A Comparison of Thermal and Flow Modulation GCxGC with dual FID-MS for Aviation Fuels

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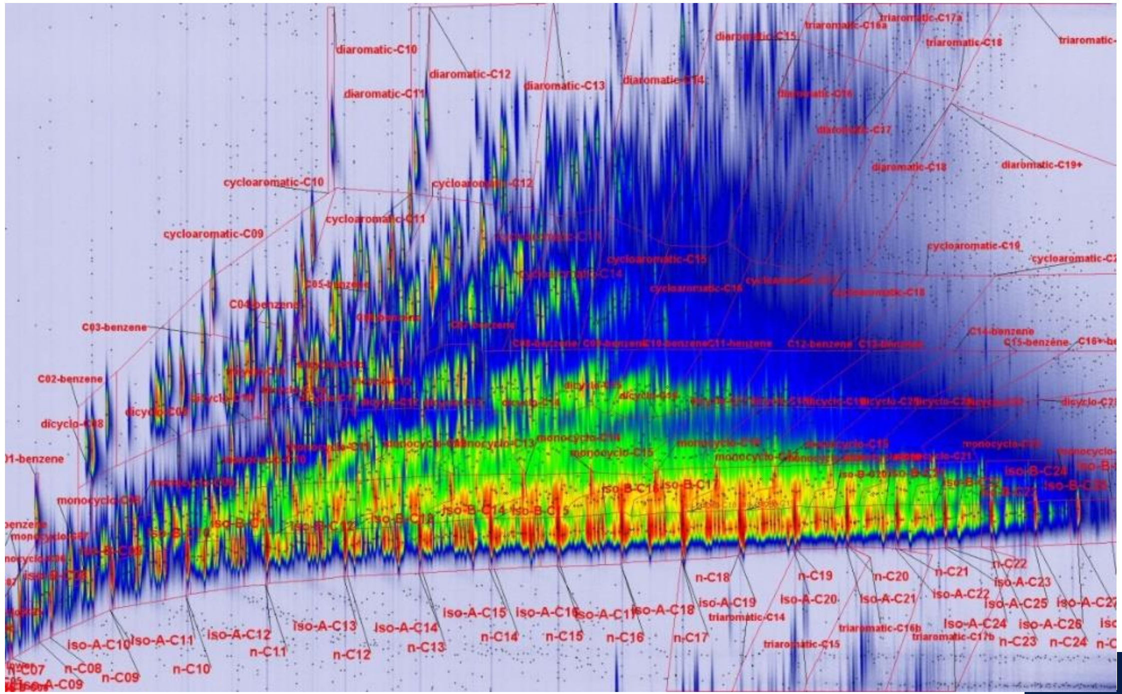
Introduction: Hydrocarbon Type Analysis, GCxGC

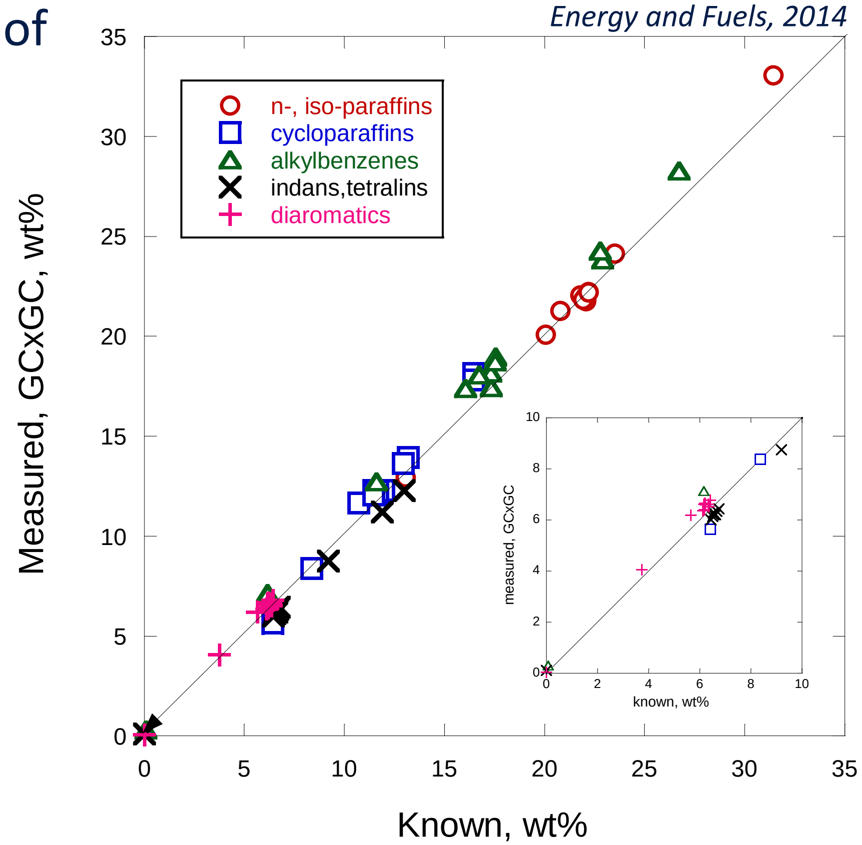
- ASTM D2425 HC type by MS is difficult
  - D2425 requires multiple instruments and analyses
    - HPLC-refractive index detection, HPLC-fraction collection, GC-MS of 2 different fraction and computing routine to examine the results
  - Quantified by MS single ion response
- GCxGC improvements
  - Improved separation in two dimensions
  - quantified by FID, simultaneous MS
- Original preference: flow modulation
  - non-polar primary column (DB-5MS)
  - moderately polar 2nd column (DB-17MS)

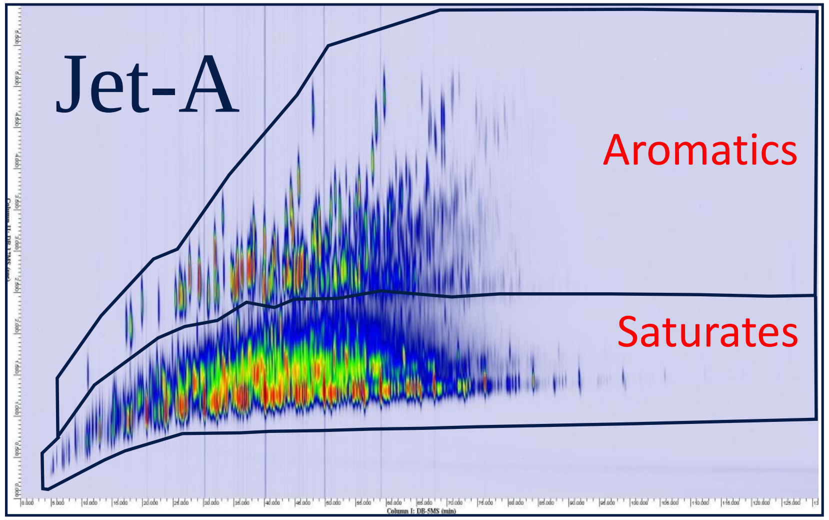


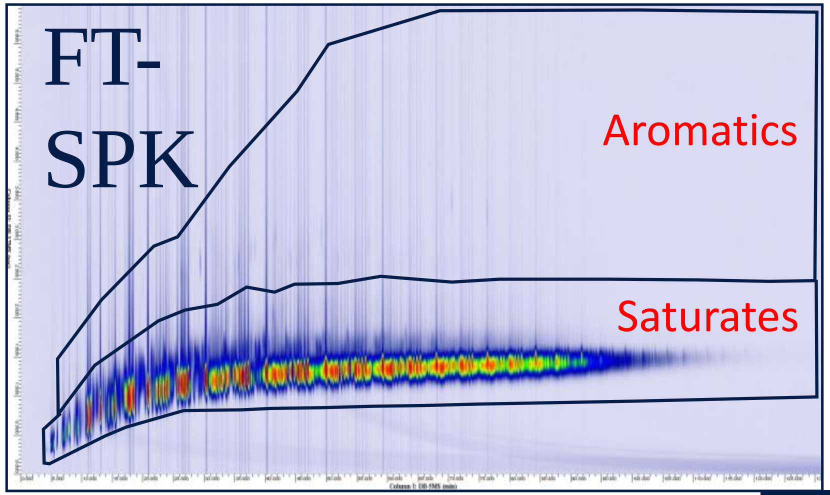
Hydrocarbon Type Analysis – Flow modulation GCxGC

- Demonstrated method with complex mixtures of standards
- Characterized petroleum and alternative Jet A plus:
  - F24
  - JP-5
  - Diesel
  - JP-7
  - Gasoline
  - RP-1,2
  - others

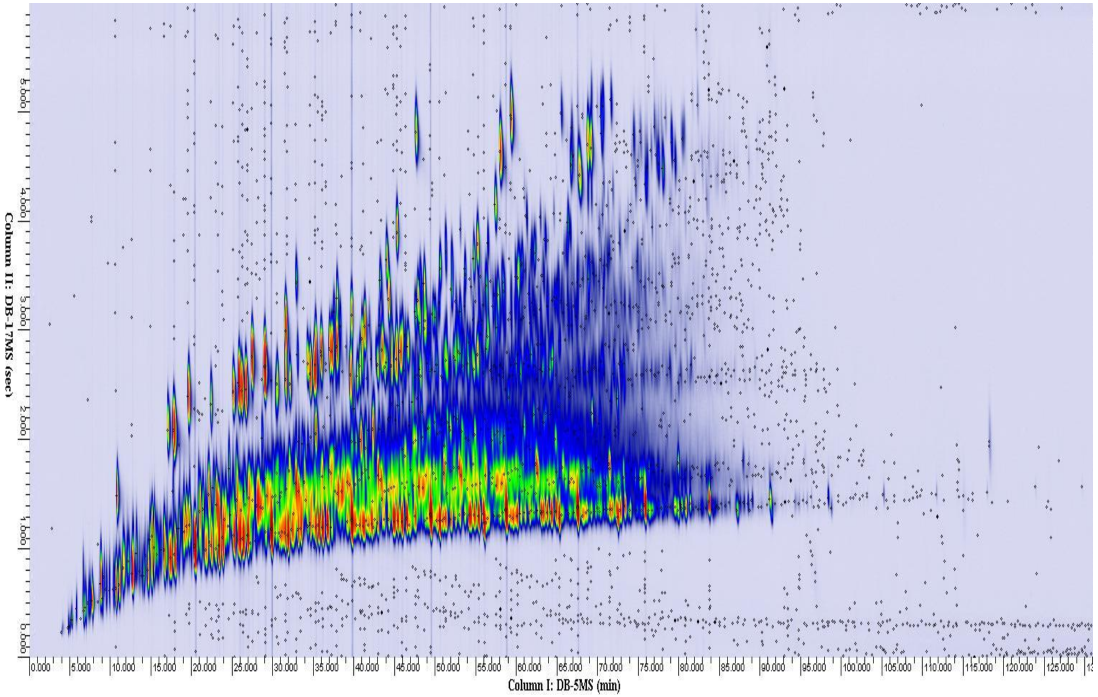
92 different jet fuel components blended into 12 different mixtures



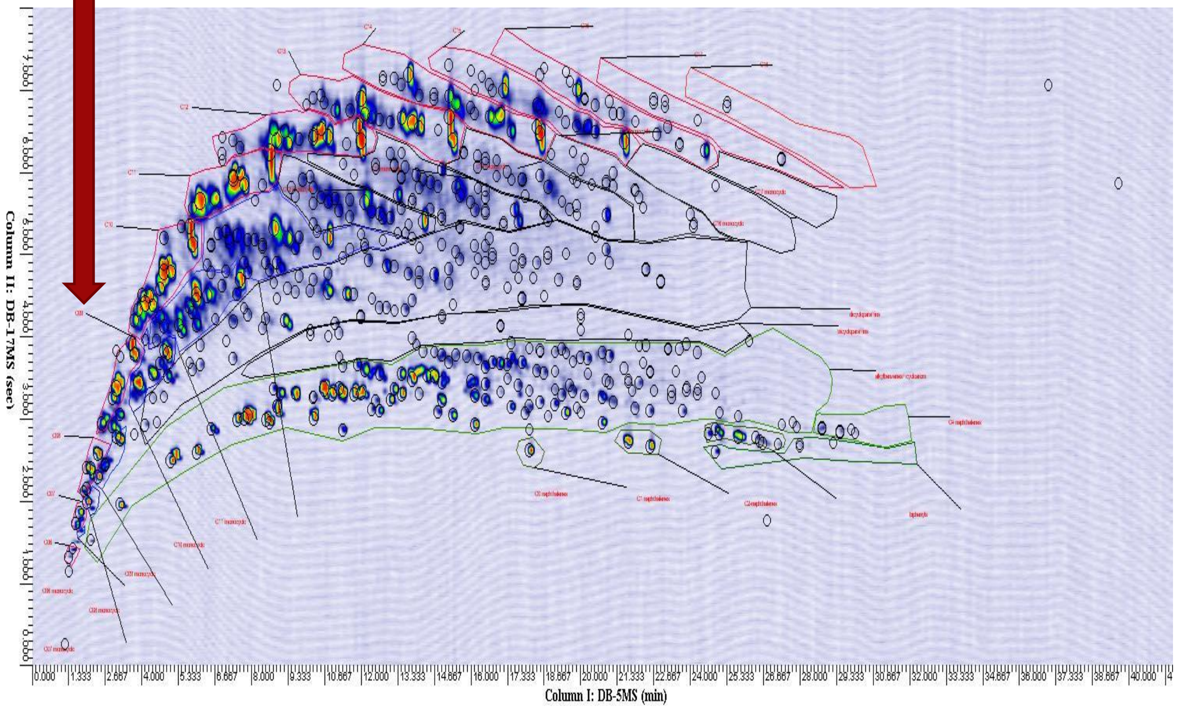




Original applications were for “normal” phase GCxGC



Difficult area



Normal phase:
non-polar primary column

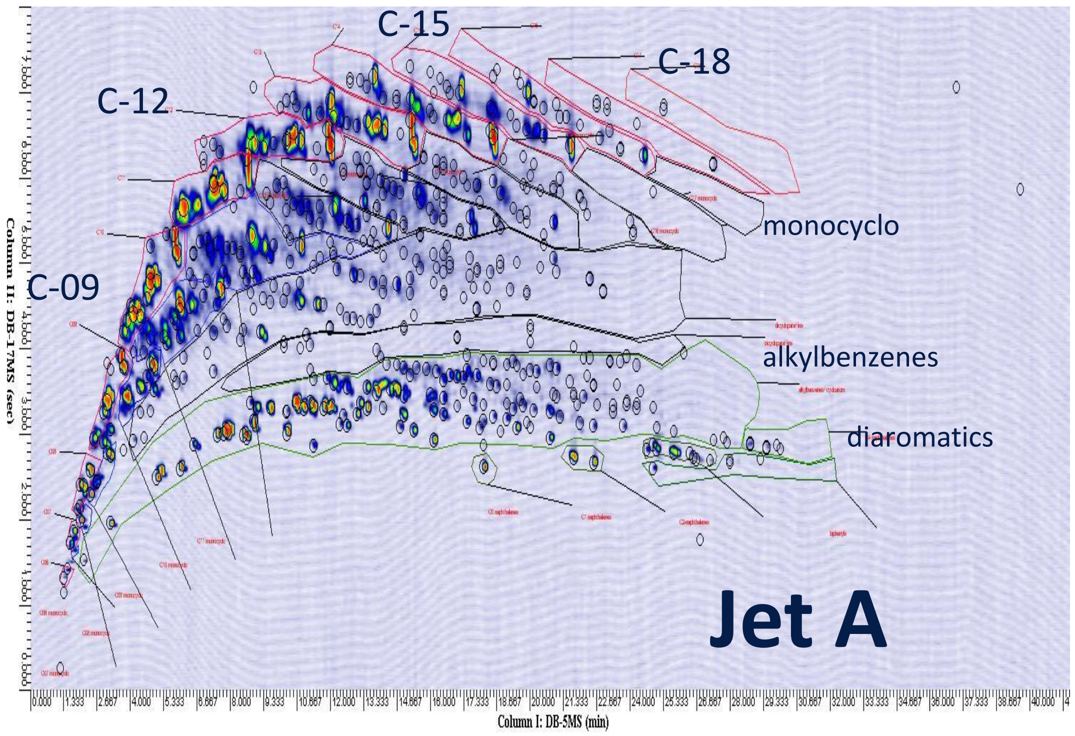
Reverse phase:
polar primary column

Hydrocarbon Type Analysis – can also determine carbon number within compound class

	10325 Jet A		12381 ATJ		12382 50/50 Blend	
	Weight %	Volume %	Weight %	Volume %	Weight %	Volume %
Aromatics						
Alkylbenzenes						
benzene (C06)	0.01	0.01	<0.01	<0.01	<0.01	<0.01
toluene (C07)	0.16	0.14	<0.01	<0.01	0.08	0.07
C2-benzene (C08)	1.10	1.00	<0.01	<0.01	0.56	0.49
C3-benzene (C09)	2.97	2.73	<0.01	<0.01	1.54	1.37
C4-benzene (C10)	3.32	3.05	<0.01	<0.01	1.71	1.52
C5-benzene (C11)	2.22	2.03	<0.01	<0.01	1.15	1.02
C6-benzene (C12)	1.45	1.33	<0.01	<0.01	0.75	0.66
C7-benzene (C13)	0.73	0.67	<0.01	<0.01	0.40	0.35
C8-benzene (C14)	0.52	0.48	<0.01	<0.01	0.24	0.21
C9-benzene (C15)	0.28	0.25	<0.01	<0.01	0.13	0.12
C10+-benzene (C16+)	0.15	0.14	<0.01	<0.01	0.05	0.04
Total Alkylbenzenes	**12.90**	11.84	**<0.01**	<0.01	**6.60**	5.87

Why thermal modulation?

- More balanced flow to the secondary column
  - More mass spec sensitivity
- Focusses solute zones on column
  - Narrower peaks
  - More resolution, in theory
- Many GCxGC users have thermal mod.
  - Systems too expensive to change
  - Any developed methods should incorporate both modulators



Thermal modulation, "reverse" column set (polar primary column)

Two experimental setups for doing GCxGC HC type

Carrier gas: Hydrogen
High Split injection, no dilution
Primary Column: DB-5MS (**20 m, 0.18 mm ID**)
Secondary Column: DB17MS **(5 m, 0.25mm ID)**
Capillary Flow technology modulator
6 seconds modulation time
Secondary Column Flow: **36 mL/min**
Quickswap tee
Agilent 5975 Mass spectrometer
Transfer line to FID detection

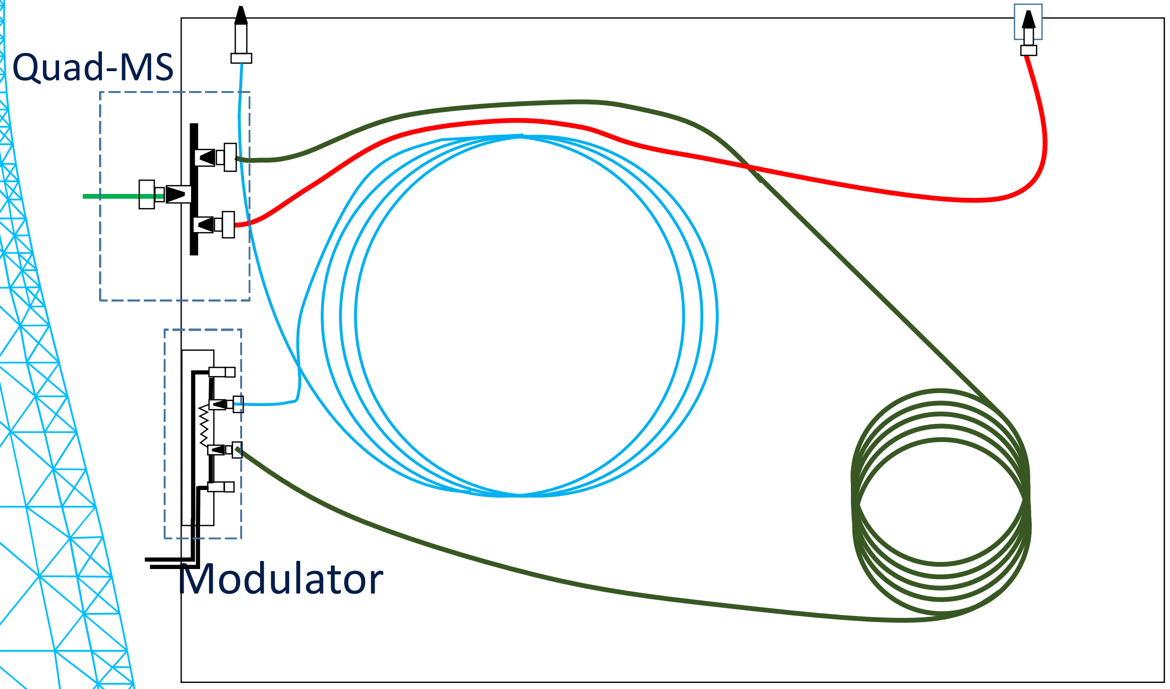
Flow modulation

Carrier gas: Hydrogen
High Split injection, no dilution
Primary Column: DB-5MS (**30 m, 0.25 mm ID**)
Secondary Column: DB17MS (**2 m, 0.25mm ID**)
LECO cryogenic modulator
6 seconds modulation time
Secondary Column Flow: **1.5 mL/min**
Capillary Flow Technology Purged Splitter
Transfer line to LECO Peg IV TOF-Mass spectrometer
Transfer line to FID detection

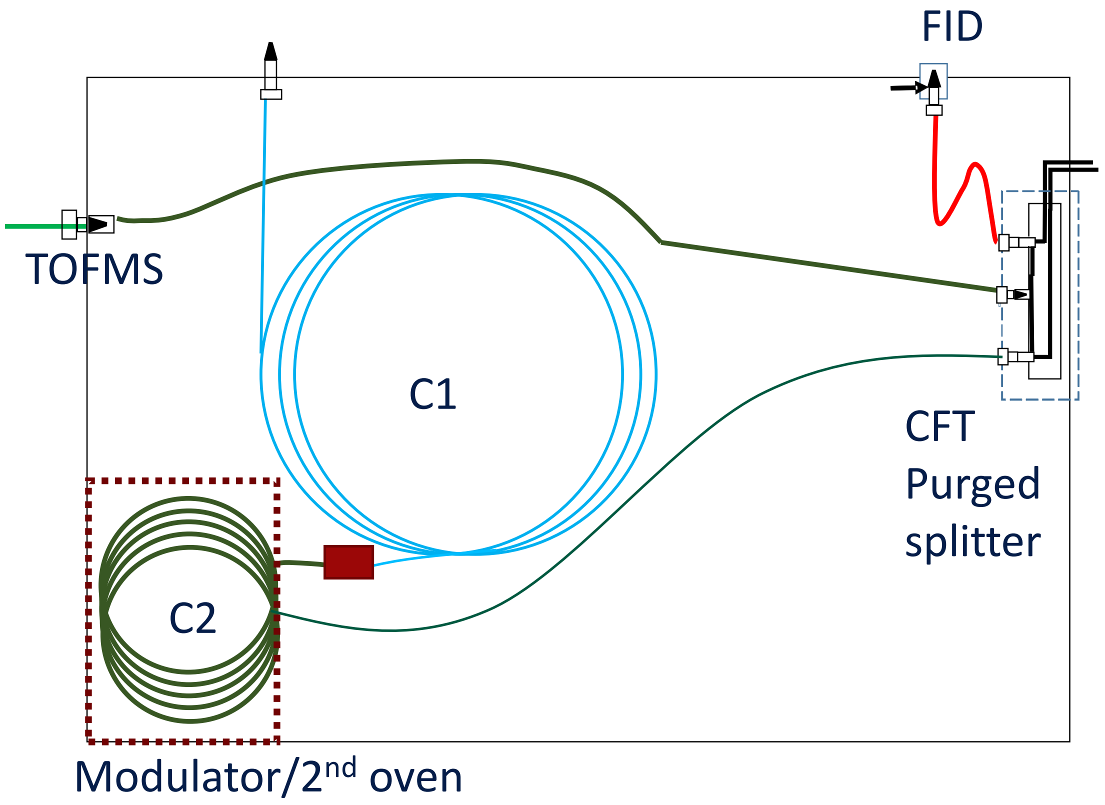
Thermal modulation

Different columns (same phases), different flows, different modulators

Two experimental setups for doing GCxGC HC type

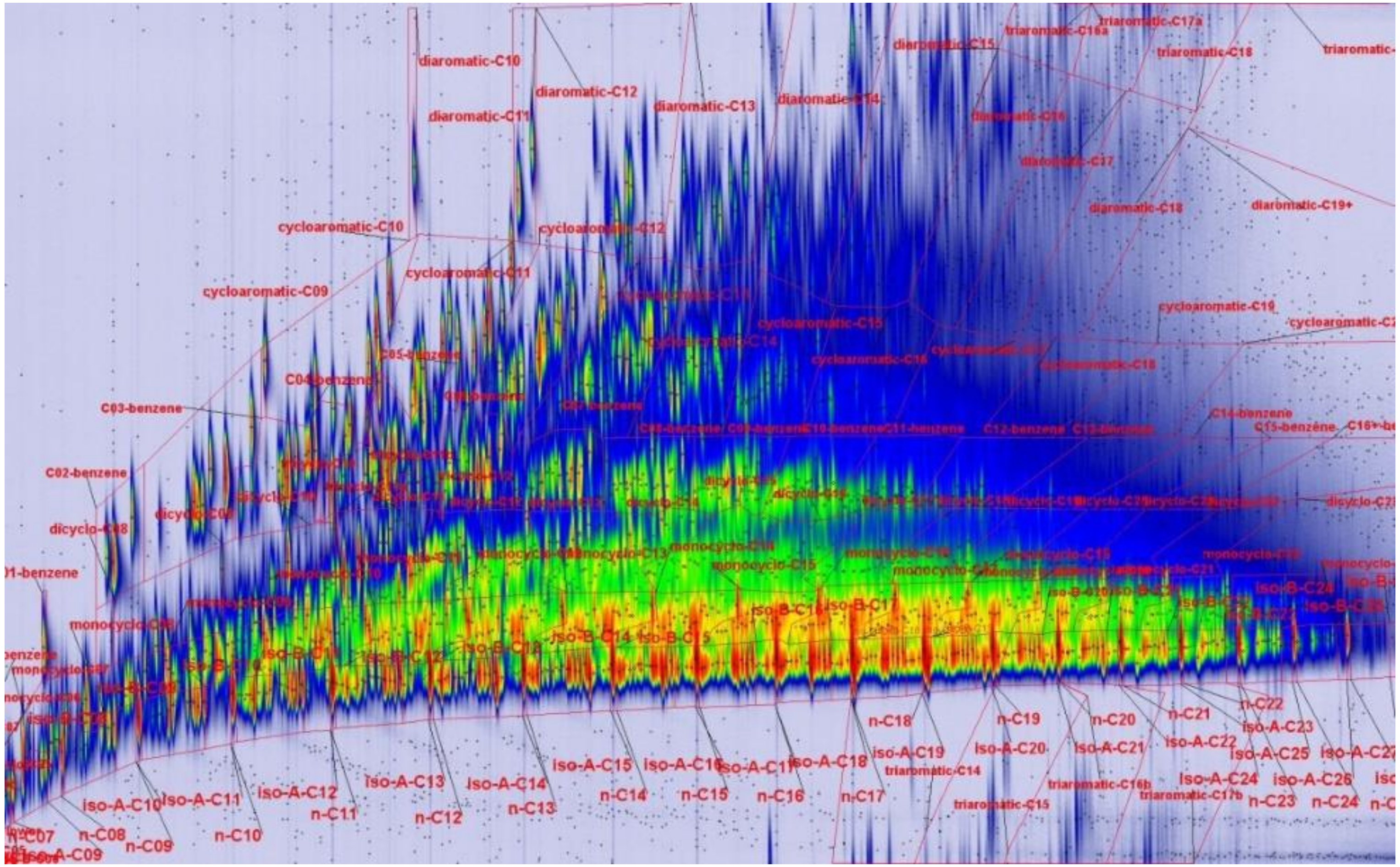


Flow modulation



Thermal modulation

Flow modulation vs thermal modulation (Similar!)

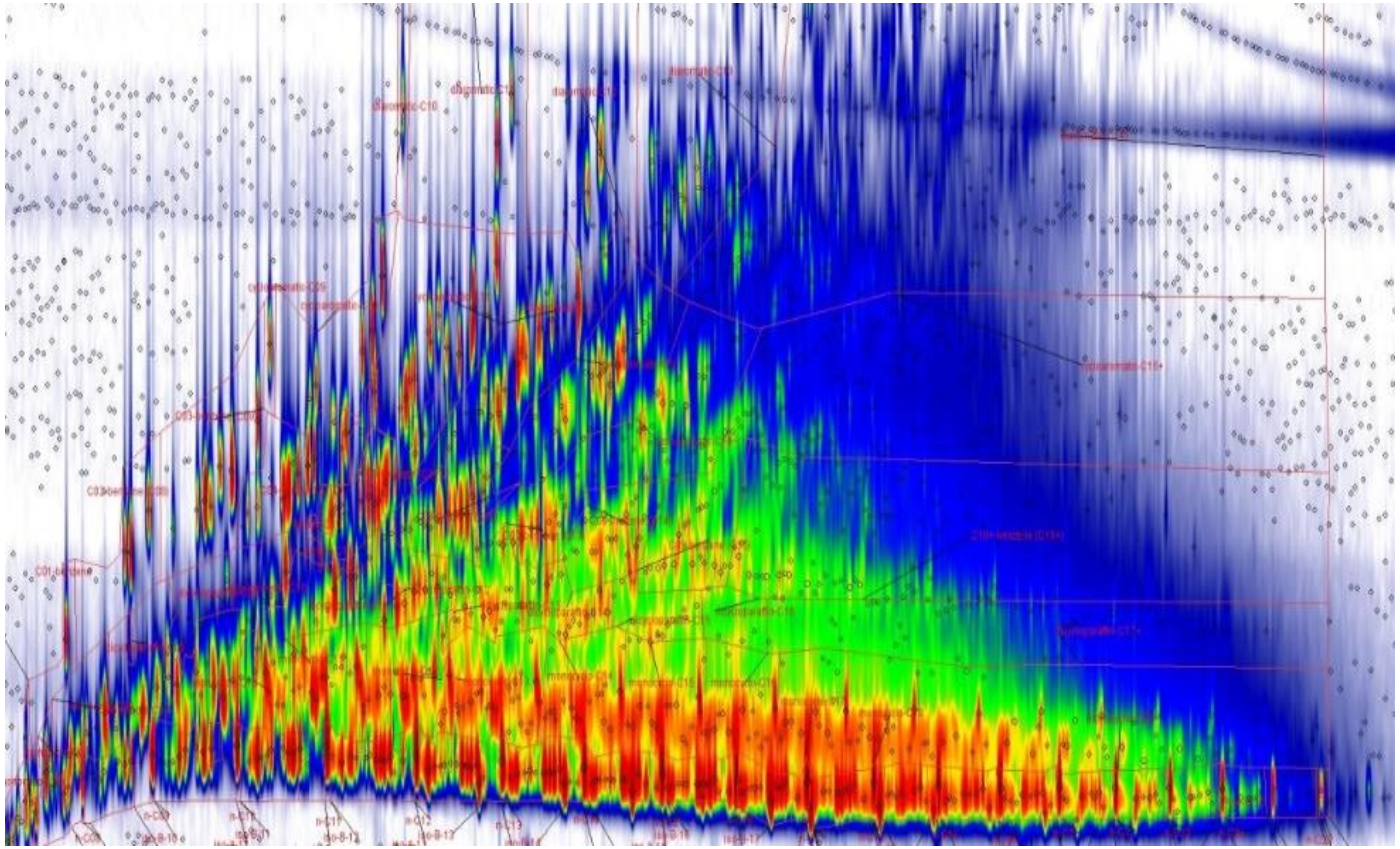


13294 F76,

Flow modulation,

Fid-quad-MS

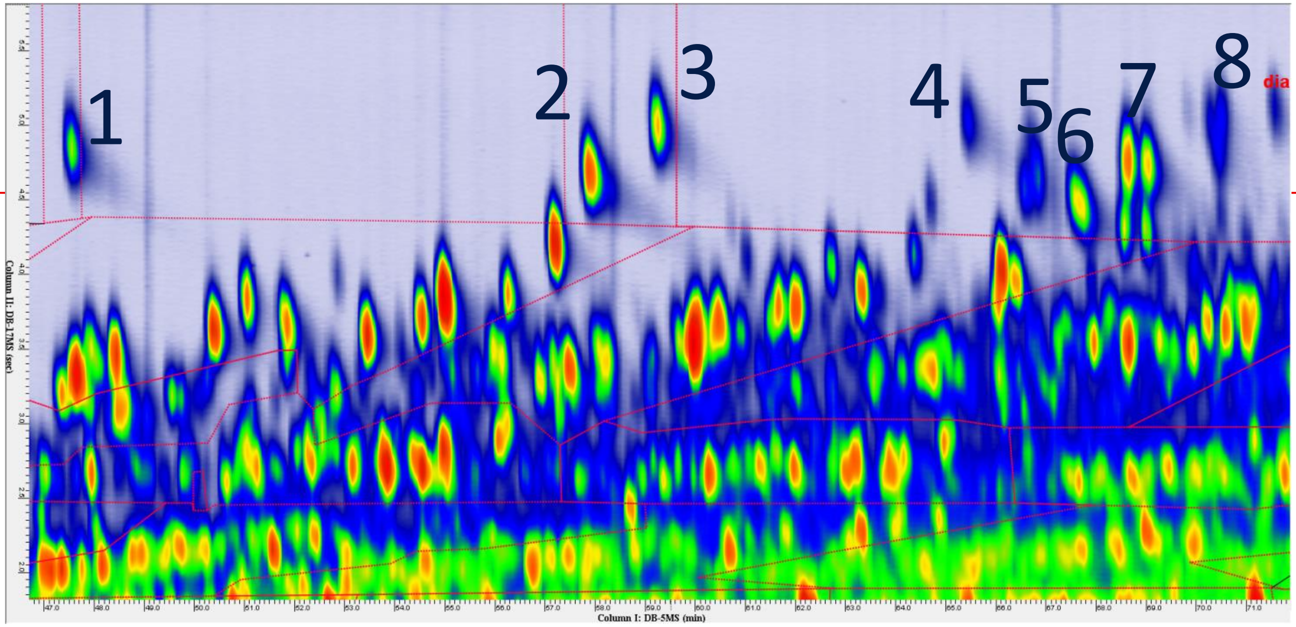
Thermal modulation example: F76



13294 F76,
Thermal modulation,
Fid-TOFMS

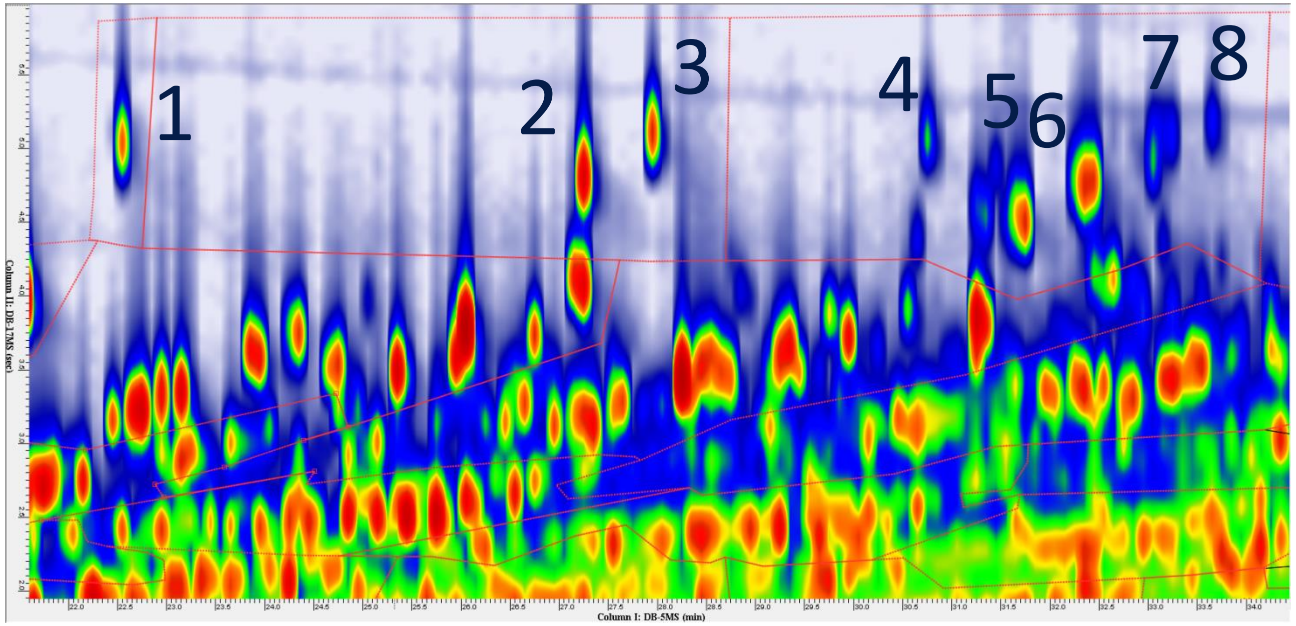
Comparison example: naphthalenes

flow



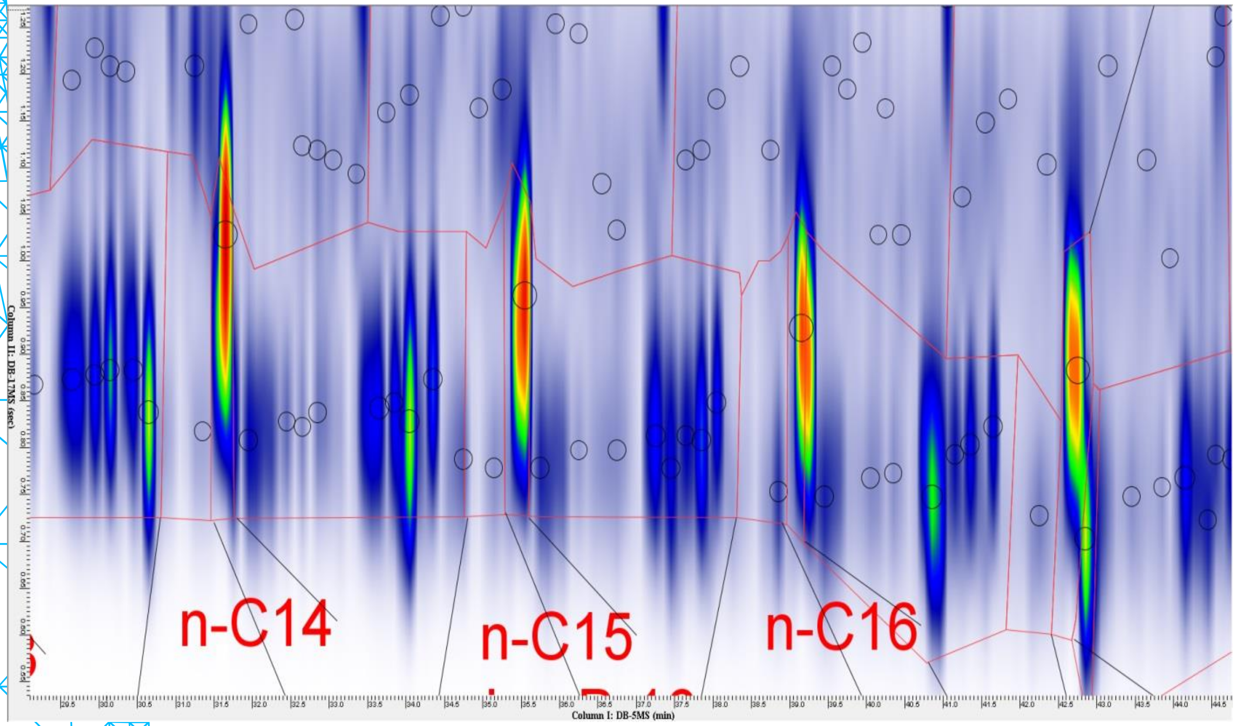
- Slight differences, but overall, very close
- Different times, different amounts, tailing (streaking different)
- Programming rates also different

thermal

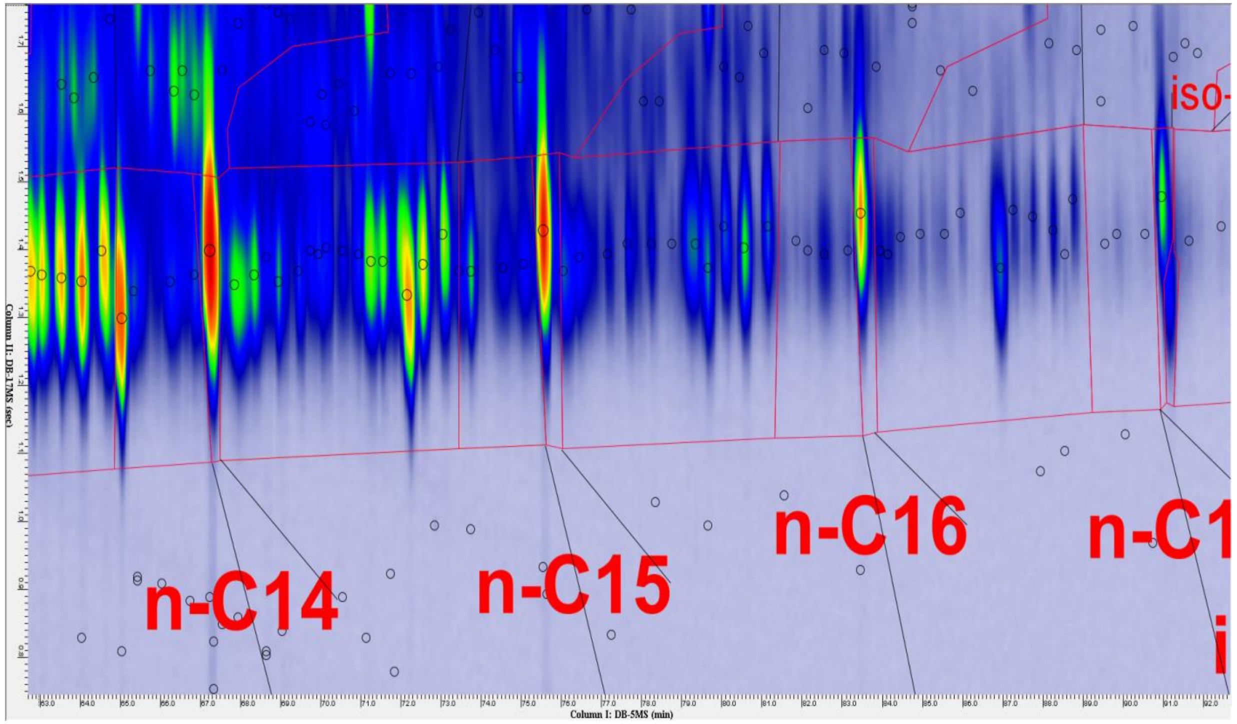


Highly branched alkanes

Thermal Modulation

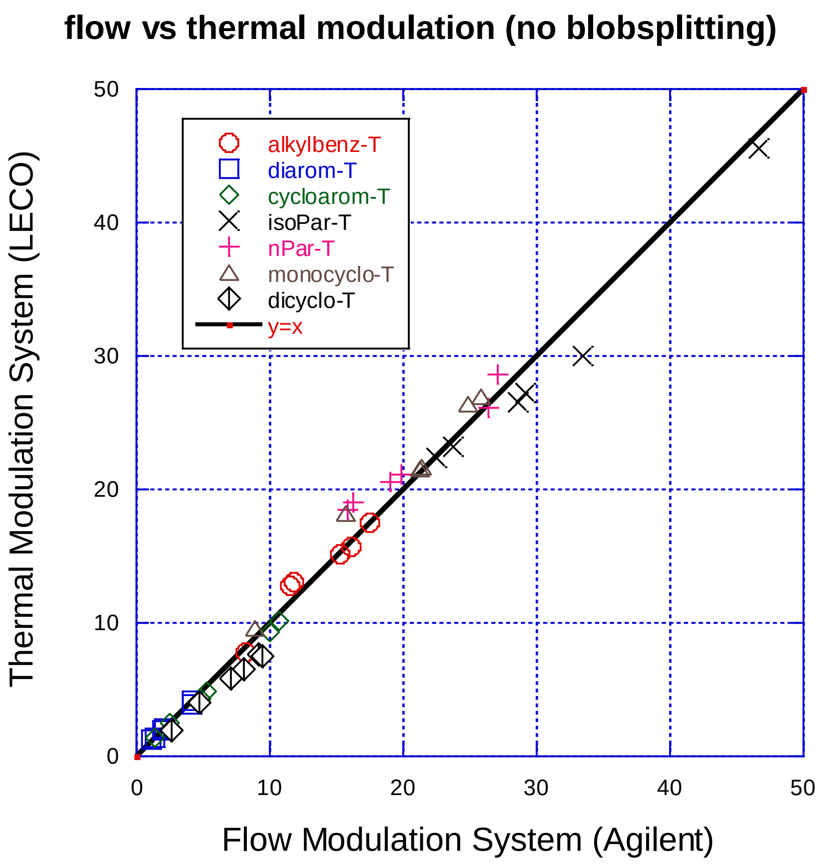


Flow Modulation



HC Type Results, comparing the thermal and flow modulation

- These are results for six different fuels, F-24s and F-76s
- The isoparaffins are lower in the flow mod system than in thermal. n-alkanes are correspondingly higher.
- Dicycloparaffins are somewhat lower for the thermal modulation system (LECO). Monos are a little higher for thermal mod.



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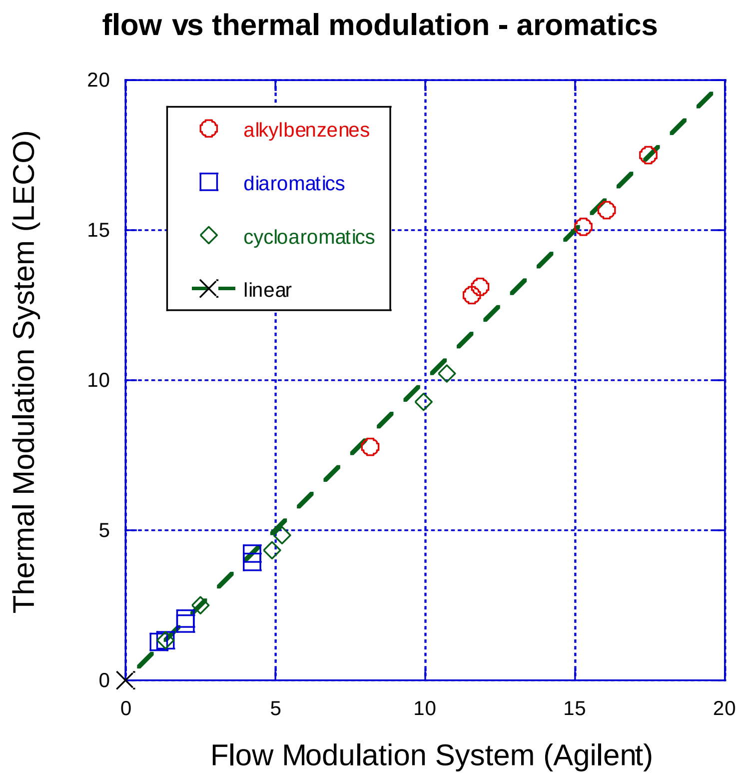

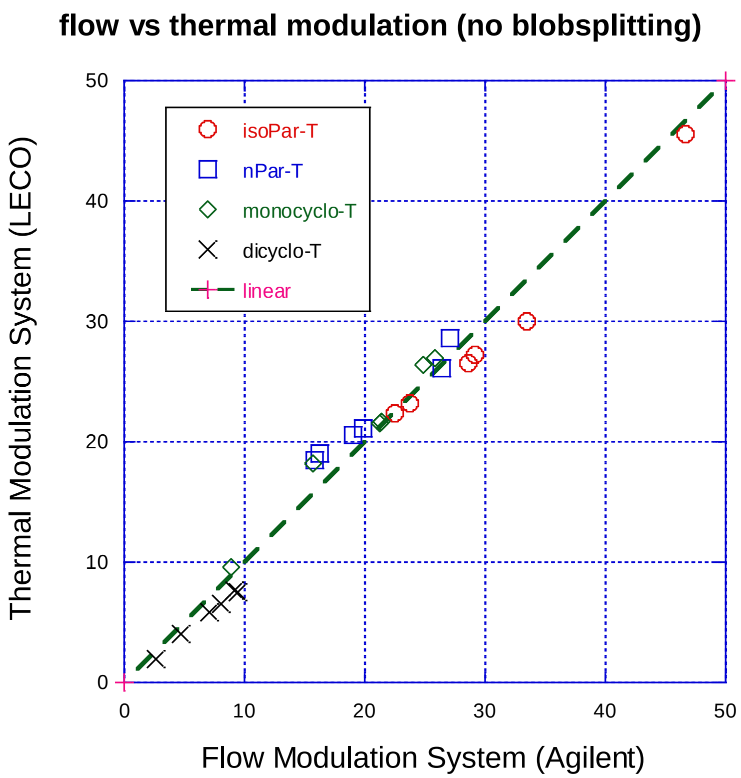

Aromatics

Alkyl-, cyclo-paraffins

Conclusions

- ASTM D2425 is a difficult technique for hydrocarbon type analysis. GCxGC has many advantages
- GCxGC: two main techniques of flow and thermal modulation.
- Thermal and flow modulation compared for Jet A, diesel fuels (6 processed so far), more now available
- Different (but similar) templates must be used
- Early work shows good agreement between modulators, in spite of other experimental differences
- Comparisons to other GCxGC systems are on-going