No More Split Ends??

Flow-Modulated GCxGC-QMS Analysis Without Splitting Off the GC Flow

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Introduction

GCxGC

Image c/o SepSolve

Thermal vs Flow Modulation

Thermal modulation

Flow modulation (if PowerPoint will play this video)

'Fill' mode

^{1}D column eluent is sampled in to the loop

The INSIGHT device that you can see here uses a consumable-free process that works by simply filling and flushing a sample loop.

Thermal vs Flow Modulation

Thermal	Flow
• Better sensitivity (in theory)	• Volatiles OK!
• Sharper peaks (in theory)	• No cryo needed
• More intuitive	• Cheaper (or is it)
	• Lends itself well to split flow
• Can’t trap smaller analytes without cryo (or at all)	• Requires high flow

But MS doesn’t like high flow 😠

But What if…

- … an MS *could* accept higher flow rates…
  - Such as the JMS-Q1600GC quadrupole GC-MS system…
    - That has a spec of 20 mL/min…

JMS-Q1600GC UltraQuad™ SQ-Zeta

LET'S TRY IT!!!!

How I should have been a plumber (Methods)

JMS-Q1600GC UltraQuad™ Zeta

- ~10^6 dy. Range
- EI, PI, CI
- Direct Probe
- 22,222 u/s scanning
- 200 L/s evac
- 20 mL/min flow

INSIGHT Flow Modulator

- Cryogen free
- No volatility restrictions
- Complete analyte xfer
- MS+FID
- ChromeSpace software
- Bleed line control kit

The Down and Dirty (method)

- D_1: Zebron ZB-5MSplus
  - 30 m x 250 µm x 0.25 µm
- D_2: Trajan BPX50
  - 5 m x 250 µm x 0.1 µm
- Bleed: Trajan Blank capillary
  - 5 m x 100 µm x 0 µm
- F_1: 0.5 mL/min
- F_2: 25 mL/min (WOW)
- $F_2/F_1 = 50$
- Bleed flow: ~ 0.5 mL/min
- Split: between 5 and 50
- Oven:
  - 80 °C (1 min) → 3 °C/min → 310 °C (up to 21 min)
  - Runtime: up to 99 min

- Mod period: 4.5 s (75% loop capacity)
- Flush 125 ms (100% loop vol + 25 ms)
- Inlet: 300 °C
- MS:
  - 70 eV EI, 50 µA
  - *m/z* 35 – 505
  - 15 Hz collection speed

(Results)

Disclaimer*

Pesticide Mix Tape (over 200 compounds!)

Pesticide Mix Tape

Pesticide Mix Tape (now in !)

Spectral Quality

- Only four compounds with MF > 800.
- Highest was 833.
- And yet, match probabilities were high.
- Many correct IDs from my own data exploration.
- Approx. 120 compounds ID’d correctly.

msFineAnalysis iQ analysis of 1D data (deconvolution)

1D Results from msFineAnalysis iQ

Famous Perfume Brand B4

Perfume Brand D

Perfume Brand D

Perfume Brand D

Perfume Brand D

Obligatory Diesel…

Soy B20

1tR 11.4113
Intensity 1.262E+06
2tR 2.1443
Soy-B20_GCxGC-FM_001_SCAN.cdf
Soy-B20_GCxGC-FM_001
Retention Time (mins)
Soy-B20_GCxGC-FM_001_SCAN.cdf: 2tR at RT=0.9 minutes
Mass (m/z) 43.5
Abundance 3.20825E+06
Soy-B20_GCxGC-FM_001_SCAN.cdf: 1tR at 2tR=0.000233 minutes
Mass (m/z)

SOY! SOY! SOY!
imgflip.com

50
40

Brand D at 50 mL/min flow into MS

50 mL/min

25 mL/min

Spectral Comparison (Ethylene Brassylate)

25 mL/min

50 mL/min

Spectral Comparison (trans-β-Ionone)

25 mL/min

50 mL/min

LE GRILLE? WHAT THE HELL IS THAT?
Max Power Memes

Things I learned along the way

- 100 PSI S/SL inlet works…but 150 is better (probably) 😣
- Takes

to set up!! But is (mostly) stable afterwards.
- Add the bleed line dimension to D1, or add it as a separate column…not both. 😣
- Smaller bore D1 is better, but gosh man, the pressure!

- Get someone else to do it.

Questions I Can’t Answer (Discussion)

Inquiring Minds Want to Know…

- How does ___ compare to thermal GCxGC?
- How come the separations aren't optimized?
- What about data speed?
- What is that ___ peak in the ___ chromatogram?
- ~~What about library searching?~~
- What about other gases?
- What is the sensitivity?

Conclusions and Future Work

Conclusions and Future Work

- Flow-modulated GCxGC-MS can be done without splitting the flow!
- Separation conditions need to be optimized
  - Higher PSI inlet
  - Better D1 column
  - Reverse phase for appropriate samples
- Sensitivity Study
- Even more flow??? Madness!!
- Helium is fun! And expensive! Switch to (insert less fun gas here).
  - QMS is a good target for the less-fun gas Hydrogen gas

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