Selection of a Capillary
GC Column - Series 3

Mark Sinnott
Application Engineer
March 19, 2009
Typical Gas Chromatographic System

Picking the appropriate stationary phase and optimum dimensions for the column will give the greatest resolution in the shortest analysis time.
Four Primary Selection Areas

Stationary Phase Type

Column Internal Diameter

Stationary Phase Film Thickness

Column Length
Resolution

\[ R_s = \frac{\sqrt{N}}{4} \left( \frac{k}{k+1} \right) \left( \frac{\alpha-1}{\alpha} \right) \]

Efficiency \quad N = f (\text{gas, L, r}_c) \quad L = \text{Length} \\
Retention \quad k = f (T, d_f, r_c) \quad r_c = \text{column radius} \\
Selectivity \quad \alpha = f (T, \text{phase}) \quad d_f = \text{film thickness} \\
T = \text{temperature}
Resolution

\[ R_s = \frac{\sqrt{N}}{4} \left( \frac{k}{k+1} \right) \left( \frac{\alpha-1}{\alpha} \right) \]

- **Efficiency** \( N = f(\text{gas}, L, r_c) \)
- **Retention** \( k = f(T, d_f, r_c) \)
- **Selectivity** \( \alpha = f(T, \text{phase}) \)

- \( L = \text{Length} \)
- \( r_c = \text{column radius} \)
- \( d_f = \text{film thickness} \)
- \( T = \text{temperature} \)
Stationary Phase - Common Types

Siloxane polymers

Poly(ethylene) glycols

Porous polymers
Capillary Column Types

Porous Layer Open Tube (PLOT)

Wall Coated Open Tube (WCOT)
Stationary Phase Polymers

\[
\begin{align*}
\text{Siloxane} & \quad R = \text{methyl, phenyl, cyanopropyl, trifluoropropyl} \\
\text{Siarylene backbone} & \\
\text{Polyethylene glycol backbone}
\end{align*}
\]
Why Is Stationary Phase Type Important?

Influence of $\alpha$

$$\alpha = \frac{k_2}{k_1}$$

$k_2$ = partition ratio of 2nd peak
$k_1$ = partition ratio of 1st peak
Selectivity

Relative spacing of the chromatographic peaks

The result of all non-polar, polarizable and polar interactions that cause a stationary phase to be more or less retentive to one analyte than another
Optimizing Selectivity

Match analyte polarity to stationary phase polarity

-like dissolves like (oil and water don’t mix)

Take advantage of unique interactions between analyte and stationary phase functional groups
# Compounds - Properties

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Polar</th>
<th>Aromatic</th>
<th>Hydrogen Bonding</th>
<th>Dipole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>induced</td>
</tr>
<tr>
<td>Hexanol</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Phenol</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Decane</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>induced</td>
</tr>
<tr>
<td>Dodecane</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>
100% Methyl Polysiloxane (boiling point column?)

1. Toluene  110°
2. Hexanol  156°
3. Phenol   182°
4. Decane (C10)  174°
5. Naphthalene  218°
6. Dodecane (C12)  216°

Strong Dispersion
No Dipole
No H Bonding
### 5% Phenyl

<table>
<thead>
<tr>
<th>Compounds</th>
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<td>Naphthalene</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>induced</td>
</tr>
<tr>
<td>Dodecane</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

#### Chart:

**5% Phenyl**

- Strong Dispersion
- No Dipole
- Weak H Bonding

**1. Toluene**
**2. Hexanol**
**3. Phenol**
**4. Decane (C10)**
**5. Naphthalene**
**6. Dodecane (C12)**

---

**100% Methyl**

- Strong Dispersion
- No Dipole
- No H Bonding
### 50% Phenyl

- **Toluene**: no, yes, no, induced
- **Hexanol**: yes, no, yes, yes
- **Phenol**: yes, yes, yes, yes
- **Decane**: no, no, no, no
- **Naphthalene**: no, yes, no, induced
- **Dodecane**: no, no, no, no

#### Strong Dispersion
- **No Dipole**
- **Weak H Bonding**

#### 100% Methyl
- **1. Toluene**: $110^\circ$
- **2. Hexanol**: $156^\circ$
- **3. Phenol**: $182^\circ$
- **4. Decane (C10)**: $174^\circ$
- **5. Naphthalene**: $218^\circ$
- **6. Dodecane (C12)**: $216^\circ
**14% Cyanopropylphenyl**

- **14% Cyanopropylphenyl**
- **Strong Dispersion**
- None/Strong Dipole (Ph/CNPr)
- Weak/Moderate H Bonding (Ph/CNPr)

**Compounds** | **Polar** | **Aromatic** | **Hydrogen Bonding** | **Dipole**
--- | --- | --- | --- | ---
Toluene | no | yes | no | induced
Hexanol | yes | no | yes | yes
Phenol | yes | yes | yes | yes
Decane | no | no | no | no
Naphthalene | no | yes | no | induced
Dodecane | no | no | no | no

**1. Toluene**
**2. Hexanol**
**3. Phenol**
**4. Decane (C10)**
**5. Naphthalene**
**6. Dodecane (C12)**

**100% Methyl**
- **Strong Dispersion**
- No Dipole
- No H Bonding

*Agilent Technologies*
### 50% Cyanopropyl

- **Compounds**
  - Toluene: no, yes
  - Hexanol: yes, no
  - Phenol: yes, yes
  - Decane: no, no
  - Naphthalene: no, yes
  - Dodecane: no, no

- **Properties**
  - Polar: no, yes
  - Aromatic: no, yes
  - Hydrogen Bonding: no, yes
  - Dipole: no, induced

### 100% Methyl

- **Compounds**
  - Decane (C10): no, no
  - Naphthalene: no, yes
  - Dodecane (C12): no, no

- **Properties**
  - No Dipole: yes
  - No H Bonding: yes

### Chromatograms

- **Column Selection**
  - 1. Toluene
  - 2. Hexanol
  - 3. Phenol
  - 4. Decane (C10)
  - 5. Naphthalene
  - 6. Dodecane (C12)
100% Polyethylene Glycol

Strong Dispersion
Strong Dipole
Moderate H Bonding

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<td>yes</td>
<td>yes</td>
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<tr>
<td>Dodecane</td>
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<td>no</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

1. Toluene
2. Hexanol
3. Phenol
4. Decane (C10)
5. Naphthalene
6. Dodecane (C12)
Selectivity is important but not everything…

Inertness and Bleed can be critical factors in column selection.

Temperature limits will play a role as well.
Stationary Phase Bleed

A thermodynamic equilibrium process that occurs to some degree in all columns, and is proportional to the mass amount of stationary phase inside the capillary tubing/carrier gas flow path.

Polysiloxane backbone releases low molecular weight, cyclic fragments

Is negligible in low temperature, O2-free, clean GC systems

Increased by increased temperature, oxygen exposure, or chemical damage
Bleed: Why Does It Happen?
“Back Biting” Mechanism of Product Formation

Cyclic products are thermodynamically more stable!
DB-5ms Structure

1. Increased stability
2. Different selectivity
3. Optimized to match DB-5
Difference in Selectivity

- **Solid line:** DB-5ms 30 m x .25 mm I.D. x .25 μm
- **Dashed line:** DB-5 30 m x .25 mm I.D. x .25 μm
- **Oven:** 60° C isothermal
- **Carrier gas:** H₂ at 40 cm/sec

1: Ethylbenzene
2: m-Xylene
3: p-Xylene
4: o-Xylene
Four Types Of Low Bleed Phases

Phases tailored to “mimic” currently existing polymers
-Examples: DB-5ms, DB-35ms, DB-17ms, DB-225ms

Phases unrelated to any previously existing polymers
-Examples: DB-XLB

Optimized manufacturing processes
-DB-1ms, HP-1ms, HP-5ms

Hand selected columns
Benefits of Low Bleed Phases
PAH Sensitivity Using DB-35MS

Commercially Available 35% phenyl column

Benzo[ghi]perylene
S/N = 15

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benz[a]anthracene
10. Chrysene
11. Benzo[b]fluoranthene
12. Benzo[k]fluoranthene
13. Benzo[a]pyrene
14. Indeno[1,2,3,-c,d]anthracene
15. Dibenz[a,h]anthracene
16. Benzo[g,h,i]perylene

Columns: 30 m x 0.32 mm x 0.35 um.
Carrier: H2, constant flow, 5 psi at 100 °C.
Injector: 275 °C, splitless, 1 ul, 0.5-5ppm.
Oven: 100 °C to 250 °C (5 min.) at 15 °C/min.; then to 320 °C (10 min.) at 7.5 °C/min.
Detector: FID, 320 °C.
Benefits of Low Bleed Phases
DB-35ms vs Standard 35% Phenyl

Benzo[g,h,i]perylene, 1ng
Higher Spectral Purity

Scan 1118 (20.560 min): 3901004.D

- Abundance 150000
- M/Z 96

Scan 1138 (20.640 min): 3901004.D

- Abundance 110000
- M/Z 50

Standard 35% Phenyl

- M/Z 35
- Abundance 253

DB-35ms

- M/Z 78
- Abundance 276
Polarity vs Stability/Temperature Range

Polarity vs Stability/Temperature Range

Polarity

Stability

Temperature Range
Stationary Phase Selection

Existing information
Selectivity/Polarity
Critical separations
Temperature limits
Application designed

Examples: DB-VRX, DB-MTBE, DB-TPH, DB-ALC1, DB-ALC2, DB-HTSimDis, DB-Dioxin, HP-VOC, etc.

Choose the column phase that gives the best separation but not at the cost of robustness or ruggedness.
Resolution

\[ R_s = \frac{\sqrt{N}}{4} \left( \frac{k}{k+1} \right) \left( \frac{\alpha - 1}{\alpha} \right) \]

Efficiency: \( N = f(\text{gas, L, } r_c) \)
Retention: \( k = f(T, d_f, r_c) \)
Selectivity: \( \alpha = f(T, \text{phase}) \)

\( L = \) Length
\( r_c = \) column radius
\( d_f = \) film thickness
\( T = \) temperature
Resolution

\[ R_s = \frac{\sqrt{N}}{4} \left( \frac{k}{k+1} \right) \left( \frac{\alpha - 1}{\alpha} \right) \]

Efficiency: \( N = f \) (gas, L, r_c)  
Retention: \( k = f \) (T, d_f, r_c)  
Selectivity: \( \alpha = f \) (T, phase)
## Column Diameter - Theoretical Efficiency

<table>
<thead>
<tr>
<th>Total Plates</th>
<th>I.D. (mm)</th>
<th>n/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>N ~ 112,000</td>
<td>0.05</td>
<td>23,160</td>
</tr>
<tr>
<td>5 m</td>
<td>0.18</td>
<td>6,660</td>
</tr>
<tr>
<td>N ~ 112,000</td>
<td>0.10</td>
<td>11,580</td>
</tr>
<tr>
<td>10 m</td>
<td>0.18</td>
<td>6,660</td>
</tr>
<tr>
<td>N ~ 112,000</td>
<td>0.20</td>
<td>5830</td>
</tr>
<tr>
<td>20 m</td>
<td>0.25</td>
<td>4630</td>
</tr>
<tr>
<td>N ~ 112,000</td>
<td>0.25</td>
<td>4630</td>
</tr>
<tr>
<td>30 m</td>
<td>0.45</td>
<td>2840</td>
</tr>
<tr>
<td></td>
<td>0.53</td>
<td>2060</td>
</tr>
</tbody>
</table>

\[ k = 5 \]
Different Column I. D.

Equal Phase Ratios

Column: DB-624
30 m, 0.53 mm, 3 μm
Carrier: Helium, 40 cm/sec
Oven: 65°C
Injection: Split
Detector: FID

Column: DB-624
30 m, 0.32 mm, 1.8 μm

Time (min)
PHASE RATIO ($\beta$)

Film Thickness

<table>
<thead>
<tr>
<th>Column Dimensions</th>
<th>Phase Ratio $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 m x 0.53 mm x 3.0 μm</td>
<td>44</td>
</tr>
<tr>
<td>30 m x 0.32 mm x 1.8 μm</td>
<td>44</td>
</tr>
</tbody>
</table>

$$K_C = k \, \beta$$

$$\beta = \frac{r}{2d_f}$$
## Column Diameter and Capacity

<table>
<thead>
<tr>
<th>I.D. (mm)</th>
<th>Capacity (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1-2</td>
</tr>
<tr>
<td>0.10</td>
<td>6-13</td>
</tr>
<tr>
<td>0.18</td>
<td>25-55</td>
</tr>
<tr>
<td>0.20</td>
<td>35-70</td>
</tr>
<tr>
<td>0.25</td>
<td>80-160</td>
</tr>
<tr>
<td>0.32</td>
<td>110-220</td>
</tr>
<tr>
<td>0.45</td>
<td>600-800</td>
</tr>
<tr>
<td>0.53</td>
<td>1000-2000</td>
</tr>
</tbody>
</table>

Like Polarity
Phase/Solute
0.25 µm film thickness
## Column Diameter - Inlet Head Pressures (Helium)

<table>
<thead>
<tr>
<th>I.D (mm)</th>
<th>Pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>275-400</td>
</tr>
<tr>
<td>0.10</td>
<td>90-130</td>
</tr>
<tr>
<td>0.18</td>
<td>30-45</td>
</tr>
<tr>
<td>0.20</td>
<td>25-40</td>
</tr>
<tr>
<td>0.25</td>
<td>15-25</td>
</tr>
<tr>
<td>0.32</td>
<td>10-20</td>
</tr>
<tr>
<td>0.45</td>
<td>3-7</td>
</tr>
<tr>
<td>0.53</td>
<td>2-4</td>
</tr>
</tbody>
</table>

30 meters
Hydrogen pressures x 1/2
Column Diameter and Carrier Gas Flow

Lower flow rates: Smaller diameter columns

Higher flow rates: Larger diameter columns

Low flow rates: GC/MS
High flow rates: Headspace, purge & trap
Diameter Summary

If you decrease the inside diameter:

- Efficiency: Increase
- Resolution: Increase
- Pressure: Increase
- Capacity: Decrease
- Flow rate: Decrease
Resolution

\[ R_s = \frac{\sqrt{N}}{4} \left( \frac{k}{k+1} \right) \left( \frac{\alpha - 1}{\alpha} \right) \]

Efficiency
\[ N = f \text{ (gas, } L, r_c) \]

Retention
\[ k = f \text{ (} T, d_f, r_c) \]

Selectivity
\[ \alpha = f \text{ (} T, \text{ phase) } \]

L = Length
\( r_c = \text{ column radius} \)
\( d_f = \text{ film thickness} \)
\( T = \text{ temperature} \)
Resolution

\[ R_s = \sqrt{N} \left( \frac{k}{k+1} \right) \left( \frac{\alpha-1}{\alpha} \right) \]

- Efficiency: \( N = f(\text{gas, L, } r_c) \)
- Retention: \( k = f(T, d_f, r_c) \)
- Selectivity: \( \alpha = f(T, \text{phase}) \)

\( L = \) Length
\( r_c = \) column radius
\( d_f = \) film thickness
\( T = \) temperature
**Film Thickness and Retention: Isothermal**

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Retention Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.40</td>
</tr>
<tr>
<td>0.25</td>
<td>1.00</td>
</tr>
<tr>
<td>1.0</td>
<td>4.00</td>
</tr>
<tr>
<td>3.0</td>
<td>12.0</td>
</tr>
<tr>
<td>5.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

*Constant Diameter Normalized to 0.25 µm*
Film Thickness and Resolution

When solute $k < 5$
(early eluters)

When solute $k > 5$
(later eluters)
Analysis of Noble & Fixed Gases
Using HP PLOT MoleSieve

Column: HP-PLOT/MoleSieve
30 m x 0.53 mm x 50 μm
HP part no. 19095P-MS0
Carrier: Helium, 4 ml/min
Oven: 35°C (3 min) to 120°C (5 min) at 25°C/min
Sample: 250 μl, split (ratio 50:1)

1. Neon
2. Argon
3. Oxygen
4. Nitrogen
5. Krypton
6. Xenon
## Film Thickness and Capacity

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Capacity (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>50-100</td>
</tr>
<tr>
<td>0.25</td>
<td>125-250</td>
</tr>
<tr>
<td>0.50</td>
<td>250-300</td>
</tr>
<tr>
<td>1</td>
<td>500-1000</td>
</tr>
<tr>
<td>3</td>
<td>1500-3000</td>
</tr>
<tr>
<td>5</td>
<td>2500-5000</td>
</tr>
</tbody>
</table>

0.32 mm I.D.  
Like Polarity Phase/Solute
Film Thickness and Bleed

More stationary phase = More degradation products
Film Thickness and Inertness

- 0.25: active
- 1.0: active
- 3.0: active
Film Thickness Summary

If you increase the film thickness:

- Retention: Increase
- Resolution (k<5): Increase
- Resolution (k>5): Decrease
- Capacity: Increase
- Bleed: Increase
- Inertness: Increase
- Efficiency: Decrease
Resolution

\[ R_S = \sqrt{N} \left( \frac{k}{k+1} \right) \left( \frac{\alpha - 1}{\alpha} \right) \]

Efficiency  \( N = f(\text{gas, } L, r_c) \)  
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Selectivity  \( \alpha = f(T, \text{phase}) \)

\( L = \text{Length} \)  
\( r_c = \text{column radius} \)  
\( d_f = \text{film thickness} \)  
\( T = \text{temperature} \)
Resolution

\[ R_s = \frac{\sqrt{N}}{4} \left( k \frac{k}{k+1} \frac{\alpha-1}{\alpha} \right) \]

Efficiency: \( N = f (\text{gas, } L, r_c) \)  
L = Length  
r_c = column radius

Retention: \( k = f (T, d_f, r_c) \)  
d_f = film thickness

Selectivity: \( \alpha = f (T, \text{phase}) \)  
T = temperature
## Column Length and Efficiency (Theoretical Plates)

<table>
<thead>
<tr>
<th>Length (m)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>69,450</td>
</tr>
<tr>
<td>30</td>
<td>138,900</td>
</tr>
<tr>
<td>60</td>
<td>277,800</td>
</tr>
</tbody>
</table>

**0.25 mm ID**

\[ \frac{n}{m} = 4630 \text{ (for } k = 5) \]
Column Length and Resolution

\[ R \alpha \sqrt{n} \alpha \sqrt{L} \]

Length X 4 = Resolution X 2

\[ t \alpha L \]
Column Length VS Resolution and Retention: Isothermal

- R = 0.84, 2.29 min (15 m)
- R = 1.16, 4.82 min (30 m)
- R = 1.68, 8.73 min (60 m)

Double the plates, double the time but not double the resolution
Column Length and Cost

15m  30m  60m

$ $ $ $ $ $
Length Summary

If you Increase Length:

- Efficiency: Increase
- Resolution: Increase
- Analysis Time: Increase
- Pressure: Increase
- Cost: Increase
Summary - Four Primary Selection Areas

Stationary Phase Type

Column Internal Diameter

Stationary Phase Film Thickness

Column Length
Still Can’t Decide Which Column to Use??????
...Call Us!!!

TECHNICAL SUPPORT

Agilent 1-800-227-9770 #4, #1

E-mail:

gc_column_support@Agilent.com