The Power of Heat and Multidimensional Separations in micro & Fast Gas Chromatography

Robert Shellie, University of Tasmania
John Crandall (presenter), President Falcon Analytical

433 AEI Drive - Lewisburg, WV 24901

info@falconfast.net *Tel: (304) 647-5860*

Broad Applicability in GC Means HEAT!!!

- Fixed Gases, O_2, N_2, H_2, CO, CO_2, H_2S
  - Sure, most micro GCs handle this type of application
  - Low concentration level analytes require specialty detectors
    - FID
    - TCD
    - FPD
    - Dielectric Barrier Discharge as HID, PID and ECD
- For light hydrocarbons and beyond… to C_{50}
  - Up to about C6 can be done at lower temperatures BUT…
  - >C6 requires HEAT… > than Si based technologies can take

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Broadly Applicable Fast and micro GC

- Requires the same parameters as traditional GC
  - Split/splitless injectors
  - Programmed temperature and/or isothermal separations
  - Detection at temperature with the right technique for target analytes
- And most especially HEAT!
  - For hydrocarbons, this means up to about 350^{o} C
  - Going beyond risks thermal cracking (we aren't doing pyrolysis GC although a pyroprobe could enable it)

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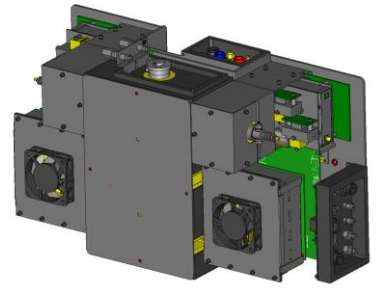
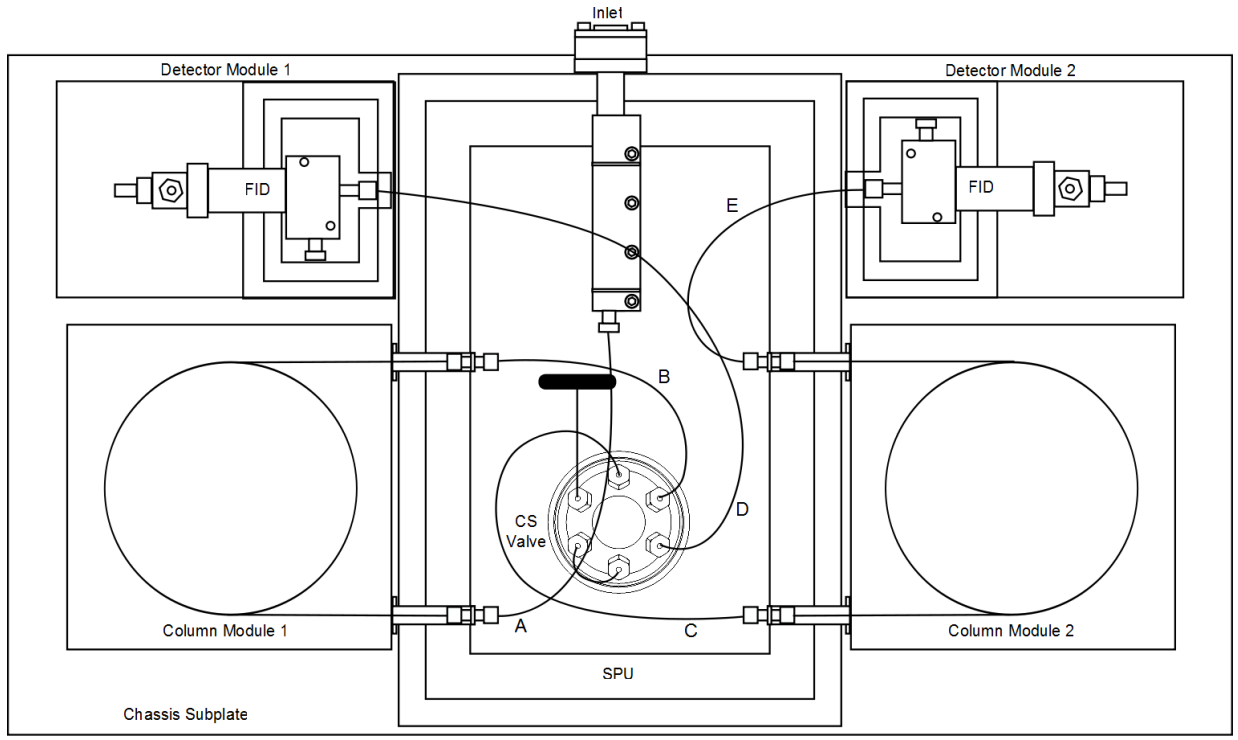
And What about Column Switching?
(multidimensional gas chromatography)





- Single injections at up to 350°C
- Single column switching valve
- Two independently controlled column modules
- Two detectors, the same or different…
- Enables surprisingly powerful fast, high resolution, high sensitivity gas chromatography

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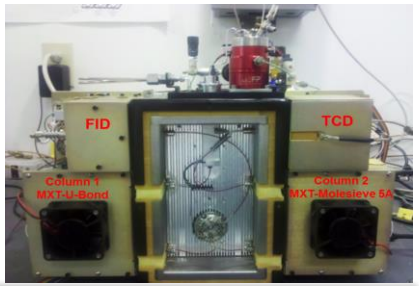
The Focus Is on Heartcut



- Several column switching schemes are possible
  - Backflush
  - Trap/bypass… but the heartcut enables many separations
- The technique uses
  - Column 1 of one type of column phase
  - Column 2 of another phase completing an incomplete separation
  - Detector selection improves probability of the correct selectivity and sensitivity for target analytes

Here are a couple of examples

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Test Mix Specifications

- Defines boiling range where the heartcut is done.
- Demonstrates operability of the Calidus CS system.
- Note 30 minute run.

RESTEK

Certificate of Analysis

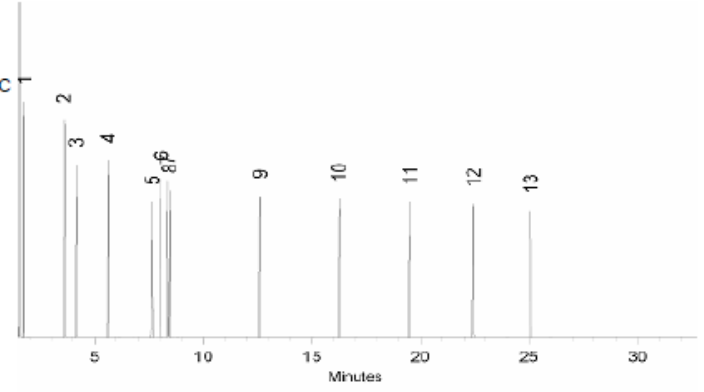
110 Benner Circle
Bellefonte, PA 16823-8812
Tel: (800)356-1688
Fax: (814)353-1309

FOR LABORATORY USE ONLY-READ MSDS PRIOR TO USE.

Catalog No. : 31224 Lot No.: A058927
Description : E1387-90 Column Resolution Check Mix
Expiration Date[1]: April 2015 Storage: Refrigerate

Elution Order	Compound	CAS #	Percent Purity [2]	Concentration [3] (weight/volume)	Percent Uncertainty [4]
1	n-Hexane (C6)	110-54-3	99%	2,019.000 ug/ml	+/-0.05 %
2	Toluene	108-88-3	99%	2,005.500 ug/ml	+/-0.05 %
3	n-Octane (C8)	111-65-9	99%	2,000.000 ug/ml	+/-0.05 %
4	p-Xylene	106-42-3	99%	2,000.000 ug/ml	+/-0.05 %
5	1-methyl-3-ethylbenzene (3-ethyltoluene)	620-14-4	99%	2,013.500 ug/ml	+/-0.05 %
5	1-methyl-3-ethylbenzene (3-ethyltoluene)	620-14-4	99%	2,013.500 ug/ml	+/-0.05 %
6	1-methyl-2-ethylbenzene (2-ethyltoluene)	611-14-3	99%	2,000.000 ug/ml	+/-0.05 %
6	1-methyl-2-ethylbenzene (2-ethyltoluene)	611-14-3	99%	2,000.000 ug/ml	+/-0.05 %
7	1,2,4-Trimethylbenzene	95-63-6	99%	2,017.000 ug/ml	+/-0.05 %
8	n-Decane (C10)	124-18-5	99%	2,000.000 ug/ml	+/-0.05 %
9	n-Dodecane (C12)	112-40-3	99%	2,000.000 ug/ml	+/-0.05 %
10	n-Tetradecane (C14)	629-59-4	99%	2,000.000 ug/ml	+/-0.05 %
11	n-Hexadecane (C16)	544-76-3	98%	2,000.180 ug/ml	+/-0.05 %
12	n-Octadecane (C18)	593-45-3	99%	2,000.000 ug/ml	+/-0.05 %
13	n-Eicosane (C20)	112-95-8	99%	2,000.000 ug/ml	+/-0.05 %
Solvent:	Methylene Chloride	75-09-2	99%		

Column: 30m x .25mm x .25um Rtx-5 (cat.#10233)
Carrier Gas: hydrogen @ 40cm/sec.
Temp. Program: 40°C (hold 2 min.) to 330°C @ 8°C/min.
Inj. Temp: 250°C
Det. Temp: 330°C
Det. Type: FID



Sara Eyster
Sara Eyster, QA Analyst

Balance 1128360905

1 Expiration date of the unopened ampul stored at recommended temperature.
2 Purity was determined by one or more of the following techniques: GC/FID, HPLC, GC/ECD, GC/MS. Value rounded to the nearest LOWER whole percentage. In addition to detectors listed above, chemical identity and purity are confirmed using 1 or more of the following: MS, DSC, solid probe MS, GC/FPD, GC/NPD, GC/TC, FTIR, melting point, refractive index, and Karl Fisher. See data pack or contact Restek for further details.
3 Based upon gravimetric preperation with balance calibration verified using NIST traceable weights (seven mass levels).
4 Percent Uncertainty based upon balance AND ASTM Class A volumetric glassware accuracy.

ISO 9001 REGISTERED

Manufactured under Restek's ISO 9001 Registered Quality System Certificate #FM90397

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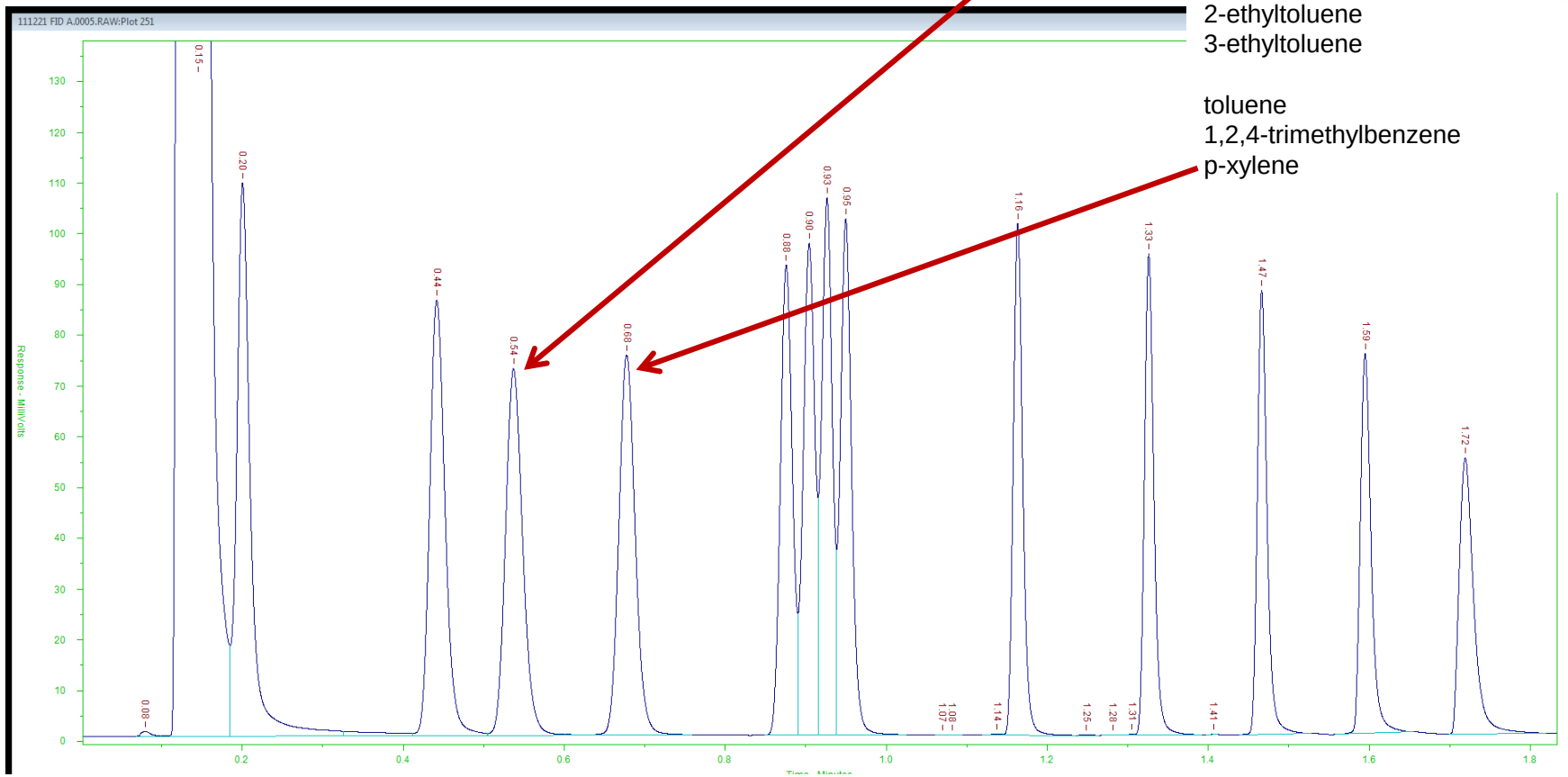
CRM through MXT-1, No Heartcut



n-hexane (C6)
n-octane (C8)
n-decane (C10)
n-dodecane (C12)
n-tetradecane (C14)
n-hexadecane (C16)
n-octadecane (C18)
n-eicosane (C20)
2-ethyltoluene
3-ethyltoluene

toluene
1,2,4-trimethylbenzene
p-xylene

Note:
2 minute run.

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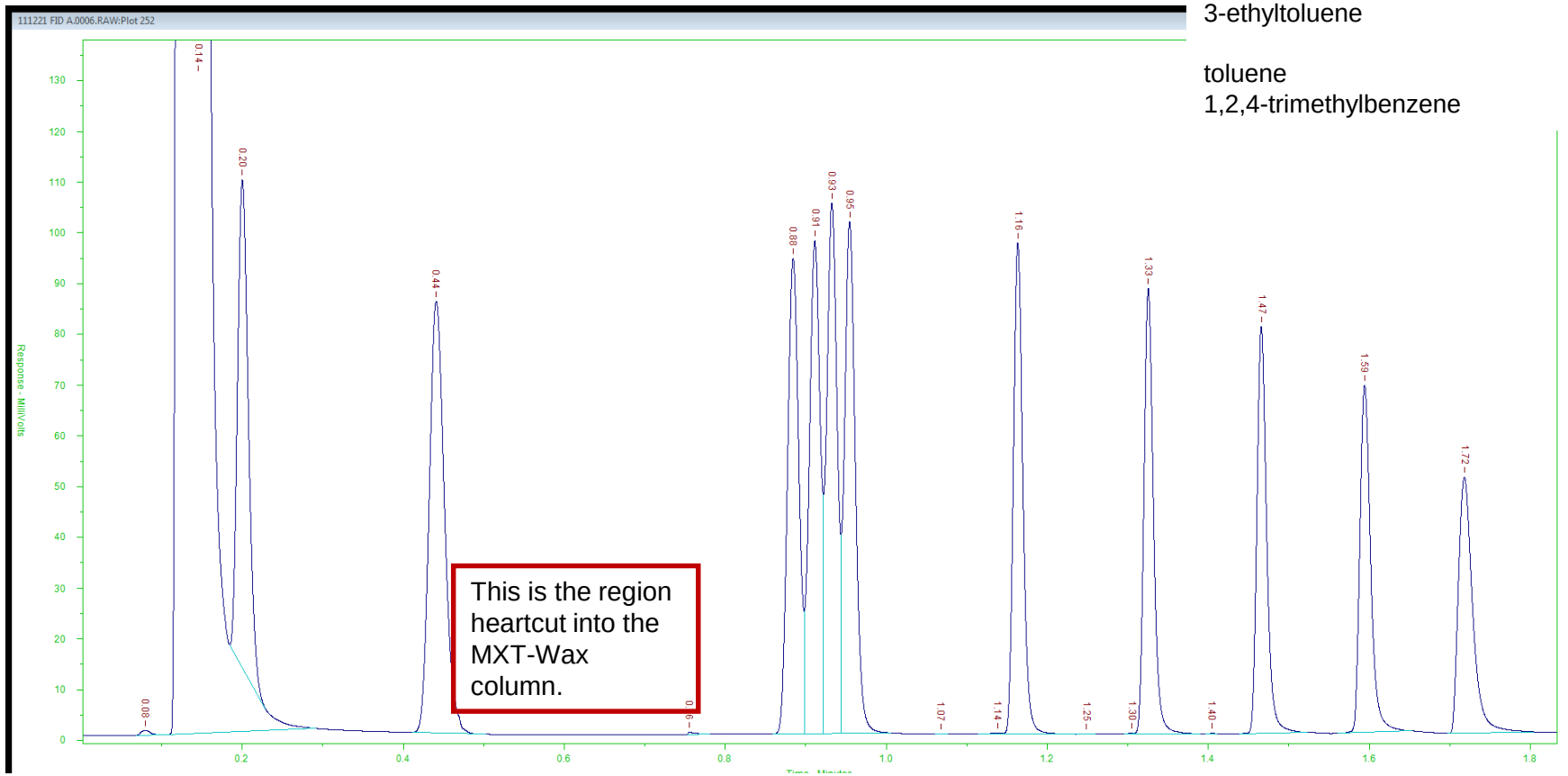
Analytical Systems & Technology

CRM through MXT-1, with Heartcut

n-hexane (C6)
n-decane (C10)
n-dodecane (C12)
n-tetradecane (C14)
n-hexadecane (C16)
n-octadecane (C18)
n-eicosane (C20)
2-ethyltoluene
3-ethyltoluene

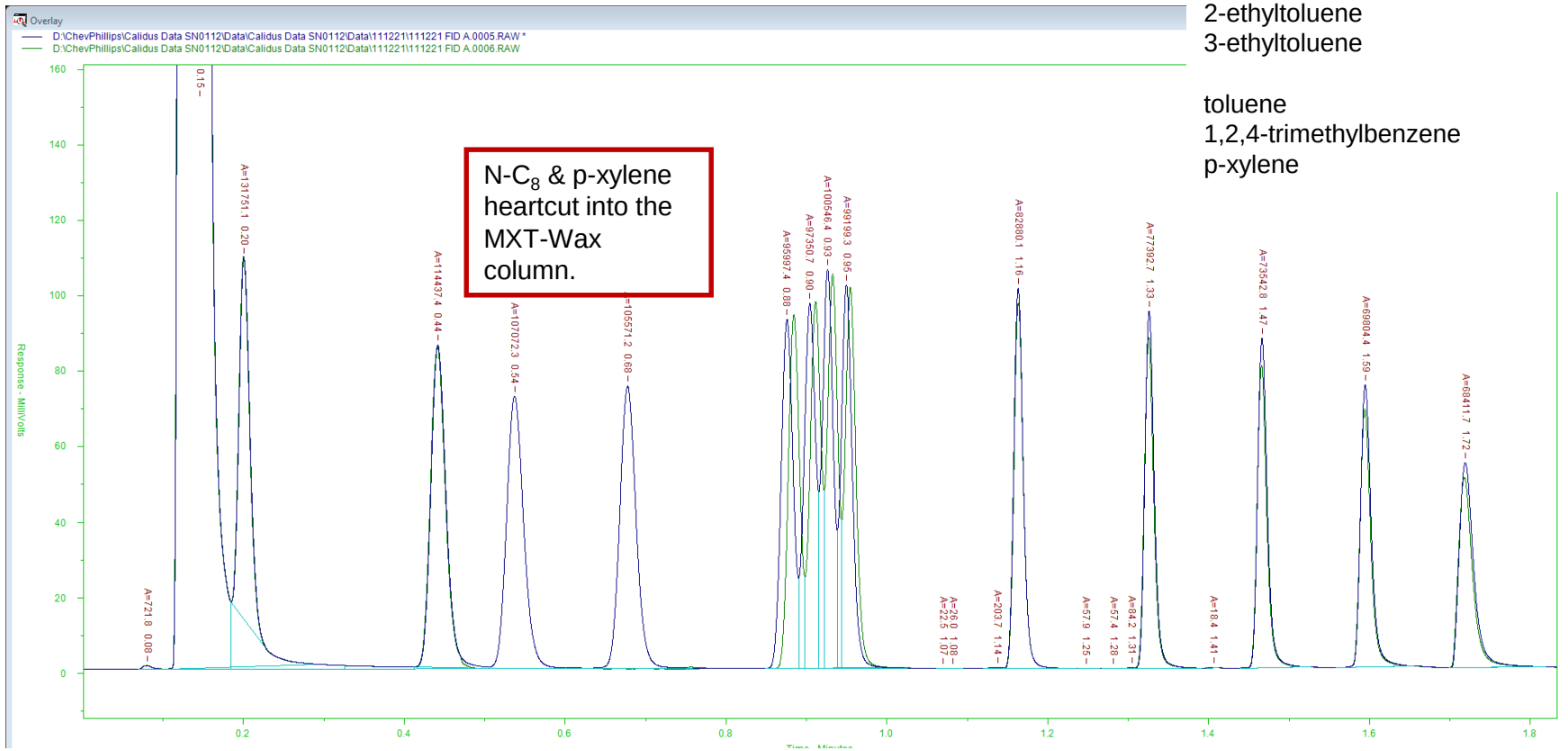
toluene
1,2,4-trimethylbenzene



CRM through MXT-1,No Heartcut Overlaid with Heartcut

n-hexane (C6)
n-octane (C8)
n-decane (C10)
n-dodecane (C12)
n-tetradecane (C14)
n-hexadecane (C16)
n-octadecane (C18)
n-eicosane (C20)
2-ethyltoluene
3-ethyltoluene

toluene
1,2,4-trimethylbenzene
p-xylene



CRM Heartcut from the MXT-1 into the MT-Wax Column

n-hexane (C6)
n-octane (C8)
n-decane (C10)
n-dodecane (C12)
n-tetradecane (C14)
n-hexadecane (C16)
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toluene
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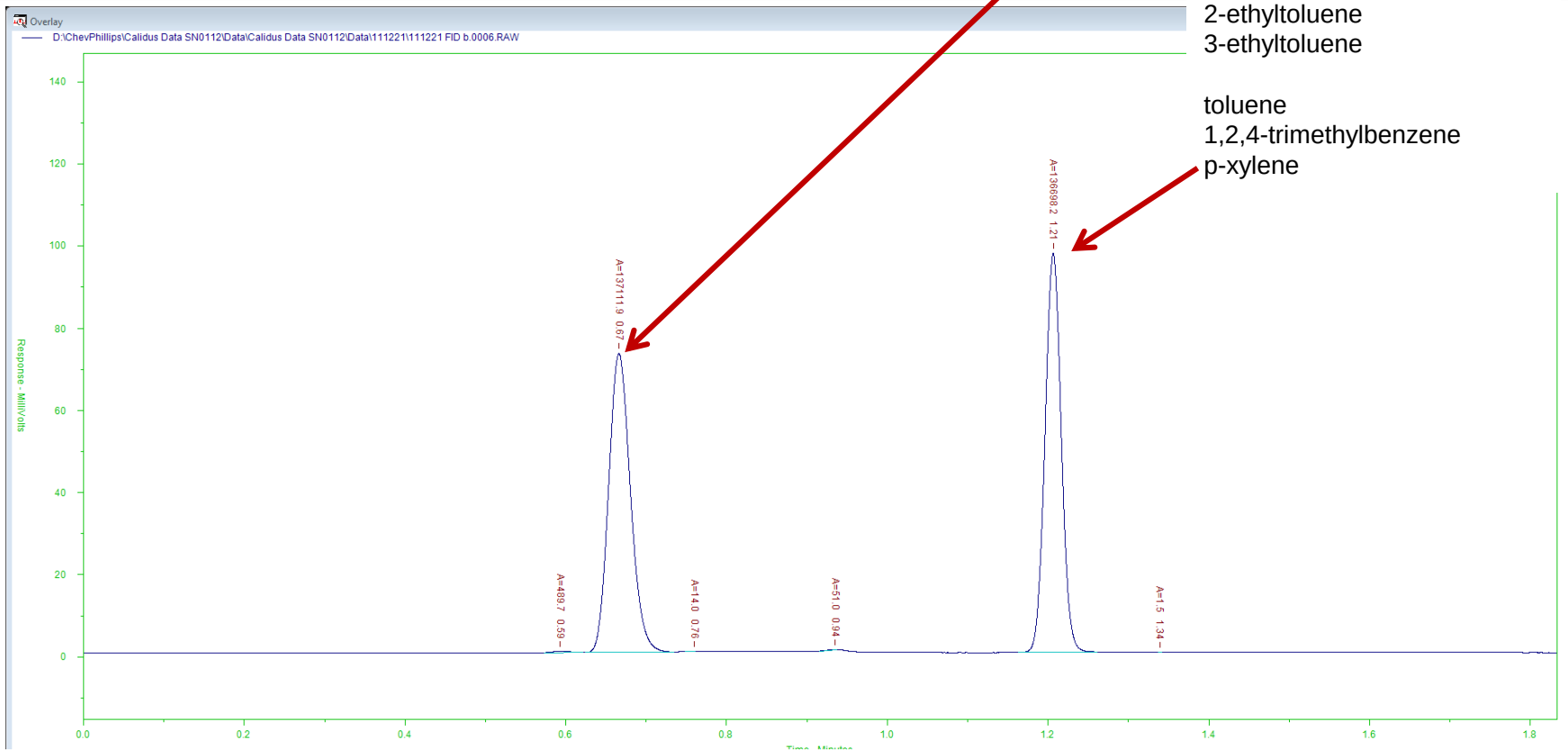
p-xylene



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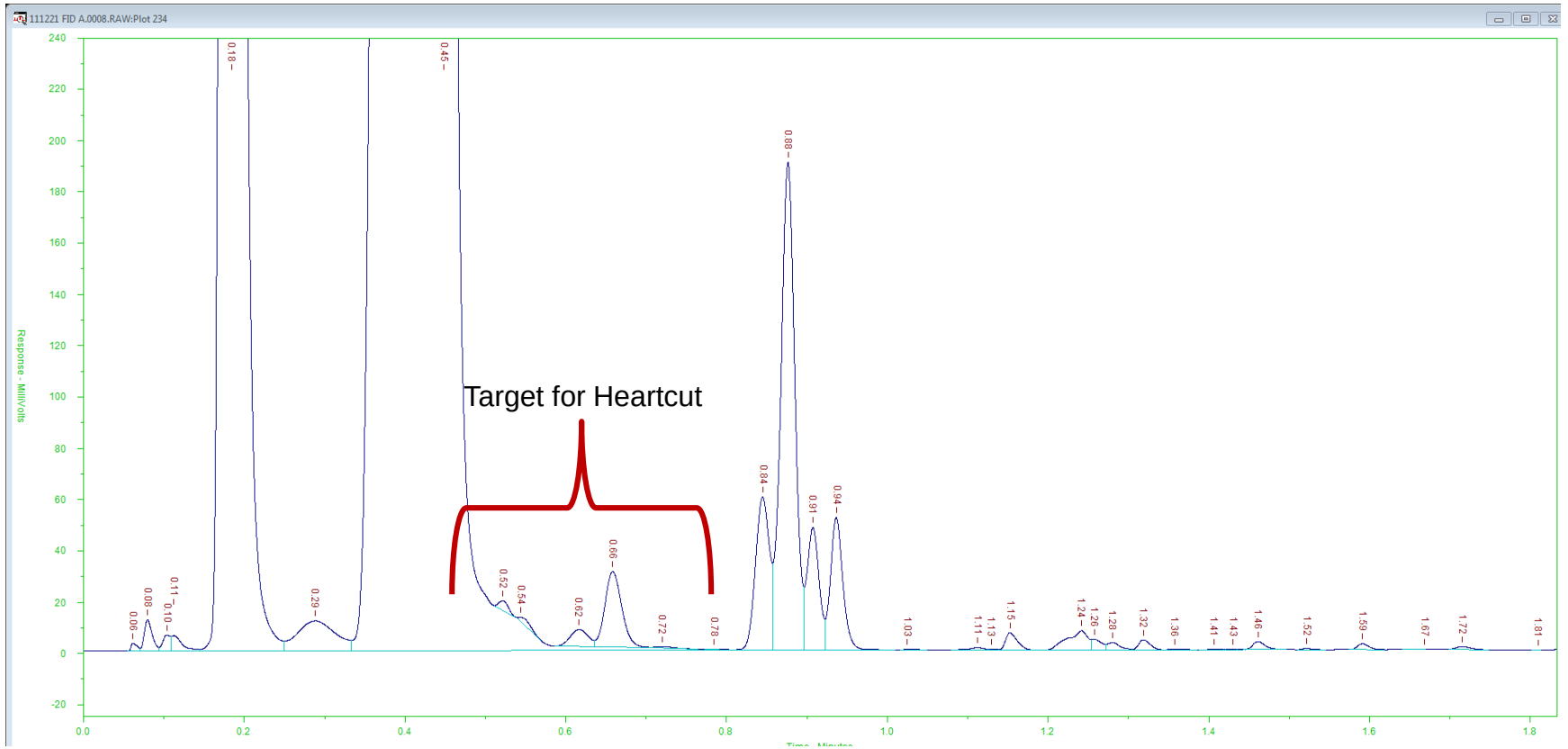
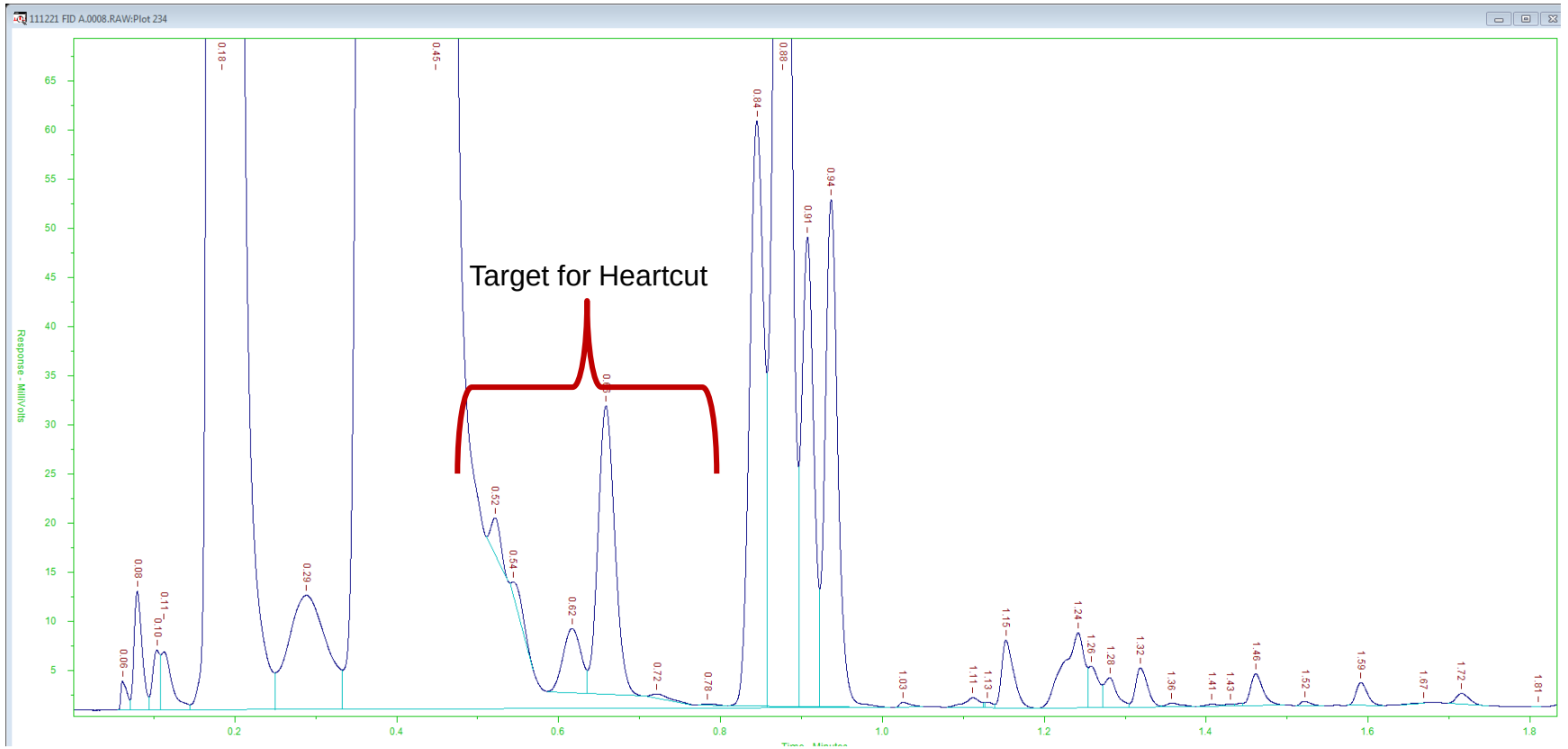
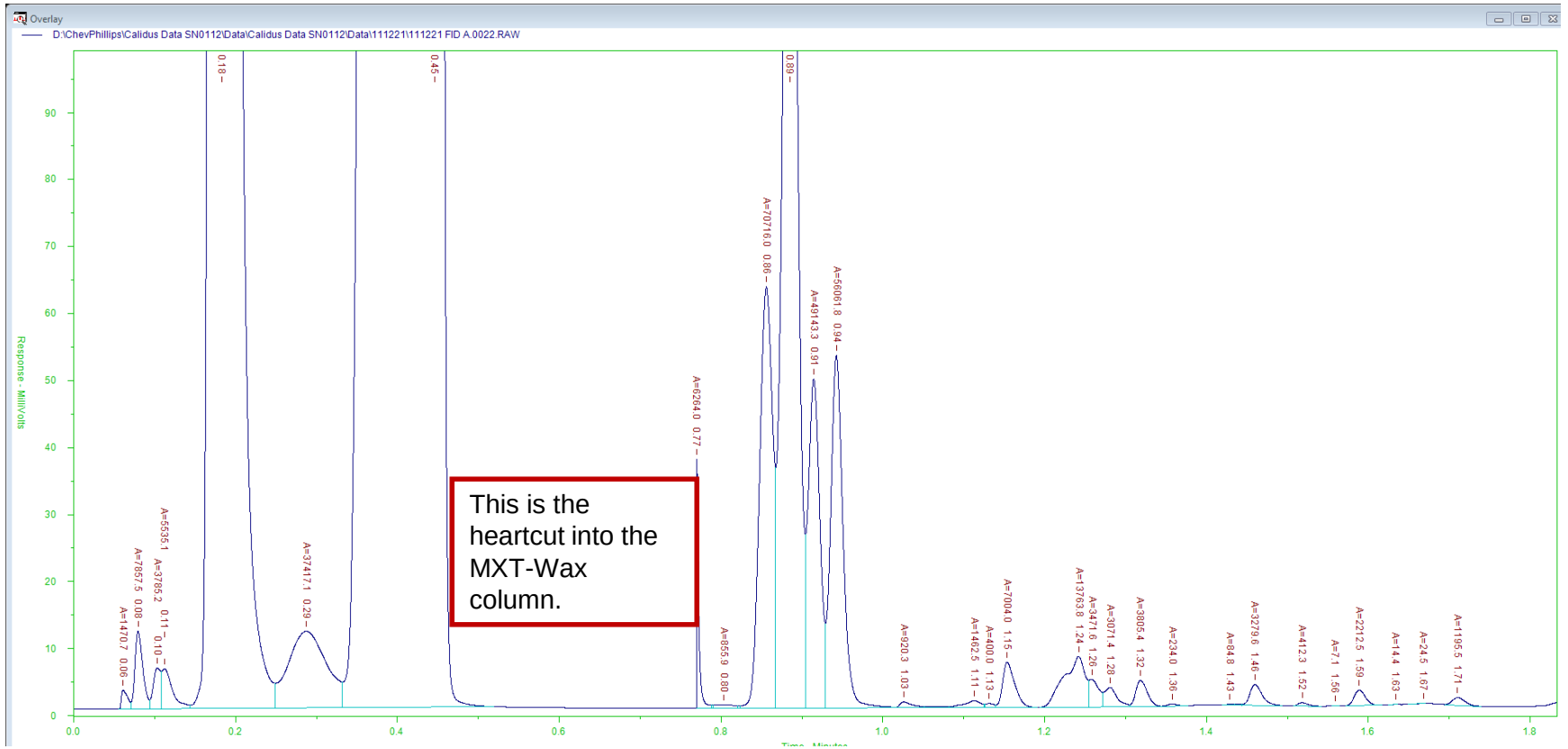
NAO Hexene Sample through the MXT-1 Channel, No Heartcut, Zoomed



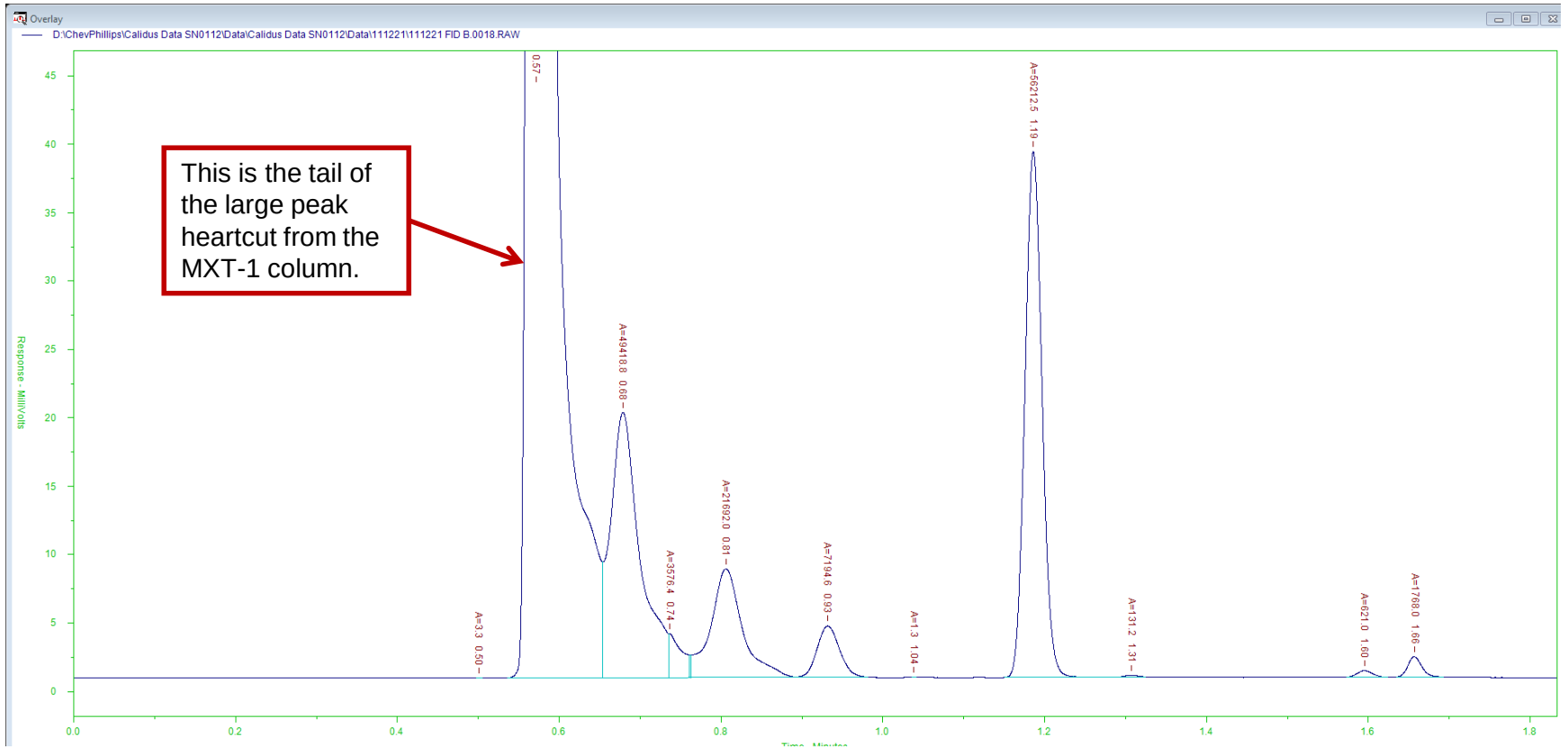
NAO Hexene Sample through the MXT-1 Channel, No Heartcut, Zoomed More



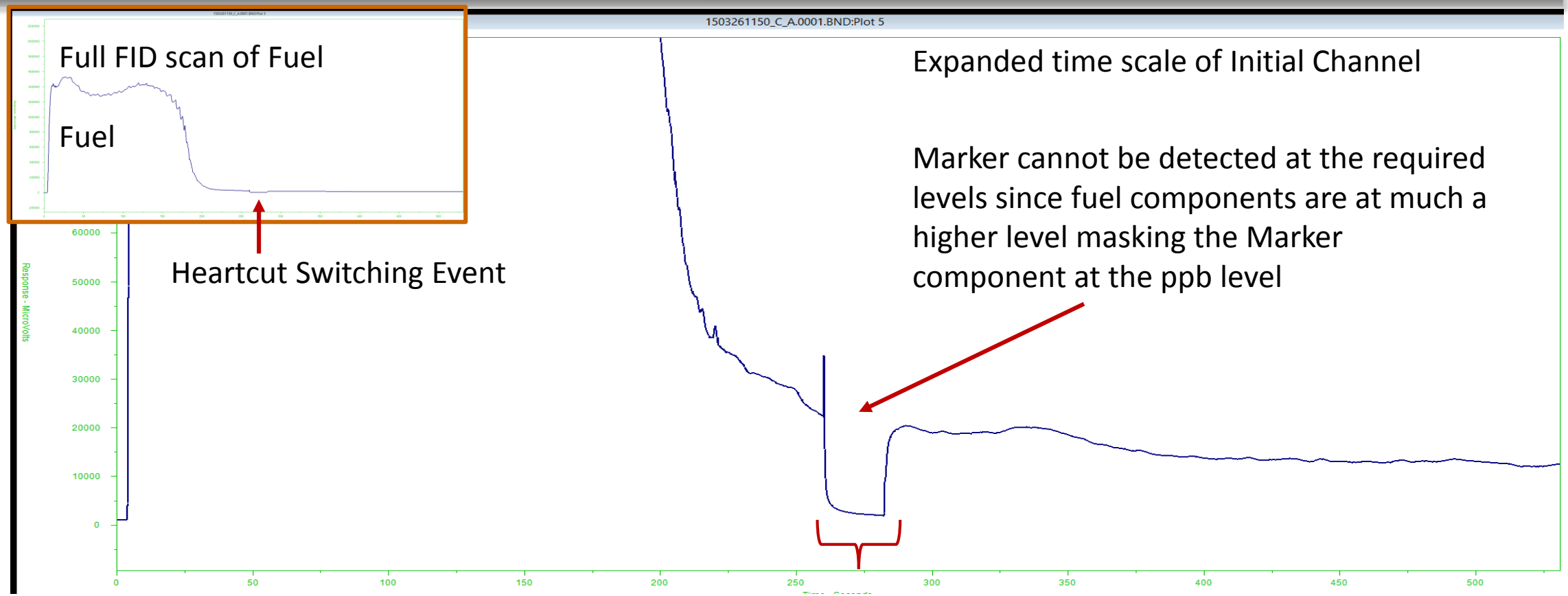
NAO Hexene Sample through the MXT-1 Channel, with Heartcut, Y-Axis Zoomed More



NAO Hexene Sample Heartcut from the MXT-1 into the MXT-Wax Column, Y-Axis Zoomed



How Does It Work in the Real World?
Marker Detection



Expanded time scale of Initial Channel

Marker cannot be detected at the required levels since fuel components are at much a higher level masking the Marker component at the ppb level

Material Heartcut into MXT-1 including where Marker would elute

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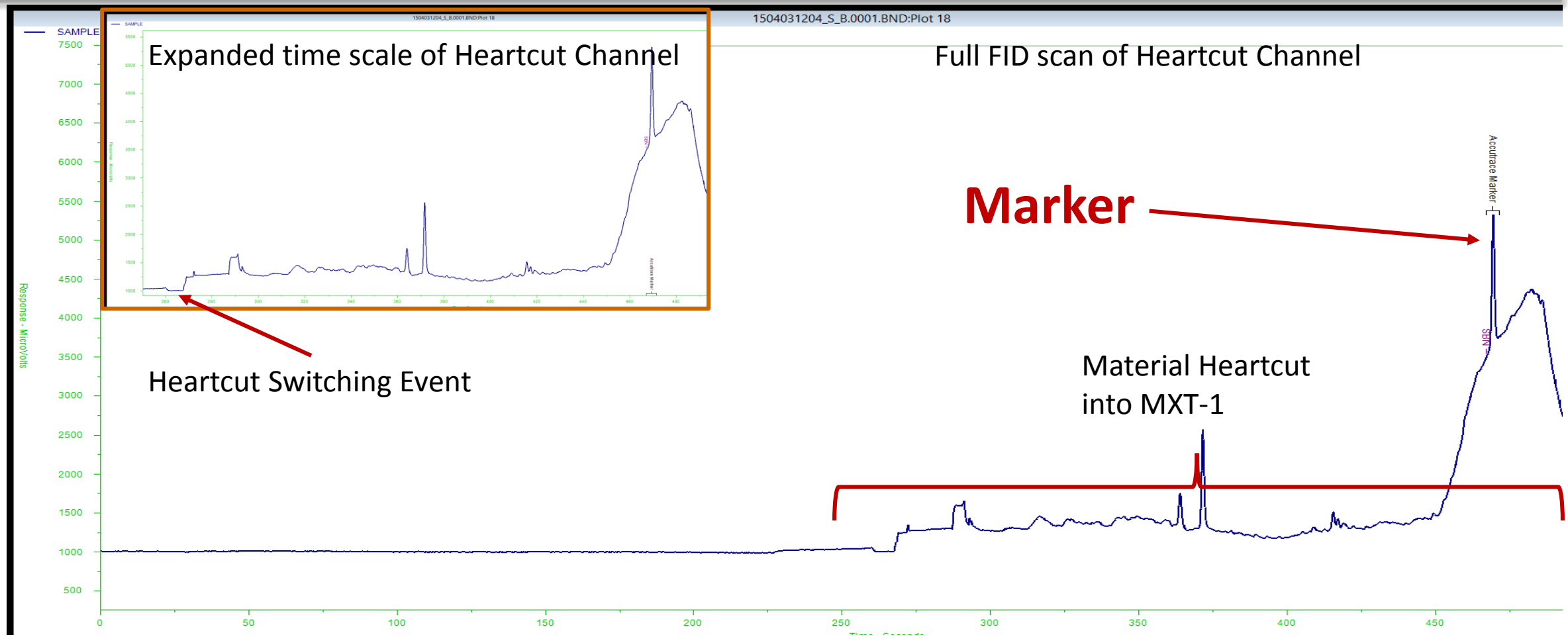
Marker at 500 ppb from the Heartcut Channel (attend Bill Winniford's presentation)



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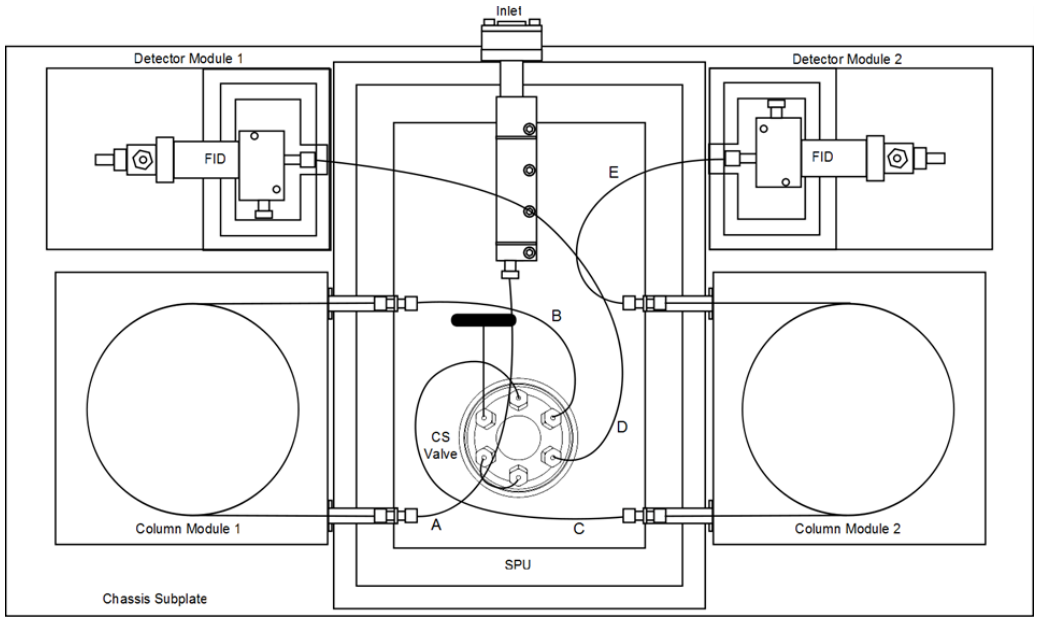
Sorry… it's just column switching… ☺

- Parallel chromatography
- Multidimensional chromatography
- 2-D Gas Chromatography
- GC by GC… GCxGC
- Comprehensive 2-D GC

OK, now that I've had my fun…



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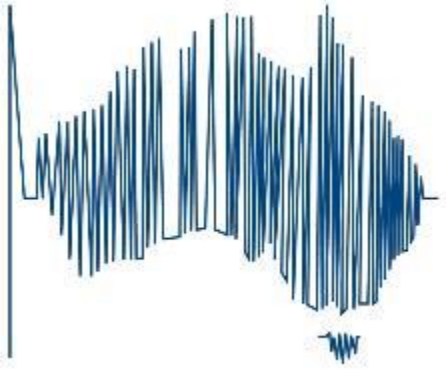
Applications of planar microfluidic devices and gas chromatography for complex problem solving

Robert A Shellie

ACROSS
Australian Centre for Research on Separation Science



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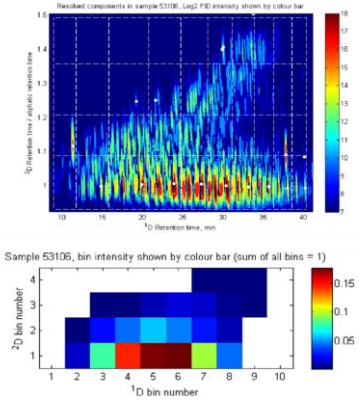
“Significant progress [in multi-dimensional separations] will depend on a judicious choice of building blocks, the development of effective means for their combination, system optimization, and the development of sophisticated detection and data reduction systems.” (Giddings 1984)



Giddings JC. Two-dimensional separations: concept and promise. Anal. Chem. 1984; 56:1258A–1270A.

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- Migration from tube based flow systems to planar microchannel systems delivers flexible and innovative chromatographic solutions

- Capillary flow technology (first generation)

- SilFlow technology (second generation)

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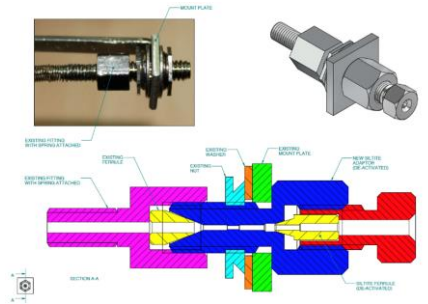
SilFlow Planar Microfluidic Devices

Like capillary flow technology:

- Chemically inert
- Low dead volume
- Reliable operational stability (thermal cycles)
- Easy to install and leak free

Unlike capillary flow technology:

- Lower thermal mass
- Substantially lower cost
- Smaller in size = flexibility for system application
- A genuine Australian product



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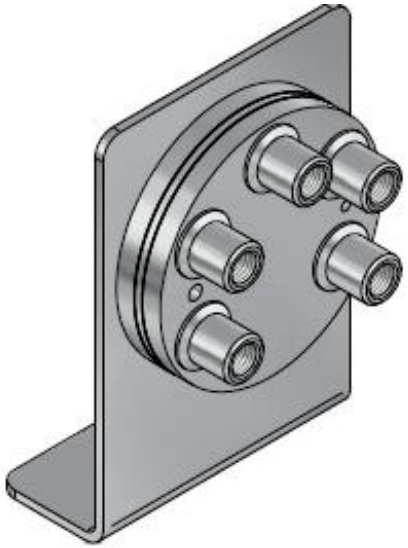

micro-GC

Bench Top

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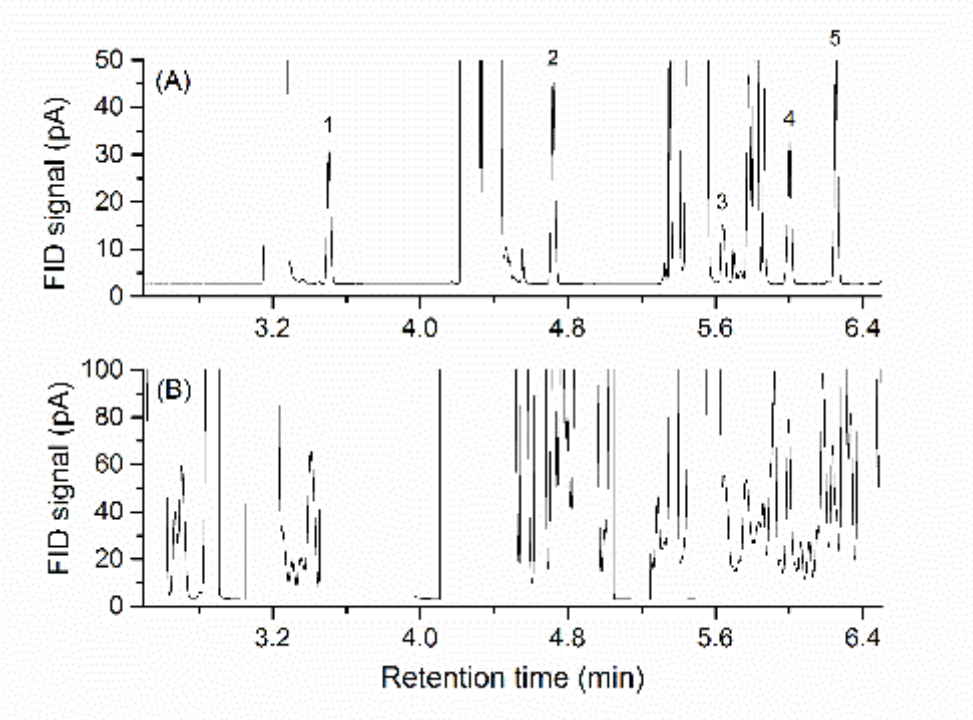
- Three-port configuration:
  - Splitting of inlet to two columns (parallel chromatography)
  - Splitting of column effluent to two different detectors

- Four port configuration:
  - Back-flush to vent
  - Column isolation

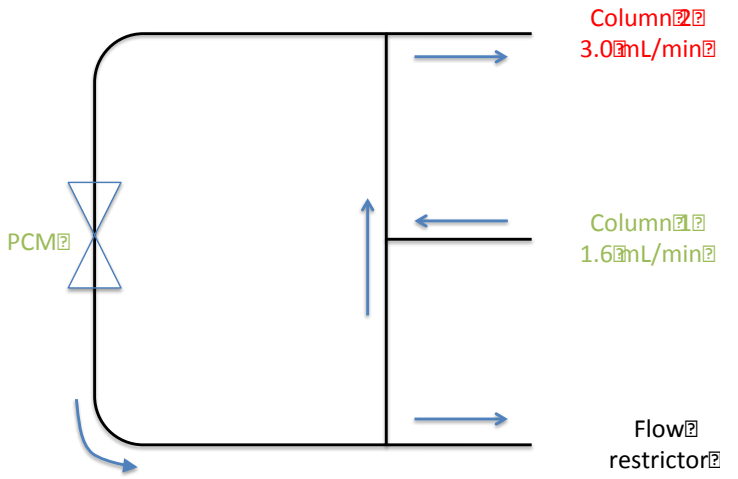
- Five-port configuration:
  - Multi-dimensional gas chromatography

- Comprehensive two-dimensional gas chromatography
  - Two three-port configuration

Five-port configuration: Multi-dimensional gas chromatography



Isoparaffins™ synthetic hydrocarbon solvent spiked with BTEX



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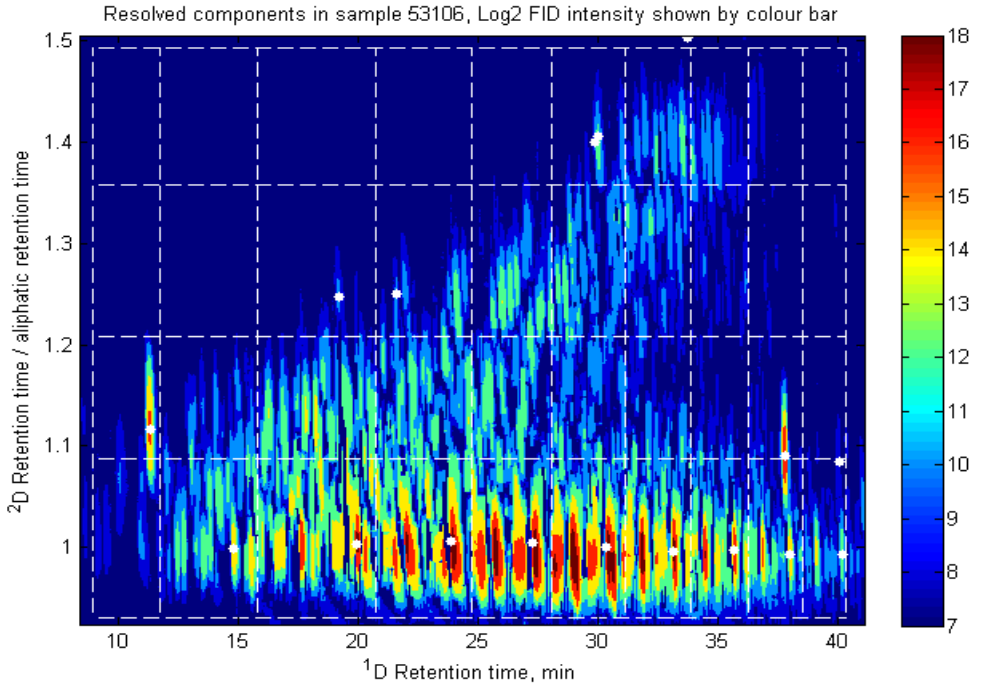

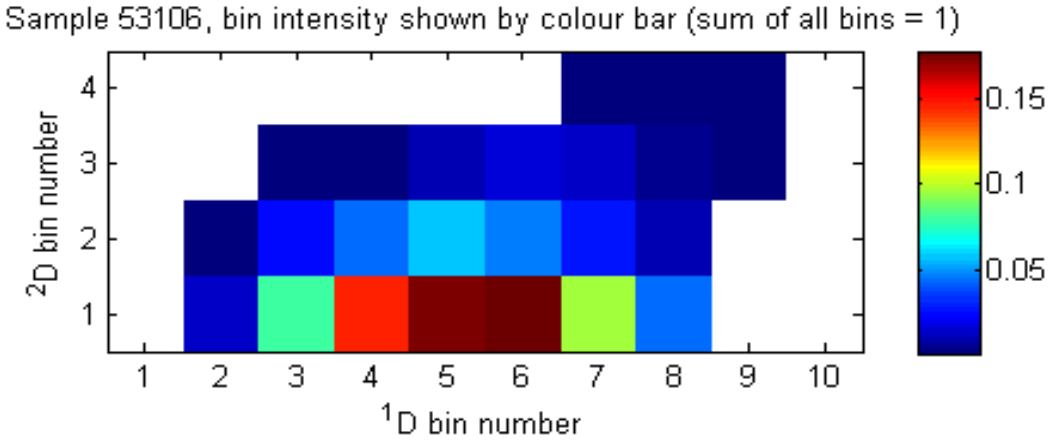

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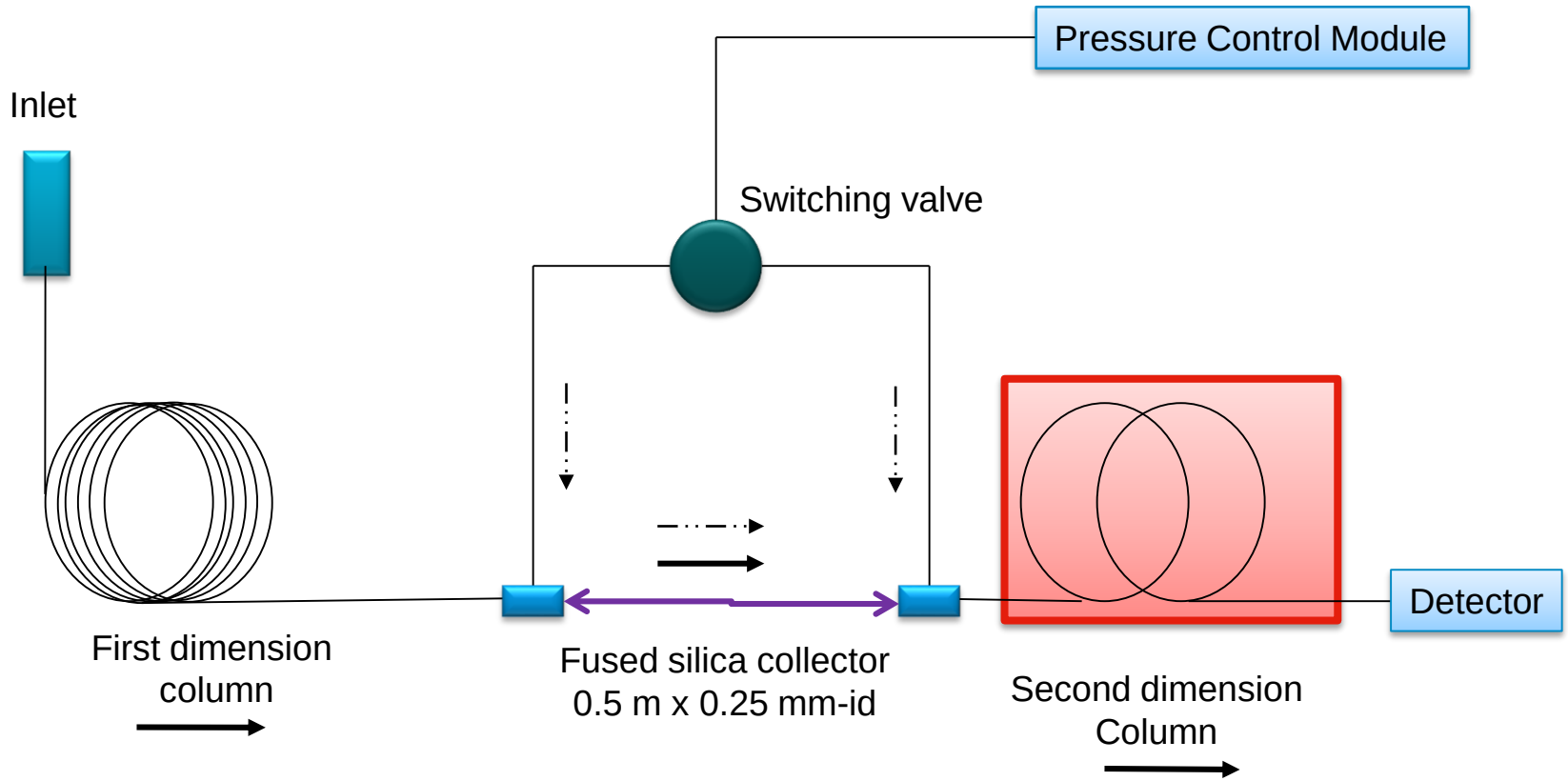
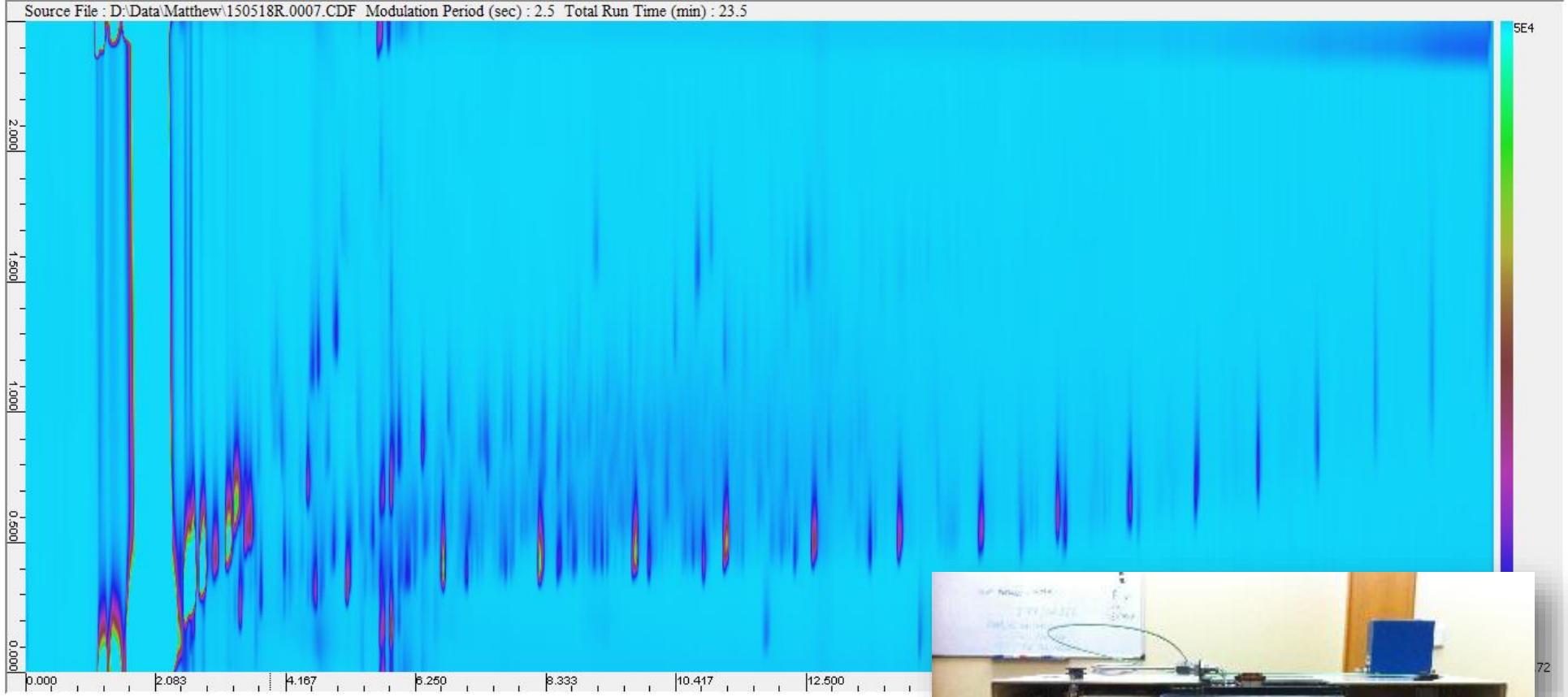
Two three-port configuration: GC×GC





Sample: Wide cut diesel, 1 uL injection
20:1 split

Comments: P_m = 2.5 s, Pi = 110 ms

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Acknowledgements

Matthew Jacobs, University of Tasmania

Jim Luong, Dow Chemical Canada

Kayte Parlevliet & Brett Barnett, Trajan Scientific & Medical

John Crandall, Ned Roques, Falcon Analytical

This work was supported by the Australian Research Council Discovery Projects Funding Scheme (DP110104923)

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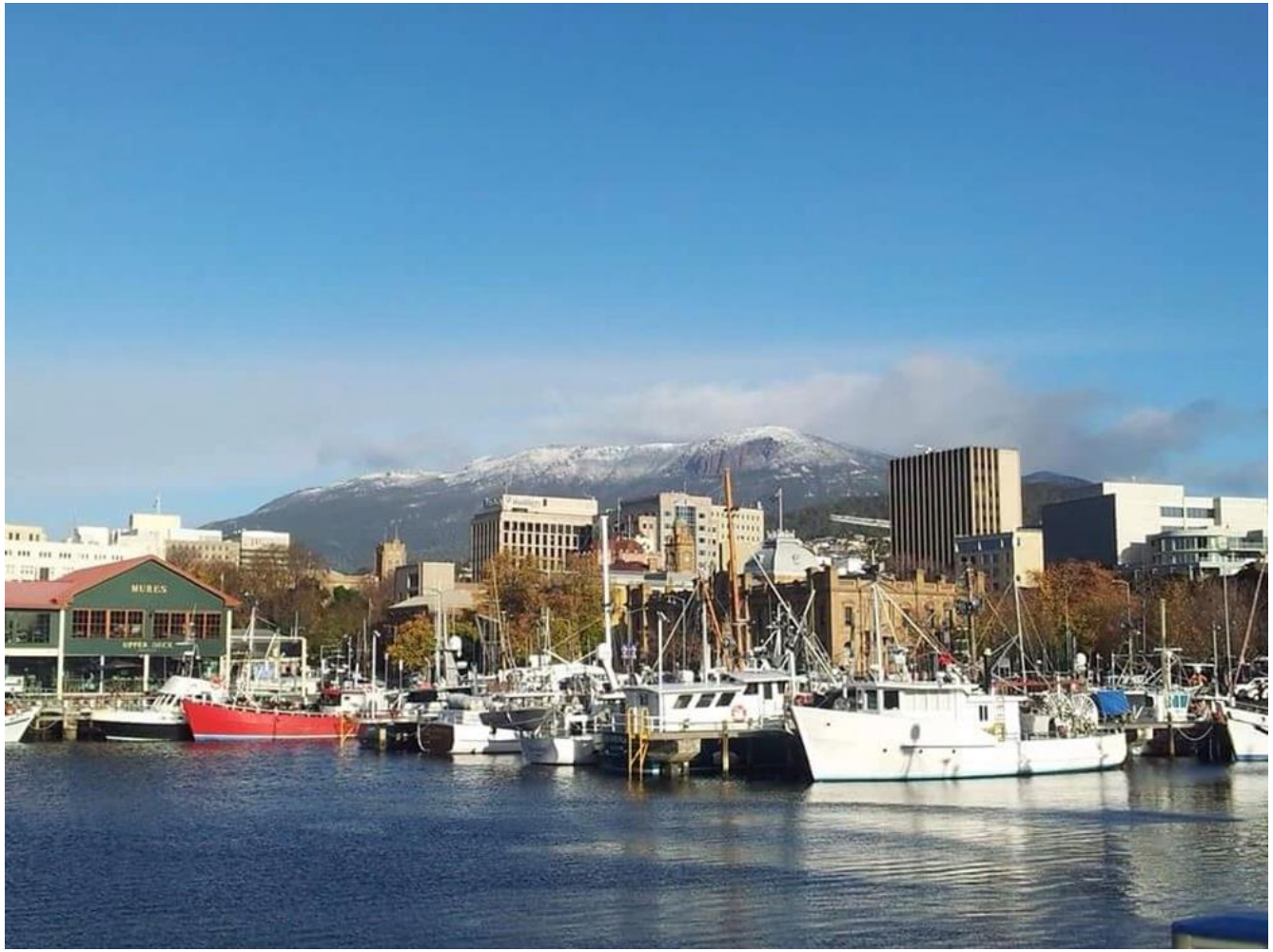
CALIDUS
micro GAS CHROMATOGRAPH

in the lab…

in the process…

in the field.



Questions

Thanks for your interest and attention.

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CALIDUS
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