Gas Chromatography

1. Introduction

2. Stationary phases

3. Retention in Gas-Liquid Chromatography

4. Capillary gas-chromatography

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6. Detectors

(Chapter 2 and 3 in The essence of chromatography)

Retention in Gas-Liquid Chromatography

A. General descriptors

B. retention and capacity factor: $t_R = t_M(1+k)$

C. Solute retention in Binary stationary phase

D. Temperature and Flow Programming

E. Problem solving

A. General descriptors

(1) t_R, t_R' , and t_M

(2) V_R, V_R' , and V_M

(3) L_R, L_R' , and L_M

(4) $V_R = t_R * F$, and $L_R = t_R * u$

(5) $\sigma_V = \sigma_t * F$, and $\sigma_L = \sigma_t * u$

$$j = \frac{3}{2} \frac{(P_i/P_0)^2-1}{(P_i/P_0)^3-1}$$

$$u_{avg} = j\, u_0\, (T_c/T_0)\, [(P_o-P_w)/P_o]$$

$$F_{avg} = j\, F_0\, (T_c/T_0)\, [(P_o-P_w)/P_o]$$

(6) $k = t_R' / t_M = \dfrac{\text{the time of solute stay in stationary phase}}{\text{the time of solute stay in mobile phase}}$

(7) $K = k^*\beta = k^* \dfrac{V_M}{V_S}$

(8) $t_R = t_M(1+k)$

(9) $\alpha = k_1/k_2$

(10) $R_s = (t_{R2}-t_{R1})/[(W_{b1}+W_{b2})/2] = [N^{1/2}/4][(\alpha -1)/(\alpha)]*[k_2/(1+ k_2)]$,

B. retention and capacity factor: $t_R = t_M(1+k)$

1. Modern methods: solute effects (Kamlet, Taft, and Abraham)

$$\log k = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + l\log L^{16} \quad \text{(Gas chromatography)}$$

Solute descriptors (R_2, π_2, $\Sigma\alpha_2$, $\Sigma\beta_2$, $\log L^{16}$, and V_x): depended on solute properties

Kamlet-Taft parameters

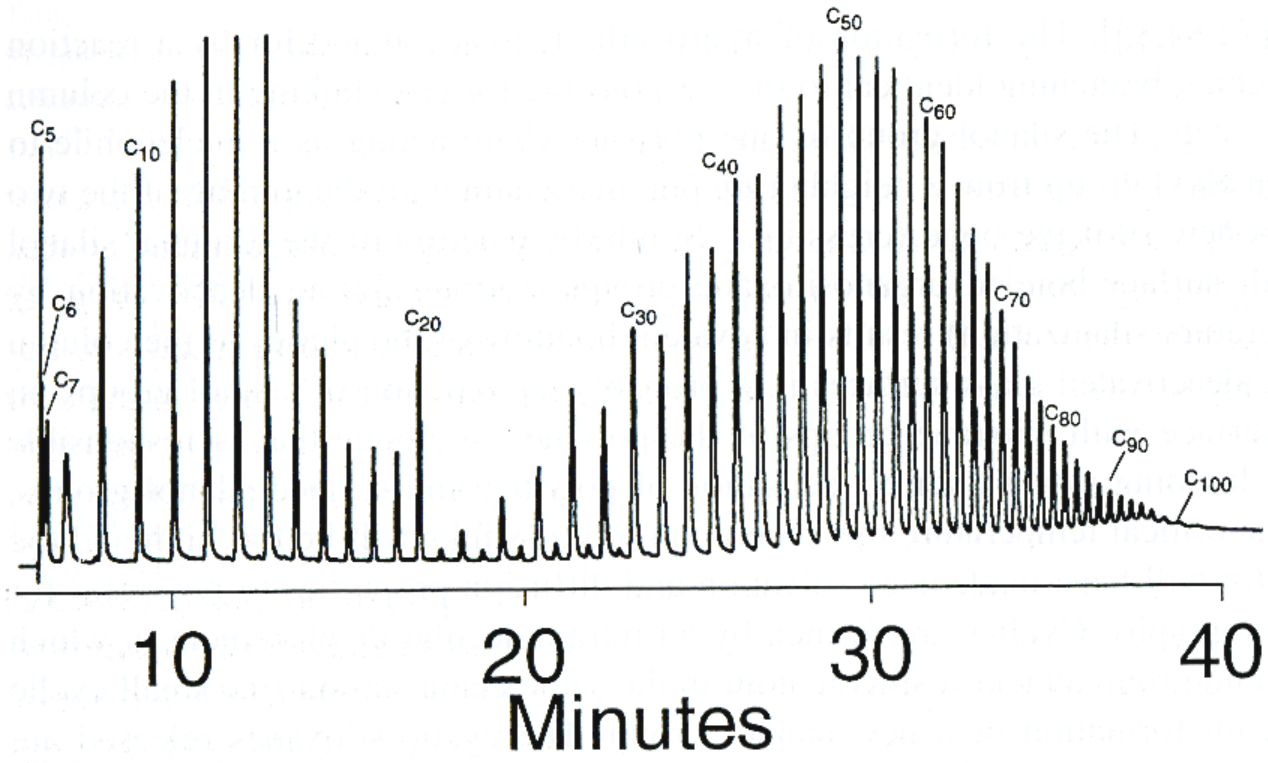
System constants (*c, m, r, s, a, b,* and *l*): depended on chromatographic system conditions: mobile phase, stationary phase, and temperature.

2. Kovat's Retention Index

$$I = 100z + 100*[\log t_R'(x) - \log t_R'(z)]/[\log t_R'(z+1) - \log t_R'(z)]$$

Where t_R' is the adjusted retention time, z the carbon number of the n-alkane eluting immediately before the substance of interest denoted by x, and z+1 the retention number of the n-alkane eluting immediately after substance x.

Kovat's approach is using retention of n-alkanes as standards to Index the retention of substance of interest on a certain chromatographic system.



$$I = 100z + 100*[\log t_R'(x) - \log t_R'(z)]/[\log t_R'(z+1) - \log t_R'(z)]$$

3. McReynolds' phase constants

$\Delta I = I_{\text{stationary phase x}} - I_{\text{squalene}}$ Squalene ($C_{30}H_{62}$)

McReynold's phase constants

$\Delta I = aX' + bY' + cZ' + dU' + eS'$

Phase constant: X': Benzene; Y': 1-butanol; Z': 2-pentanone; U': 1-nitropropane; S': Pyridine

a, b, c, d, e, constants for the solute of interest.

Comparison to the method by Kamlet, Taft, and Abraham

Table 2.15
Prototypical solutes used by McReynolds (Rorschneider solutes in parentheses) to characterize stationary phase properties
R_2 = excess refraction, π_2^H = dipolarity/polarizability, $\Sigma\alpha_2^H$ hydrogen-bond acidity, $\Sigma\beta_2^H$ = hydrogen-bond basicity and log L^{16} partition coefficient on hexadecane at 25°C.

Symbol	Solute	Solute descriptors				
		R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	log L^{16}
X′	Benzene	0.610	0.52	0	0.14	2.786
Y′	1-Butanol (Ethanol)	0.224	0.42	0.37	0.48	2.601
Z′	2-Pentanone (2-Butanone)	0.143	0.68	0	0.51	2.143
U′	1-Nitropropane (Nitromethane)	0.242	0.95	0	0.27	2.894
S′	Pyridine	0.631	0.84	0	0.52	3.022
H′	2-Methyl-2-pentanol	0.180	0.30	0.31	0.60	1.963
J′	Iodobutane	0.628	0.40	0	0.15	3.628
K′	2-Octyne	0.225	0.30	0	0.10	3.850
L′	Dioxane	0.329	0.75	0	0.64	2.892
M′	cis-Hydrindane	0.439	0.25	0	0	4.635

Idea is same: use constants from systems and solute to describe retention

Difference: Kamlet et al use solvatochromic parameters to index the constant of solute of interest.
McReynolds uses properties of specific molecules to index constant of solute of interest.

Method by McReynolds

McReynold's phase constants

$$\Delta I = aX' + bY' + cZ' + dU' + eS'$$

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Method by Kamlet, Taft, and Abraham

$$\log k = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + l\log L^{16} \quad \text{(Gas chromatography)}$$

Solute descriptors (R_2, π_2, $\Sigma\alpha_2$, $\Sigma\beta_2$, $\log L^{16}$, and V_x): depended on solute properties

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C. Solute retention in Binary stationary phase
(combinatorial approach)

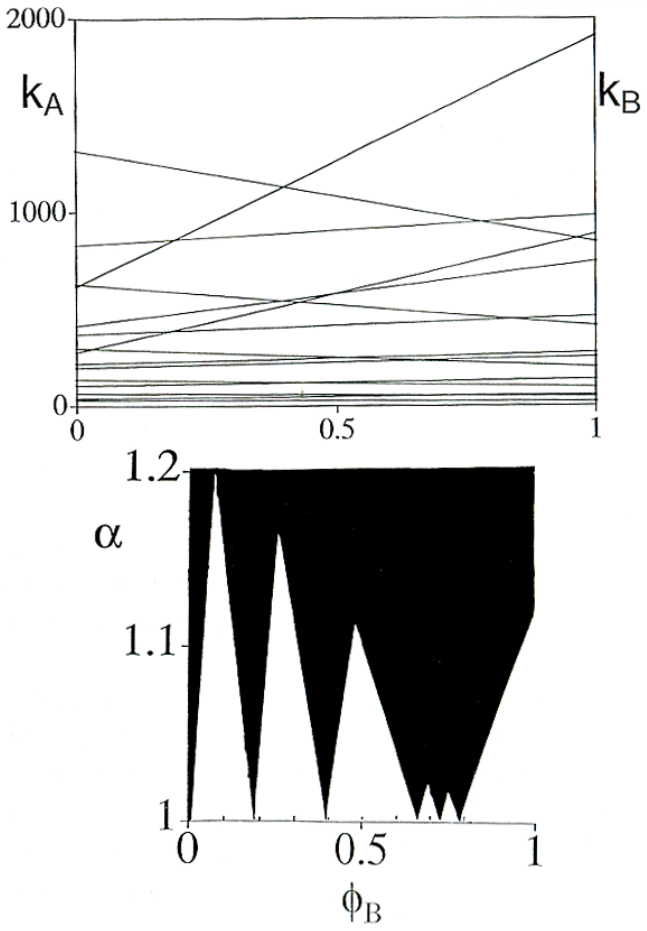
1. Mixture of stationary phases

$$K_s = \Phi_A K_A + \Phi_B K_B$$

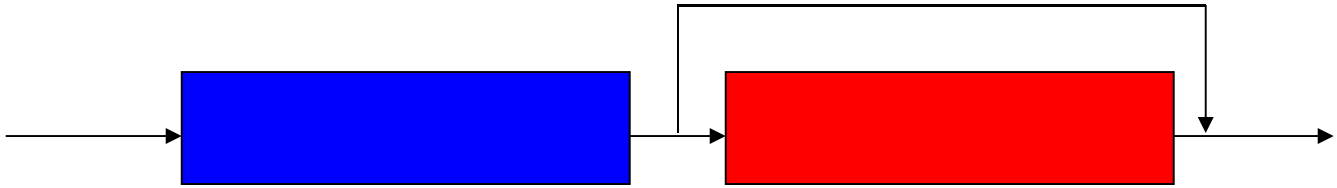
$$\Phi_A + \Phi_B = 1$$

Where: K_s is the gas-liquid partition coefficient for a solute on a mixed bed stationary phase. K_A or K_b are the gas-liquid partition coefficients for a solute on a pure stationary phase A or B, respectively.

$$\alpha = k_1/k_2 = K_1/K_2$$



2. Coupled columns



Column A Column B

$K_s = \Phi_A K_A + \Phi_B K_B$

$K_s = (PK_A + K_B) / (P+1)$ $P = t_{MA}/t_{MB}$

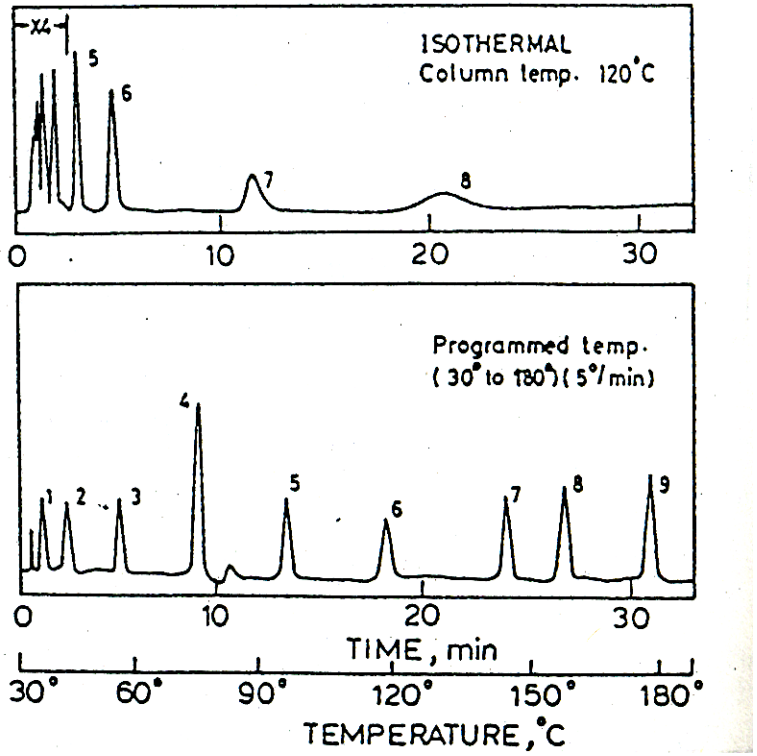
Question: After two solutes achieve baseline separation in the first GC column, what is the consequence if let them go through the second column?

$R_s = [N^{1/2}/4][(\alpha -1)/(\alpha)]/[k_2/(1+ k_2)]$,

The essence of Chromatography: p128

D. Temperature and Flow Programming

1. Temperature programming:



2. Flow programming:

$H_{tot} = A + B/u + Cu$ (van Deemter equation)

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13. A mixture of two solutes in injected into a 25 m X 0.2 mm ID capillary GC column using nitrogen as the carrier gas and a column temperature of 150 ^{o}C; the average flow rate of nitrogen through the column is 10 mL/min. The first solute in the injected mixture eluted with a retention time of 10.23 min and a baseline width of 0.15 min; the second solute in the mixture elutes at 10.41 min with a baseline width of 0.18 min. Injection of air (a non-retained solute) produces a peak at 0.08 min. The diffusion coefficient for both solute 1 and 2 under these conditions is roughly 1 X 10^{-1} cm^2/sec. Please determine each of the following values for this system.

(a) Separation factor α between solute 1 and 2. (b) the plate number for solute 1 and 2. (c) Is baseline resolution is achieved in this separation. (d) The average time it takes solute 1 to travel across the diameter of the GC capillary (i.e., 0.2 mm).