Planar Microfluidics in Multidimensional Chromatography

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Planar Microfluidic Devices in Gas Chromatography - Drivers

- Migration from tube based flow systems to planar microchannel systems to deliver flexible and innovative chromatographic solutions
  - 1. Suitable for fast moving molecules
  - 2. Doesn’t require cryogen
  - 3. In-Oven with no moving parts

- Capillary flow technology (first generation)
- SilFlow technology (second generation)
Benefits and impact

Like capillary flow technology:
- Chemically inert
- Low to no dead volume
- Super operational stability (thermal cycle)
- Easy to install and leak free

Unlike capillary flow technology:
- Much lower thermal mass; by 300%
- Substantially lower cost, by 400%
- Smaller in size = flexibility for system application
Configuration of a three-port splitter device for parallel chromatography

30 m x 0.32 mm-id x 20 µm **HP-PLOT Q**

30 m x 0.32 mm-id x 10 µm **Rtx-Alumina BOND MAPD**


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Overlay of chromatograms of 1000 ppm (v/v) each of hydrocarbons in helium

PW1/2=0.007648 min
PW1/2=0.0102 min

1. Methane
2. Acetylene
3. Ethylene
4. Ethane
5. Propylene
6. Propane


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Configuration of a three-port splitter device for column effluent splitting

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An overlay of chromatograms obtained on the FID and P-SCD of a natural gas sample spiked with 10 ppm (v/v) each of hydrogen sulfide, carbonyl sulfide, methyl mercaptan and ethyl mercaptan respectively.

1. Hydrogen sulfide
2. Carbonyl sulfide
3. Methyl mercaptan
4. Ethyl mercaptan
5. Impurity
6. Impurity
Configuration of a four-port splitter device to perform back-flush with a mid-point pressure source

Inlet Pressure (P1)

Fused silica restrictor

Pressure control module (P2)

Transfer line

FID-1

FID-2

10 m x 0.32 mm-id x 1 µm VF-Waxms

30 m x 0.32 mm-id x 10 µm Rtx-Alumina BOND MAPD

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Accurate back-flush with four-port splitter device

Column 1: 10 m x 0.32 mm x 1 µm VF-WAXms
Column 2: 30 m x 0.32 mm Rtx-AluminaBOND MAPD

1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Propylene
6. Acetylene
7. Butane
8. Pentane
9. Hexane

Water if present


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Configuration of a twin three-port splitter device for valveless switching and column isolation

Inlet Pressure (P1)

Flow profiles:
• P1>>P2 = forward
• P1>P2 = isolate Column 2
• P2>>P1 = backflush

Pressure control module (P2)

Transfer line

FID

TCD

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Overlay of chromatograms for the separation of fixed gases and hydrocarbons in one single analysis with a configuration of a twin three-port splitter device (valveless switching and column isolation).

FID – PoraBOND Q/Methanizer

1. Carbon monoxide
2. Methane
3. Carbon dioxide
4. Ethylene
5. Ethane
6. Acetylene
7. Propylene
8. Propane

TCD – MS5A

9. Hydrogen
10. Oxygen
11. Nitrogen

Overlay of chromatograms for the separation of oxygenated compounds and hydrocarbons in one single analysis with a configuration of a twin three-port splitter device (valveless switching and column isolation).

VF-WAXms

1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Propylene
6. Acetylene
7. Butane
8. Pentane
9. Hexane
10. Methanol
11. Ethanol
12. Propanol
13. Butanol

Configuration for multi-dimensional gas chromatography (Deans switch) with a five-port SilFlow device

First detector

Restrictor

Column 1

Inlet (P1)

Second detector

Column 2

Backflow protection restrictor

Pressure control Module (P2)

Three-way solenoid

= Connection port


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Overlay of chromatograms of hydrocarbons and oxygenated compounds with a five port SilFlow device used for the configuration of multidimensional gas chromatography (Deans switch, heart-cutting)

1. Light hydrocarbons
2. Methanol
3. Ethanol
4. Propanol

• Flow modulation with SilFlow
• Performance and operating characteristics
• Configurations and applications with auxiliary ovens (LTM)
• Industrial Applications
• Summary
• Acknowledgements
Flow modulation is an option for implementation of comprehensive GCxGC

Strengths:
• Does not require cryogen
• Simple to construct (connection fittings, three-way gas switching valve, a timing device)
• Ideal for fast moving molecules
• Handles heavy hydrocarbons

Limitations:
• Unlike thermal modulation where modulation period can be readily changed, parameter optimization can be more intensive and careful attention to k in the second dimension is important
Suggested internal diameters for the collection loop: 0.45mm, 0.32mm, 0.53mm

Be aware of peak broadening as collection channel size increases
Schematic Diagram of FM-GCxGC

Inlet

Pressure control module
20 mL/min

First dimension column
1 mL/min

Modulator with two
Three-three port
SilFlow

Second dimension column
22 mL/min

Detector

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# Implementations of Flow Modulation

<table>
<thead>
<tr>
<th>Design</th>
<th>Key Attribute</th>
</tr>
</thead>
<tbody>
<tr>
<td>External Channel</td>
<td>Easy to setup and use</td>
</tr>
<tr>
<td>Variable External Loop [1]</td>
<td>Fine tune for application</td>
</tr>
<tr>
<td>External Loop with reverse flow pulse [2]</td>
<td>Can improve modulated peak shapes with larger ID columns in 1st dimension</td>
</tr>
</tbody>
</table>

Along with other commercially available fluidic devices, aids in reducing FM-GCxGC to practice:

- No moving parts
- Low thermal mass
- Inert
- In-column switching
Modulation Period as Function of 1st Column Flow

First column flow ml/min vs. Modulation Period in seconds

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RT Stability and Effect on Modulated Area: $C_{13}$
GC x GC: Higher Resolution First Dimension

- Column 1: 10 m x 0.18 mm x 0.18 µm DB1
- Column 2: 5 m x 0.25 mm x 0.15 µm DB-INNOwax
- Column 1 flow: 0.4 mL/min
- Column 2 flow: 21 mL/min
- **Modulation Timing**
  - Load: 2.895 sec.
  - Inject: 0.114 sec.
  - Period: 3.009 sec.

Lower primary flow allows longer modulation period

Typical “general purpose” setup
Column 1: 10 m x 0.18 mm x 0.18 um DB1
Column 2: 5 m x 0.25 mm x 0.15 um DB-INNOwax

Jet Fuel

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Dual LTM System

Three Independent temperature programs

S/S Inlet

Column 1

PCM

Micro Valve

Modulator

LTM

FID

Column 2

LTM

FID

Column 3

Splitter

LTM = Low Thermal Mass

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Polarity Dimensionality

3D Phase Polarity Scale

‘Van der Waals’
BP1, BP1 PONA, BPX1, SolGel-1ms
BP1, BP1 PONA, BPX1, SolGel-1ms
BPX5
BPX5
BPX35 & BPX608
BPX35 & BPX608
BP225
BP225
BP02
BP02
BP1
BP1
BPX90
BPX90
π-bonding
π-bonding
H-bonding
H-bonding

Dimethyl Polysiloxane
Cyanopropylphenyl Siloxane
Phenyl Polysilphenylene Siloxane
Cyanopropyl Polysilphenylene Siloxane
Polycarborane Siloxane
Polyethylene Glycol

Picture courtesy of Dr. Peter Dawes, SGE Analytical Science, Australia

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## LTM GCxGC System

<table>
<thead>
<tr>
<th>Column</th>
<th>Heated By</th>
<th>Column Dimensions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>First D</td>
<td>7890 Oven</td>
<td>20 m x 0.18um x 0.10 µm VF-5ms</td>
<td>Rugged</td>
</tr>
<tr>
<td>2nd D - I</td>
<td>LTM I</td>
<td>5 m x 0.25 mm x 0.15 µm INNOwax</td>
<td>Polar</td>
</tr>
<tr>
<td>2nd D - II</td>
<td>LTM II</td>
<td>5 m x 0.25 mm x 0.15 µm DB17 HT</td>
<td>Mid-polarity</td>
</tr>
</tbody>
</table>
1. Nonane
2. 3-methyl nonane
3. Decane
4. 3-methyl decane
5. Undecane
6. 3-methyl 1-undecane
7. Dodecane
8. 4-methyl-dodecane
9. 3-methyl-dodecane
10. Tridecane
11. Tetradecane
12. Butyl benzene
13. 1-methyl 4 propyl benzene
14. 1-methyl-4-(1-methylpropyl)-benzene
15. Penty lbenzene
16. 1-methyl butyl benzene
17. Hexyl benzene
18. 1,3 dimethyl butyl benzene
19. 1-methyl hexyl benzene
20. 1-methyl 2-n-hexyl benzene
21. 1-butylhexyl-benzene
22. 1-propyl heptyl-benzene

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Fast Moving Molecules
Light Hydrocarbons
D1: 27 m x 0.25 mm id x 1 um CP-Sil 5CBMS
D2: 5 m x 0.25 mm id x 3 um CP-PoraBOND Q

PoraBOND Q works on second dimension without upsetting the pressure
Unlike silicaPLOT, alcohols elute very nicely

1. Methane
2. Ethylene
3. Acetylene
4. Propylene
5. Propane
6. Methanol
7. Ethanol
8. Propanol
Because pulsed flow modulation does not rely on thermal focusing, hydrocarbons to over C70-C80 can be successfully modulated.
Drivers for use of FM-GCxGC for Fuels and Lubricant Characterization

- Fuels and lubricants are complex samples, often encountered in manufacturing processes - knock-out pots, pipelines, exchangers etc.

- Current analytical tools for the identification of fuels and lubricants are adequate but not ideal

- FM-GCxGC has the potential of offering fast, efficient and accurate identification of oils

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Comparison Between

Classical GC

Comprehensive 2D-GC

Diesel

Mine Oil
Various type of fuels and lubricants by FM-GCxGC

Gasoline

Diesel

Petroleum Distillate

Mine Oil
Characterization of Mine Oil
System cleanliness is essential for successful implementation of the technique

FM-GCxGC typically requires longer method development when compared to conventional GC or thermally modulated GCxGC
Acknowledgements

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Relevant Publications

  - Ultra trace analysis of morpholine, cyclohexylamine and diethylaminoethanol in steam condensate by GC with MMI-FID

  - Direct measurement of part-per-billion level of dimethyl sulfoxide in water by GC with stacked injection and chemiluminescence detection

  - Multi-dimensional gas chromatography with a planar microfluidic device for the characterization of oxygenated compounds

  - Temperature Programmable low thermal mass silicon micromachined gas chromatography and differential mobility detection for the fast analysis of trace level of ethylene oxide in medical work place atmospheres

  - Resistively heated temperature programmable silicon micromachined gas chromatography with differential mobility spectrometry

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

  - Multidimensional gas chromatography for the characterization of permanent gases and Light Hydrocarbons in catalytic cracking process

  - Planar microfluidic device and low thermal mass GC in multi-dimensional gas chromatography for the characterization of targeted volatile organic compounds