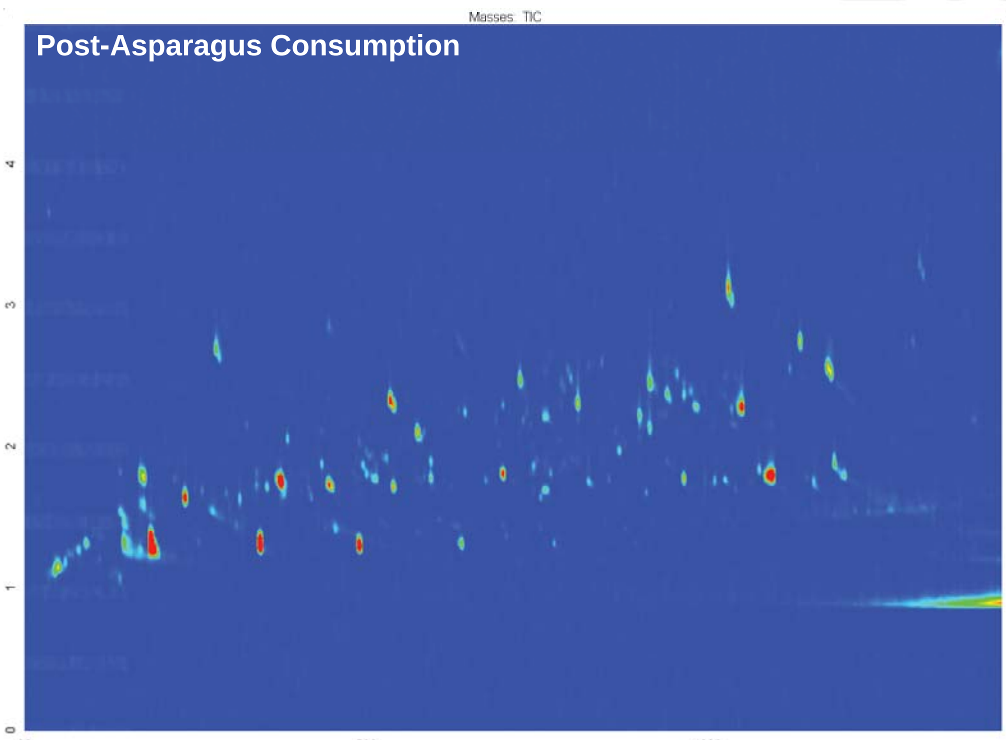

Masses: TIC
Pre-Asparagus Consumption
0
1
2
3
4
30
530
1030


Masses: TIC
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0
1
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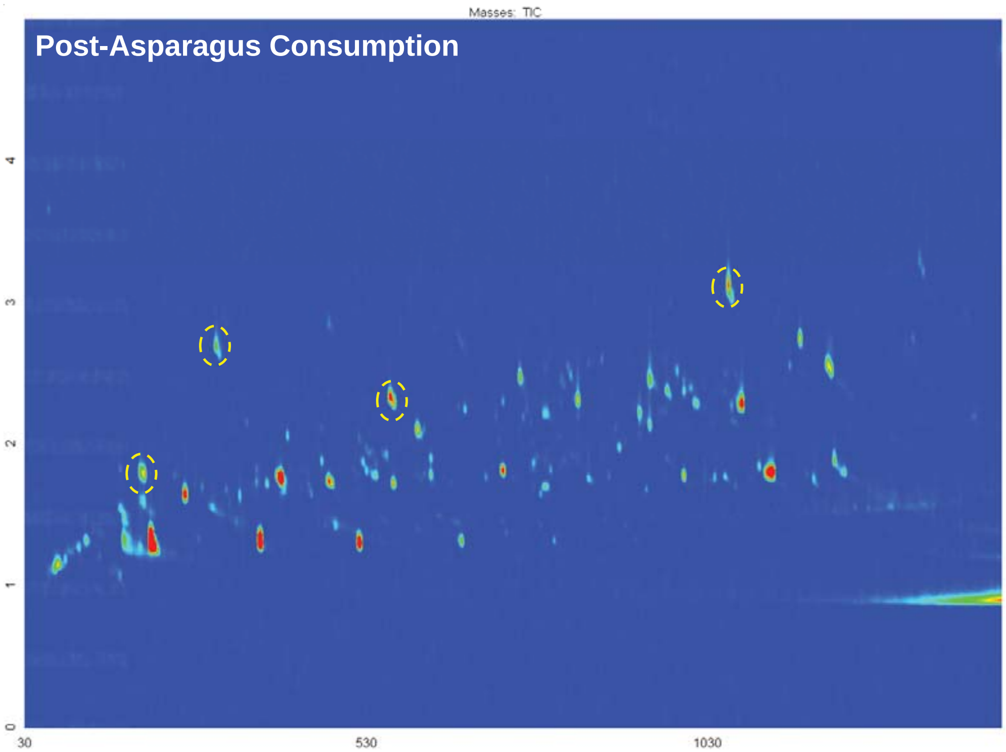
530
1030


Masses: TIC
Post-Asparagus Consumption
0
1
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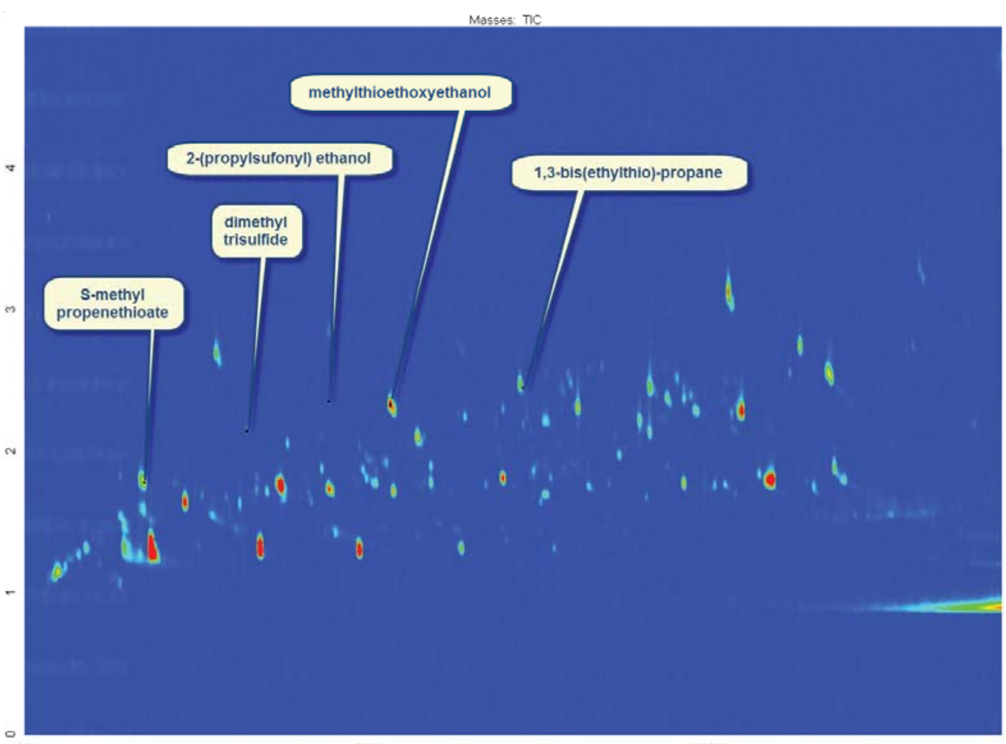
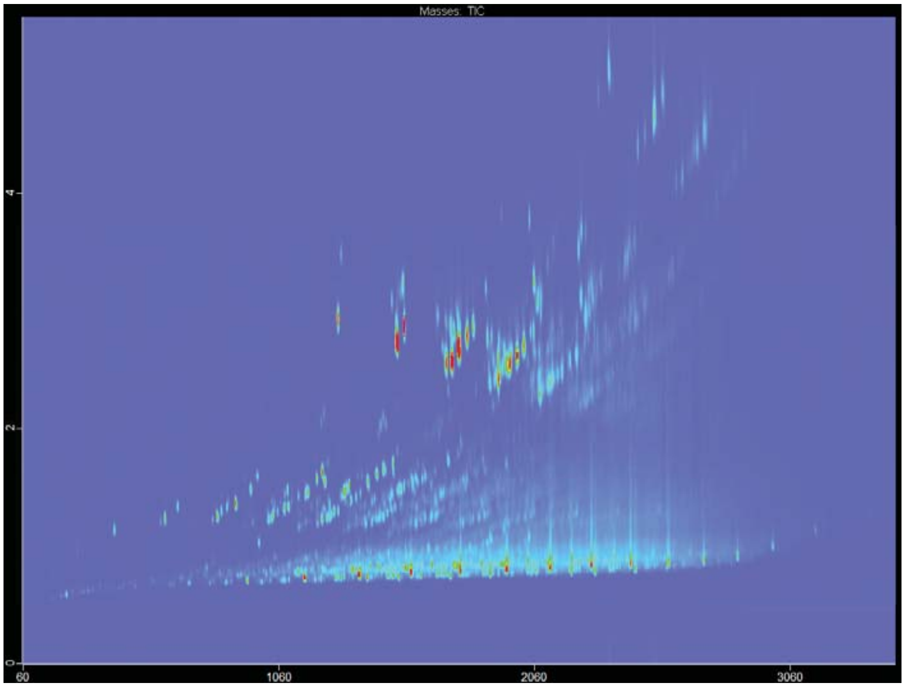
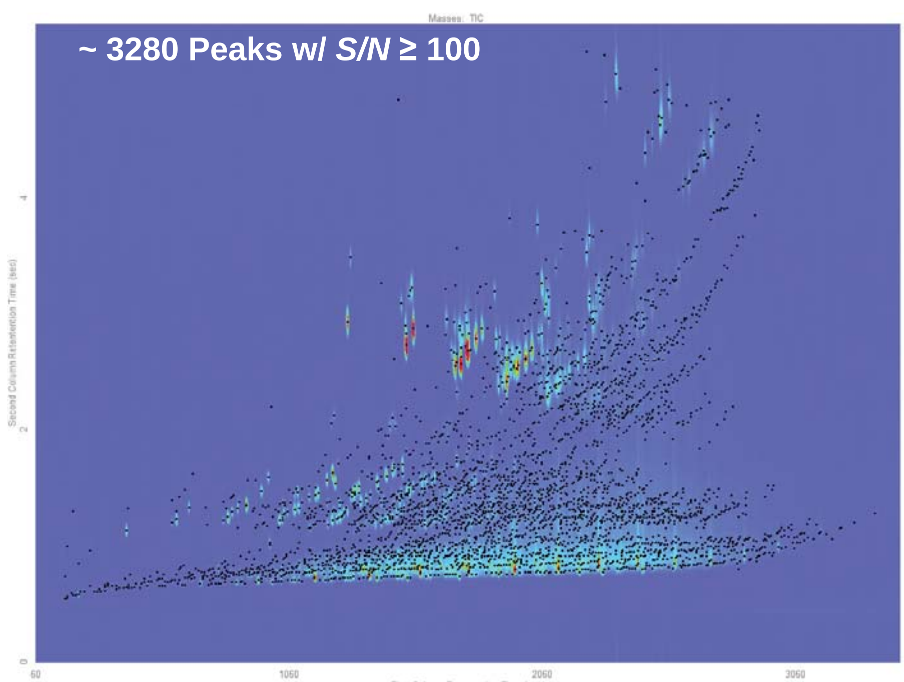

Masses: TIC
methylthioethoxyethanol
2-(propylsufonyl) ethanol
1,3-bis(ethylthio)-propane
dimethyl trisulfide
S-methyl propenethioate
0
1
2
3
4
30
530
1030

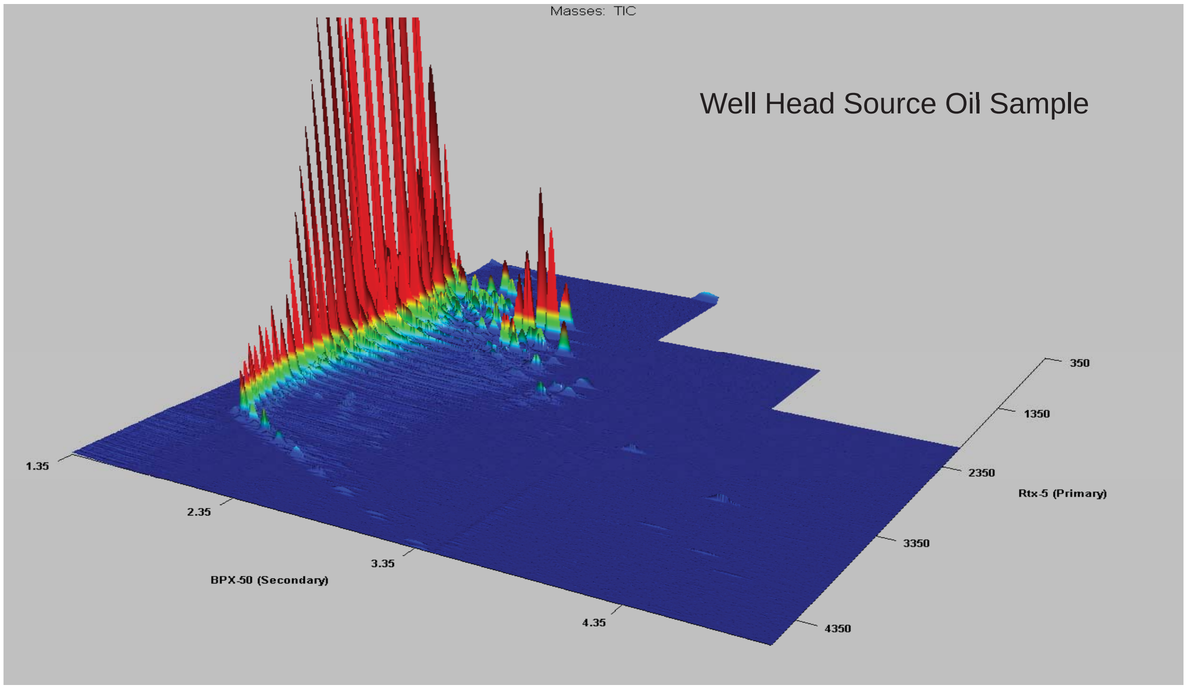
Petroleum - Diesel



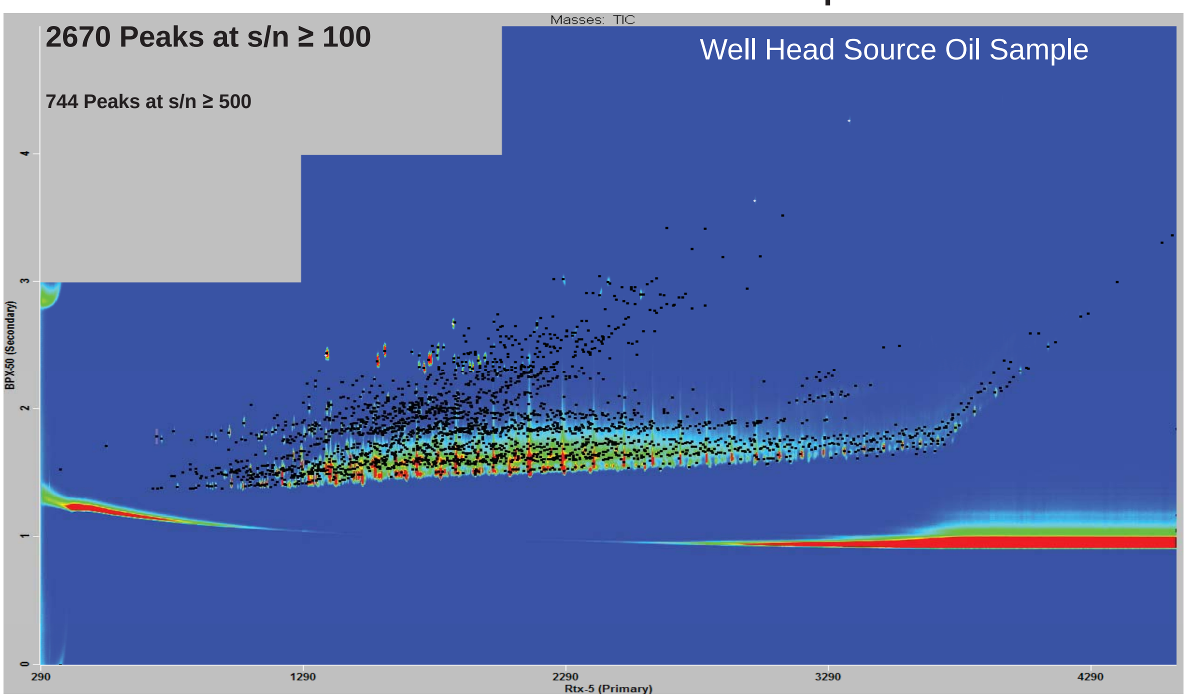
Petroleum - Diesel



Petroleum – Gulf Oil Spill



Petroleum – Gulf Oil Spill



Conclusion

- GCxGC is a versatile technique that is well-suited to the analysis of complex mixtures

- GCxGC provides benefits over a conventional 1DGC separation including:
    - Increased Detectability
    - Increased Chromatographic Resolution
    - Increased Peak Capacity

- LECO's ChromaTOF software offers advanced data processing, such as Classifications and Scripting, which take advantage of the structured nature of GCxGC data