Gas Chromatography

1. Introduction

2. Stationary phases

3. Retention in Gas-Liquid Chromatography

4. Capillary gas-liquid chromatography

5. Sample preparation and injection

6. Detectors

(Chapter 2 and 3 in The essence of chromatography)
Capillary Gas-Liquid Chromatography

A. Separation efficiency and rate theory

B. Preparation of Capillary Column

C. Evaluation of Capillary Column

<table>
<thead>
<tr>
<th>Column type</th>
<th>Phase ratio</th>
<th>$H_{\text{min}}$ (mm)</th>
<th>$u_{\text{opt}}$ (cm/s)</th>
<th>Permeability ($10^7 \text{cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classical Packed</td>
<td>4-200</td>
<td>0.5-2</td>
<td>5-15</td>
<td>1-50</td>
</tr>
<tr>
<td>Micropacked</td>
<td>50-200</td>
<td>0.02-1</td>
<td>5-10</td>
<td>1-100</td>
</tr>
<tr>
<td>Packed Capillary</td>
<td>10-300</td>
<td>0.05-2</td>
<td>5-25</td>
<td>5-50</td>
</tr>
<tr>
<td>SCOT</td>
<td>20-300</td>
<td>0.5-1</td>
<td>10-100</td>
<td>200-1000</td>
</tr>
<tr>
<td>WCOT</td>
<td>15-500</td>
<td>0.03-0.8</td>
<td>10-100</td>
<td>300-20000</td>
</tr>
</tbody>
</table>

Representative properties of different column types for gas chromatography

$H_{\text{min}} = \text{minimum plate height at the optimum mobile phase velocity } u_{\text{opt}}$
Capillary GC has much higher separation efficiency than packed-bed GC!
Rate theory-- Van Deemter Equation

1. Packed-bed system

\[ H = A + \frac{B}{u} + (C_S + C_M)u \]

\[ 2\lambda \frac{d_p}{u} + \frac{2}{(1+\varepsilon_p/\varepsilon_e)} \frac{D_m}{u} + q_s \frac{k}{(1+k)^2} \frac{d_f^2}{D_s} u + f(k) \frac{d_p^2}{D_m} u \]

\( \lambda \): column packing factor (0.5~1.5)
\( d_p \): average size of the filling particles
\( \varepsilon_p \): intraparticle porosity
\( \varepsilon_e \): interparticle porosity
\( D_m \): solute diffusion coefficient in mobile phase.
\( k \): capacity factor \( k = K \frac{V_s}{V_m} \)
\( D_s \): solute diffusion coefficient in stationary phase.
\( q_s \): shape factor for the stationary phase coating (2/3 for a thin layer).
\( d_f \): thickness of stationary phase
2. Capillary system—open tubular system

No eddy diffusion!

\[
H = \frac{B}{u} + Cu
\]

\[
H = \frac{B}{u} + (C_S + C_M)u
\]

\[
H = \left( \frac{2D_m}{u} \right) + \left( \frac{2k}{3(1+k)^2} \right) \left( \frac{d_f^2}{D_s} \right) u + \left( \frac{1+6k+11k^2}{96(1+k)^2} \right) \left( \frac{d^2}{D_m} \right) u
\]

\[
H_{\text{min}} = 2^*(BC)^{1/2}
\]

\[
u_{\text{opt}} = (B/C)^{1/2}
\]
\[ C_m = \left( \frac{1+6k+11k^2}{96(1+k)^2} \right) \left( \frac{d^2}{D_m} \right) \]

Figure 1.7. Variation of the resistance to mass transfer in the mobile phase, \( C_M \), as a function of the retention factor for open tubular columns of different internal diameters (mm).
The ratio of \( C_S \) and \( C_M \) contributions to the term of resistance to mass transfer is determined by the phase ratio.

\[
C_S + C_M = \left( \frac{2k}{3(1+k)^2} \right) \left( \frac{d_f^2}{D_s} \right) + \left( \frac{1+6k+11k^2}{96(1+k)^2} \right) \left( \frac{d^2}{D_m} \right)
\]

\[
H = B/u + (C_S + C_M)u
\]

\[
(V_m/V_s) = d/4d_f , \text{ when, } d >> d_f
\]
The Effect of Carrier Gas

H = B/u + (C_S + C_M)u

H_{min} = 2^*(BC)^{1/2}

u_{opt} = (B/C)^{1/2}

gas

\[ D_{AB} = \frac{1.00 \times 10^{-3} T^{1.75}}{P[(\text{sum } v_i)_A^{1/2} + (\text{sum } v_i)_B^{1/2}]} \left( \frac{1}{MW_A} \frac{1}{MW_B} \right) \]

\[ D_{AB} = kT/(6\pi\eta_B r_A) \]

Figure 2.1. Van Deemter plots indicating the influence of the choice of carrier gas on column efficiency for thin-film (A) and thick-film (B) open tubular columns for solutes with different retention factors.
Parameters affecting plate height

\[ H = \frac{B}{u} + (C_S + C_M)u \]

\[ \left( \frac{2D_m}{u} \right) + \left( \frac{2k}{3(1+k)^2} \right) d_f^2 u + \left( \frac{1+6k+11k^2}{96(1+k)^2} \right) \left( \frac{d^2}{D_m} \right) u \]
Preparation of Capillary Column

1. Materials
   a. glass: soda-lime (soft) *alkaline*
      SiO2 67.7%, Na2O 15.6%, CaO 5.7%, MgO 3.9%, Al2O3 2.8%, BaO 0.8%, and K2O 0.6%
      
      borosilicate (hard), *acidic*
      SiO2 67.7%, B2O3 13 %, Na2O 3.0%, Al2O3 2.0%, and K2O 1.0%
   
   b. fused silica
      
      \[ \text{SiCl}_4 + \text{O}_2 \rightarrow \text{SiO}_2 \]
      
      Surface: Si—OH, O--SiH-O
      
      Silanol Siloxane

Polymer coating
Fused silica tube
Coated stationary phase
2. Film Formation on Inner Surface of Tubes

(A) Uniform stationary film is essential for high-efficiency separation

Thin, smooth, and homogeneous film

(1) Surface tension (wettability): the surface tension of stationary phase should be smaller than that of glass or fused silica.

(2) The stability of the film depends on the viscosity of liquid and thickness of film (surface tension).

(B) Surface modification

(1) Improvement of wettability of glass surface: HCl (gas)
(2) Deactivation: silylation

(C) Coating Techniques

Dynamic coating, and Static coating
Evaluation of Column Quality

1. Activity test for uncoated columns

2. Grob test for coated columns

Figure 2.15. Activity test for an uncoated fused silica capillary column after (A) deactivation with poly(phenylmethylhydrosiloxane) and (B) before deactivation. Precolumn: 15 m x 0.20 mm I.D. coated with SE-54. Test columns 10 m x 0.20 mm I.D. The column tandem was programmed from 40 to 180°C at 4°C/min after a 1 min isothermal hold with a hydrogen carrier gas velocity of 50 cm/s. The test mixture contained C_{10} = n-decane, C_8NH_2 = 1-aminoctane, PY = 3,5-dimethylpyrididine, C_{12} = n-dodecane, C_{10}NH_2 = 1-aminodecane, DMA = 2,6-dimethylaniline, DCHA = N,N-dicyclohexylamine, C_{12}NH_2 = 1-aminododecane, and C_{17} = n-heptadecane. (From ref. [355]. ©Wiley-VCH).
Grob Test

Table 2.16
Test mixture composition and optimum experimental conditions for the Grob test.
Test compounds dissolved in 20 ml of hexane except for 2,3-butanediol, which is dissolved in chloroform. Working solution is prepared by mixing 1.0 ml of each standard solution and diluting 1.0 ml of this solution to 20 ml in hexane. To reduce the likelihood of peak overlap on non-polar stationary phases n-dodecane is used instead of n-undecane.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Abbreviation</th>
<th>Amount (mg)</th>
<th>Substance</th>
<th>Abbreviation</th>
<th>Amount (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl decanoate</td>
<td>E₁₀</td>
<td>242</td>
<td>1-Octanol</td>
<td>o₁</td>
<td>222</td>
</tr>
<tr>
<td>Methyl undecanoate</td>
<td>E₁₁</td>
<td>236</td>
<td>Nonanal</td>
<td>a₁</td>
<td>250</td>
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<tr>
<td>Methyl dodecanoate</td>
<td>E₁₂</td>
<td>230</td>
<td>2,3-Butanediol</td>
<td>D</td>
<td>380</td>
</tr>
<tr>
<td>n-Decane</td>
<td>10</td>
<td>172</td>
<td>2,6-Dimethylaniline</td>
<td>A</td>
<td>205</td>
</tr>
<tr>
<td>n-Undecane</td>
<td>11</td>
<td>174</td>
<td>2,6-Dimethylphenol</td>
<td>P</td>
<td>194</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>12</td>
<td>176</td>
<td>Dicyclohexylamine</td>
<td>am</td>
<td>204</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-Ethylhexanoic Acid</td>
<td>S</td>
<td>242</td>
</tr>
</tbody>
</table>

Optimized experimental conditions
Carrier gas measurements at or close to room temperature. Initial temperature 40°C for program.

<table>
<thead>
<tr>
<th>Column length (m)</th>
<th>Hydrogen Methane elution (s)</th>
<th>Temperature program (°C/min)</th>
<th>Helium Methane elution (s)</th>
<th>Temperature program (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>20</td>
<td>5.0</td>
<td>35</td>
<td>2.5</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>3.3</td>
<td>53</td>
<td>1.65</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>2.5</td>
<td>70</td>
<td>1.25</td>
</tr>
<tr>
<td>30</td>
<td>60</td>
<td>1.67</td>
<td>105</td>
<td>0.84</td>
</tr>
<tr>
<td>40</td>
<td>80</td>
<td>1.25</td>
<td>140</td>
<td>0.63</td>
</tr>
<tr>
<td>50</td>
<td>100</td>
<td>1.0</td>
<td>175</td>
<td>0.5</td>
</tr>
</tbody>
</table>
(1) The height of the peaks
(2) The shape of the peaks
3. Columns Thermal Stability

The bleed products from stationary phase consist primarily of low molecular weight impurities. Fused silica columns show very low levels of thermally induced catalytic phase decomposition.

Figure 2.17. Standardized column bleed test. (From ref. [369]. ©Elsevier)
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