The Design of High Temperature Capillary Gas Chromatography Columns Based on Polydimethylsiloxane

Jarl Snider, D. J. Hotnisky, Kristi Sellers, Dinesh V. Patwardhan Ph. D.
Outline

Background
Definition of Terminology
Unique Attributes of High Temperature Column
Applications
Conclusions
Polydimethylsiloxane

\[
\text{HO-Si-O}_n\text{-H}
\]

\[
\text{H}_3\text{C-Si-O-Si-O}_n\text{-Si-CH}_3
\]
Thermal Stability of PDMS

Adapted from Siloxane Polymers, ed. Clarson & Semlyen, 1993.
Bleed

- Chromatography of “loose” silicones from the column
Typical Chemical Structure of Bleed

D₃

D₄
Challenge

• Since the decomposition temperature for PDMS is 343°C, it is a challenge to make a column that is stable and has low bleed at 380°C.
Origin of Bleed

- **Polymer Synthesis**
- **Oligomers that are “created” in a column’s lifetime**
Origin of Bleed...

- Polymer Synthesis

Adapted from Inorganic Polymers, Mark, Allcock, & West 1992.
Polymer Synthesis

- Silicone Polymers can be synthesized using well known catalysts (KOH, HCl) under equilibration polymerization conditions.
- We use newer, more advanced catalysts, better synthetic techniques.
Origin of Bleed...

- Polymer Synthesis
- Oligomers that are “created” in a column’s lifetime
Origin of Bleed...

- Oligomers that are “created” in a column’s lifetime

(FS tubing)

(polymer coating)

PDMS

D₃/D₄ bleed
Enhancement of Thermal Stability by Using “Additives”

Silphenylene
A column with true “One” selectivity cannot be obtained by having silphenylene in the backbone.
Stx™-1 HT

- The polymer or the phase is PDMS.
Origin of Bleed...

deaconation

fused silica
Origin of Bleed...

deaconization

fused silica
Deactivation of the Fused Silica Surface

- We are using an advanced deactivation called Siltek™. It is a deposition process, unlike silazane or silicone deactivation.
Aroclor® 1254
Aroclor® 1260
<table>
<thead>
<tr>
<th><strong>Column:</strong></th>
<th>Stx-HT1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Serial #:</strong></td>
<td>215041</td>
</tr>
<tr>
<td><strong>Description:</strong></td>
<td>30m, 0.32mmID, 0.10µm</td>
</tr>
<tr>
<td><strong>Sample:</strong></td>
<td>Aroclor Solutions Part #32009, 32011, 32012</td>
</tr>
<tr>
<td><strong>Concentration:</strong></td>
<td>400ppb</td>
</tr>
<tr>
<td><strong>Solvent:</strong></td>
<td>Hexane</td>
</tr>
<tr>
<td><strong>Sample Size:</strong></td>
<td>1.0µL</td>
</tr>
<tr>
<td><strong>Instrument:</strong></td>
<td>HP5890</td>
</tr>
<tr>
<td><strong>Injector:</strong></td>
<td>Splitless/275°C</td>
</tr>
<tr>
<td><strong>Splitless Hold Time:</strong></td>
<td>1.0min.</td>
</tr>
<tr>
<td><strong>Split Vent Flow:</strong></td>
<td>40cc/min.</td>
</tr>
<tr>
<td><strong>Septa Purge:</strong></td>
<td>5cc/min.</td>
</tr>
<tr>
<td><strong>Carrier Gas:</strong></td>
<td>Helium</td>
</tr>
<tr>
<td><strong>Head Pressure:</strong></td>
<td>8.5psi</td>
</tr>
<tr>
<td><strong>Column Flow Rate:</strong></td>
<td>1.9cc/min.</td>
</tr>
<tr>
<td><strong>Linear Velocity:</strong></td>
<td>31cm/sec.</td>
</tr>
<tr>
<td><strong>Detector:</strong></td>
<td>ECD/310C</td>
</tr>
<tr>
<td><strong>Make up Gas Flow:</strong></td>
<td>40cc/min.</td>
</tr>
<tr>
<td><strong>Temp. Program:</strong></td>
<td>75°C(1.0min.) 15°C/min. to 150°C(0) 5°C/min. 300°C(10min.)</td>
</tr>
</tbody>
</table>
PCB Congeners

Column: Stx-HT1
Serial #: 215041
Description: 30m, 0.32mmID, 0.10µm

Sample: PCB Congener Standard #2
Part #32294
Concentration: 100ng
Solvent: Iso-Octane
Sample Size: 1.0µL

Instrument: HP5890
Injector: Splitless/275°C
Splitless Hold Time: 0.80min.
Split Vent Flow: 40cc/min.
Septa Purge: 5cc/min.
Carrier Gas: Helium
Head Pressure: 8.5psi
Column Flow Rate: 1.9cc/min.
Linear Velocity: 31cm/sec.
Detector: ECD/310°C
Make up Gas Flow: 40cc/min.

Temp. Program: 100°C(0.80min.) 15°C/min. to 325°C(10min.)

Elution Order:
1. BZ#28
2. BZ#52
3. BZ#101
4. BZ#118
5. BZ#153
6. BZ#138
7. BZ#180

*PCBs numbered according to Ballschmiter
10ppm Aliphatics

1. C24 30m, 3.32mmID, 0.01µm Stx™-1HT (cat.# 11709)
2. C26 Solvent: Hexane
3. C28 Oven temp.: 30°C (hold 0.5 min.) to 240°C at 15°C/min. to 380°C at 10°C/min. (hold 10 min.)
4. C30 Det.: FID at 340°C
5. C36 Inj.: splitless at 250°C
Carrier: hydrogen
Flow rate: 4.0cc/min. at 30°C
Make-up gas flow: 40cc/min.
Bleed Comparison

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rtx®-1MS</th>
<th>Stx™-1HT</th>
</tr>
</thead>
<tbody>
<tr>
<td>340°C</td>
<td>4.34pA</td>
<td>6.94pA</td>
</tr>
<tr>
<td>360°C</td>
<td>15.61pA</td>
<td>6.07pA</td>
</tr>
<tr>
<td>380°C</td>
<td>39.02pA</td>
<td>11.27pA</td>
</tr>
</tbody>
</table>
50ppm Hydrocarbons

Aliphatic hydrocarbons:

1. C9
2. C10
3. C12
4. C14
5. C16
6. C18
7. C19
8. C20
9. C22
10. C24
11. C26
12. C28
13. C30

Aromatic Hydrocarbons:

1. napthalene
2. 2-methylnaphthalene
3. acenaphthylene
4. acenaphthene
5. fluorene
6. phenanthrene
7. anthractene
8. fluoranthene
9. pyrene
10. benzo(a)anthracene
11. chrysene
12. benzo(b)fluoranthene
13. benzo(k)fluoranthene
14. benzo(a)pyrene
15. indeno(1,2,3-cd)pyrene
16. dibenzo(a,h)anthracene
17. benzo(g,h)perylene
Analysis Conditions

30m, 3.32mmID, 0.01µm Stx™-1HT (cat.# 11709)
Oven temp.: 30°C (hold 0.5 min.) to 240°C at
  15°C/min. to 380°C at 10°C/min.
  (hold 10 min.)
Det.: FID at 340°C
Inj.: splitless at 250°C
Carrier: hydrogen
Flow rate: 4.0cc/min. at 30°C
Make-up gas flow: 40cc/min.

1.0µL injections of MA EPH Aliphatic Hydrocarbon
standard (cat.# 31459, solvent: hexane) & MA EPH
Aromatic Hydrocarbon standard (cat.# 31458, solvent:
methylene chloride) @ 50ppm concentration.
ASTM D2887

30m, 3.32mmID, 0.01µm Stx™-1HT (cat.# 11709)
Oven temp.: 30°C to 380°C at 10°C/min.
Det.: FID at 380°C
Inj.: cool on-column
Carrier: helium
Flow rate: 1.3cc/min. at 30°C
Linear velocity: 22cm/sec. at 30°C
Make-up gas flow: 45cc/min.
Head pressure: 6.0psi
XTI Mix on Rtx-1 & Stx-1HT

1. 1,2-hexanediol
2. nitro-di-N-propylamine
3. benzoic acid
4. C14
5. 2,4-dinitrophenol
6. nitrophenol
7. nitroaniline
8. pentachlorophenol
9. carbazole
10. C20
11. C21
12. C22
13. benzo(b)fluoranthene
14. benzo(k)fluoranthene
Summary

- Definitions
- The design of low bleed & stable column system was discussed
- Several applications were shown