Operation and Applications of Differential Flow Modulation

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Flow Modulator
Outline

• GC X GC Basics
• Flow modulation using CFT (Capillary Flow Technology)
• Performance and operating characteristics: GC and MSD
• Configurations and applications for heavy hydrocarbons
• Configurations and applications for light hydrocarbons
• Summary
Comprehensive 2-D GC (GCxGC) basics

Consists of four parts:
1. A primary column (conventional separation)
2. A modulator
3. A second column (very fast separation)
4. Fast detector

The peak capacity of the system is the product of the peak capacities of the two columns: result – increased separation power

The modulator does two jobs:
1. It collects effluent from the primary column
2. It transfers the collected effluent (in whole) to the secondary column

This process is repeated approximately every 1.5 seconds, synchronized with the start of data acquisition

GC x GC Chromatogram
Overview

Pulsed flow modulation (PFM) 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
• Low cost of ownership

Limitations:
• Unlike thermal modulation where modulation period can be readily change, parameter optimization can be more intensive

Objectives:
• Demonstrate the reliability, flexibility, and ease of use of Agilent capillary flow modulator in PFM-GCxGC
• Articulate utility of said device with practical industrial applications
  – Compatibility with both partition (WCOT) and adsorption (PLOT) chromatography
Capillary Flow Technology Modulator
Feature Set

Aids in reducing PFM-GCxGC to practice:

- No moving parts
- Low thermal mass
- Inert
- In-column switching
- Low part counts
Basic Configuration

**Hardware**

7890A GC
Split/splitless inlet, hydrogen carrier gas
PCM module
Valve driver and timing board (7890A)
Three way modulation valve
Capillary Flow Technology modulator device
Two columns: 30m x 0.25mm non-polar, 5m x 0.25mm polar (typical)
FID at 200 Hz
7683 Auto Injector

**Data processing software**

CG Image, LLC, Lincoln NE 68505
Zoex Corporation, Pasadena, TX 77505
Flow Modulator Diagram

S/S Inlet

Column 1

PCM

Micro Valve

Modulator

S/S inlet: constant flow mode
PCM: Pressure control mode, column in constant flow
Micro 3-way valve, 24VDC, 0.25ms response time

Column 2

FID

Column 1: 15 to 60M, 0.25mm ID
Column 2: 2 to 5M, 0.25mm ID
Constraints

Since the collection channel is fixed …

- Flow rates cannot be varied by large amounts
- Modulation timing depends on first column flow rate
- Second column flow is always high, typically 21 ml/min
- Hydrogen carrier should be used although Helium is possible
CFT Modulation Device

• Modulator geometry is optimized for use with 0.25mm ID and smaller 1st dimension columns

• Various lengths of both first and second dimension columns can be used
Schematic Diagram of PFM-GCxGC

- **Inlet**
- **PCM B-1** In forward pressure, constant flow
- **First dimension column** In constant flow
- **CFT Modulator**
- **Second dimension column**
- **Detector**

GCxGC eseminar Oct. 2010
Load and Inject Sequence

LOAD

- Column 1 (25 – 60 M, typical)
- Collection channel
- Split/Splitless Inlet 0.8 ml/min
- FID
- Collect Flow direction approx. 21 ml/min
- CFT Flow Modulator

INJECT

- Column 1 (25 – 60 M, typical)
- Collection channel
- Split/Splitless Inlet 0.8 ml/min
- FID
- Collect Flow direction approx. 21 ml/min
- CFT Flow Modulator

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Peak Width as a Function of Carbon Number

Flow modulation performs well over a wide boiling point range.
Effect of Flow Rate on Modulation

Hydrogen carrier

Modulations as Function of Flow Rate
n-C11, Modulation: 1.40s load, 0.09s inject

No. of Modulations

Column 1 Flow
Modulation Period as Function of 1st Column Flow

Hydrogen carrier

![Graph showing modulation period as a function of 1st column flow.](image-url)

- Y-axis: First column flow (ml/min)
- X-axis: Modulation Period (in seconds)

The graph illustrates the decrease in first column flow with an increase in modulation period, indicating a direct relationship between the two variables.
Light Cycle Oil

Column 1: 15 m x 0.25mm x 0.10 DB-5ms
Column 2: 3m x 0.25mm x 0.15 DB17HT
Flow Modulation Applied to a Gas Oil FeedStock

Flow modulation performance does not degrade with temperature

Gas Oil feedstock

Sample Range: C6 to C40+

Column 1: 15 m x 0.25 mm x 0.10um DB-5ms
Column 2: 3 m x 0.25 mm x 0.15 DB17HT
Gas Oil

Easiest way to reduce “wrap around”: increase oven ramp rate

6 C/min

5 C/min
Flow Modulator Diagram for Operation with the 5975C MSD

Flow Modulation Interface for the MSD

MSD

171mm x 110um restrictor

Second column

Restrictor (0.4M x 0.25mm)

MOD

FID

MS Tee

171mm x 110um restrictor

Restrictor (0.4M x 0.25mm)
TIC 2D Image of E85 Fuel

- C5 alcohols
- Iso Butanol
- 1-Propanol

ETOH
TIC of Gasoline Sample

GC Image 2D plot showing Mass spectrum

Approximately 28 scans/second: 5975 MSD
**5975C GCxGC**

**TIC Light Cycle Oil**

Scan: 50 -375 amu

19 scans/sec. (2.3 scans)

<table>
<thead>
<tr>
<th>Scan range</th>
<th>Scans/sec</th>
<th>Scans/peak</th>
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</thead>
<tbody>
<tr>
<td>50 - 200</td>
<td>28</td>
<td>3.3</td>
</tr>
<tr>
<td>50 - 300</td>
<td>22</td>
<td>2.6</td>
</tr>
</tbody>
</table>

1. Naphthalene
2. Methyl naphtalenes
3. Dimethy naphthalenes
4. 1 methyl 4- phenyl methyl benzene
5. Anthracene
6. Methly phenanthrene
7. 9,10 dimethyl phenanthrene
8. n-C23
<table>
<thead>
<tr>
<th></th>
<th>Compound</th>
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<tbody>
<tr>
<td>1</td>
<td>Nonane</td>
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<tr>
<td>2</td>
<td>3-methyl nonane</td>
</tr>
<tr>
<td>3</td>
<td>Decane</td>
</tr>
<tr>
<td>4</td>
<td>3-methyl decane</td>
</tr>
<tr>
<td>5</td>
<td>Undecane</td>
</tr>
<tr>
<td>6</td>
<td>3-methyl 1-undecane</td>
</tr>
<tr>
<td>7</td>
<td>Dodecane</td>
</tr>
<tr>
<td>8</td>
<td>4-methyl-dodecane</td>
</tr>
<tr>
<td>9</td>
<td>3-methyl-dodecane</td>
</tr>
<tr>
<td>10</td>
<td>Tridecane</td>
</tr>
<tr>
<td>11</td>
<td>Tetradecane</td>
</tr>
<tr>
<td>12</td>
<td>Butyl benzene</td>
</tr>
<tr>
<td>13</td>
<td>1-methyl 4 propyl benzene</td>
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<tr>
<td>14</td>
<td>1-methyl-4-(1-methylpropyl)-benzene</td>
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<tr>
<td>15</td>
<td>Pentyldiethylbenzene</td>
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<tr>
<td>16</td>
<td>1-methyl butyl benzene</td>
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<tr>
<td>17</td>
<td>Hexyl benzene</td>
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<td>18</td>
<td>1,3-dimethyl butyl benzene</td>
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<td>19</td>
<td>1-methyl hexyl benzene</td>
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<td>20</td>
<td>1-methyl 2-n-hexyl benzene</td>
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<tr>
<td>21</td>
<td>1-butylhexyl-benzene</td>
</tr>
<tr>
<td>22</td>
<td>1-propyl heptyl-benzene</td>
</tr>
</tbody>
</table>
GC x GC: Higher Resolution First Dimension

Column 1: 10M x 0.18um x 0.18 DB1
Column 2: 5M x 0.25mm x 0.15um DB-INNOWAX
Column 1 flow: 0.4ml/min
Column 2 flow: 21ml/min

Modulation Timing
Load: 2.895 sec.
Inject: 0.114 sec.
Period: 3.009 sec.
Jet Fuels
Diesel Fuel

Column 1: 10M x 0.18um x 0.18 DB1
Column 2: 5M x 0.25mm x 0.15um DB-Innowax
Fresh Sanfrac™ Oil

D1:  15 m x 0.15 mm id x 0.6 um VF-1ms at 0.35 mL/min, hydrogen
D2:  5 m x 0.25 mm id x 0.25 um INNOWAX at 22 mL/min, hydrogen

Oven profile:
40C (2min) – 10C/min – 270C – 15 min

Inlet:
275C, S/SL in Split mode 600:1, sample size: 0.2 uL

Modulation time: 3 seconds
Inject time: 0.13 second
Sampling time: 2.87 seconds
Weathered Sanfrac™ Oil

D1: 15 m x 0.15 mm id x 0.6 um VF-1ms at 0.35 mL/min, hydrogen
D2: 5 m x 0.25 mm id x 0.25 um INNOWAX at 22 mL/min, hydrogen

Oven profile:
40C (2min) – 10C/min – 270C – 15 min

Inlet:
275C, S/SL in Split mode 600:1, sample size: 0.2 uL

Modulation time: 3 seconds
Inject time: 0.13 second
Sampling time: 2.87 seconds
Light Hydrocarbons Including $C_4$ Isomers
Column Set (PDMS/SilicaPLOT)

40C-1min-20C/min-200C-5min

1. Methane
2. Ethylene
3. Acetylene
4. Ethane
5. Propylene
6. Propane
7. Cyclopropane
8. 2-methylpropane
9. 2,2-dimethylpropane
10. 2-methylbutane
11. 2-methylpentane
12. 3-methylpentane

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Typical Hydrocarbons and Aromatics in Light Hydrocarbon Processing

1. Methane (5%)
2. Ethylene (35%)
3. Acetylene (0.4%)
4. Ethane (20%)
5. Propylene (0.5%)
6. Propane (0.1%)
7. Iso-butane (0.1%)
8. 1-Butene (0.1%)
9. N-butane (0.1%)
10. 1,3-Butadiene (0.5%)
11. Iso-pentane (0.1%)
12. 1-Pentene (0.1%)
13. Pentane (0.1%)
14. 1,4-Pentadiene (0.1%)
15. 1-Hexene (0.1%)
16. Hexane (0.1%)
17. Benzene (0.2%)
18. Toluene (0.1%)

In hydrogen

1D: 27 m x 0.25 mm id x 1 um CP-Sil 5CBMS@ 0.8 mL/min
2D: 5 m x 0.25 mm id x 3 um CP-SilicaPLOT@ 22 mL/min
Modulation time: 1.7 sec  Sampling time: 1.57sec  Inject time: 130 msec
40C (2min) – 15C/min – 250C – 10 min
C1 to C3

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
Light Hydrocarbons and Oxygenated

Column set: (PoraBOND/VF-WAXms)
Modulation time: 1.7 sec, Sampling time: 1.57 sec, Inject time: 130 msec
40C (5 min) – 10C/min – 250C

1. Methane
2. Acetylene
3. Ethylene
4. Ethane
5. Methanol
6. Propylene
7. Propane
8. Cyclopropane
9. EO/AA
10. Ethanol
11. 1-Propanol

Improved separation for C1/C3
Better space utilization for oxygenated

Acetaldehyde and EO
Combining Pre-column Backflush with GCxGC

• Investigate possibility of analyzing heavy crudes with comprehensive gas chromatography
• Apply chemometrics to identify source or contamination
• Process 50 Hz raw data files
• Analyze four different crudes
• Column set
  • First Dimension: 30 m x 0.25 mm x 0.10 um DB-5HT
  • Second Dimension : 5 m x 0.25 mm x 0.15 um DB-17HT
Flow Modulator Diagram: Backflush

MMI: ramped flow, negative ramp at backflush time

Aux: Controls Column 1 in constant flow

PCM: Pressure control mode, column in constant flow

Restrictor/ Pre-column

Column 1

Micro Valve

Modulator

G3186B

21-25 ml/min typical

Column 2

FID
Crude Oil GCxGC: Pre-column Backflush

BF at 30 min, Oven programmed to 390 C
Principal Component Analysis: 2D view

Four crudes
Key Observations

- Higher separation power achieved by using narrow bore columns in first dimension.
- Samples at the extreme ends of the boiling point range can be separated.
- Various combinations of WCOT/PLOT can be configured to address a variety of light hydrocarbon separations as an alternative of traditional valved systems.
- PoraBOND or SilicaPLOT columns can be used for either the first or second dimension column.
- Due to the high second dimension column flow, care must be taken to avoid backpressure that would upset operation of pulsed flow modulation.
Summary

PFM-GCxGC is particularly useful for:

- Fast moving molecules, light hydrocarbons, light chlorinated hydrocarbons, and oxygenated compounds
- Well suited for heavy hydrocarbon, can operate over 400°C
- Complimentary technique for GC/MS for characterization of fuel and lubricants

- Capillary flow technology modulator can be implemented in production laboratories

- Compatibility with adsorption chromatography as illustrated with Silica and DVB based columns

- Hardware available as G3440A Opt #887 and G3487A (“kit”) on the 7890A