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

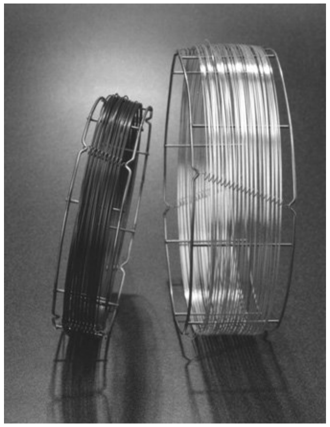
(Chapter 2 and 3 in The essence of chromatography)

Capillary Gas-Liquid Chromatography

A. Separation efficiency and rate theory

B. Preparation of Capillary Column

C. Evaluation of Capillary Column



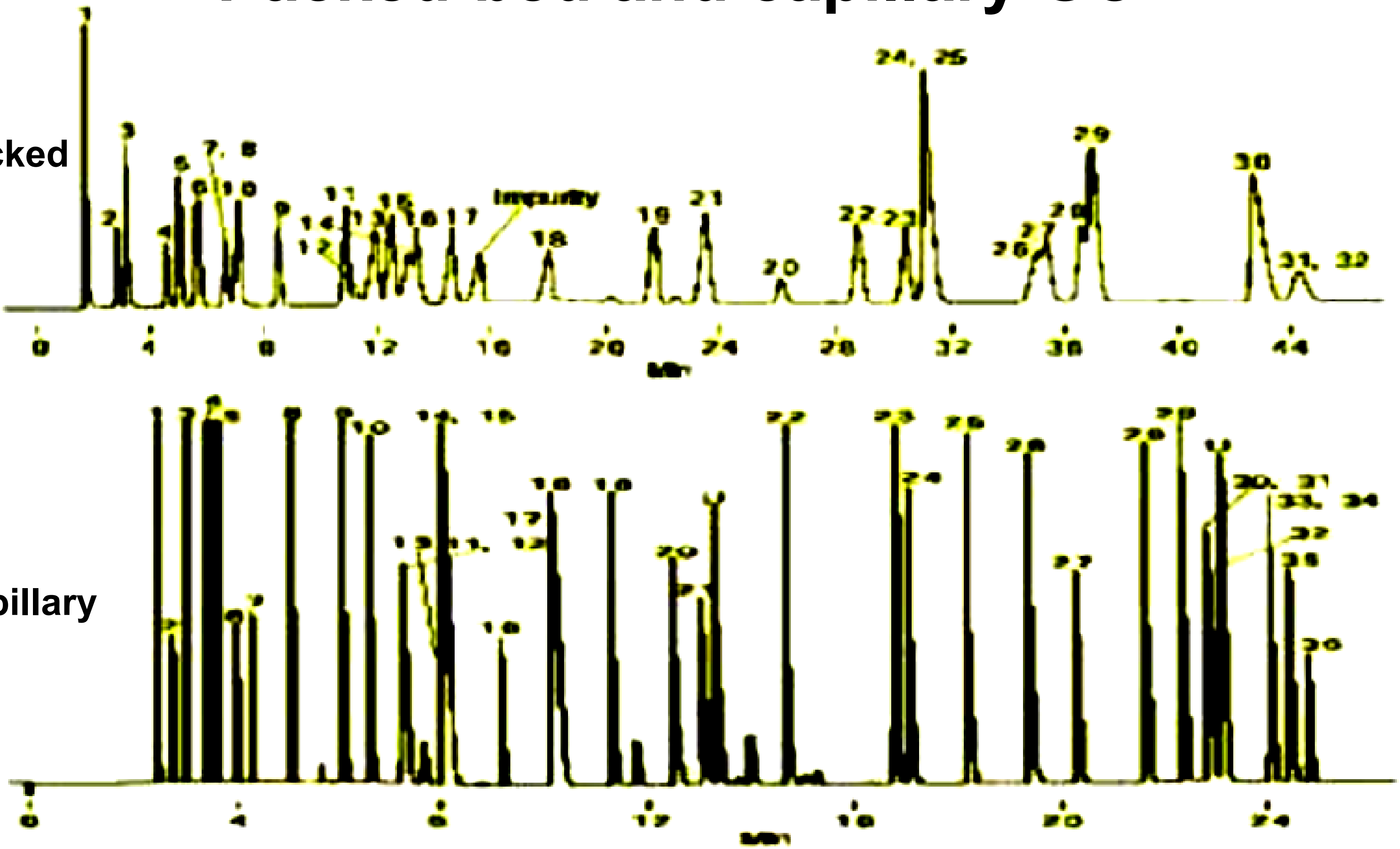
Representative properties of different column types for gas chromatography
H_{min} = minimum plate height at the optimum mobile phase velocity u_{opt}

Column type	Phase ratio	H_{min} (mm)	u_{opt} (cm/s)	Permeability (10^7.cm^2)
Classical Packed	4-200	0.5-2	5-15	1-50
Micropacked	50-200	0.02-1	5-10	1-100
Packed Capillary	10-300	0.05-2	5-25	5-50
SCOT	20-300	0.5-1	10-100	200-1000
WCOT	15-500	0.03-0.8	10-100	300-20000

Packed-bed and capillary GC

packed

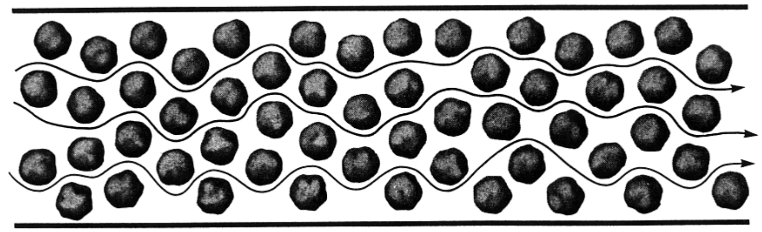
capillary



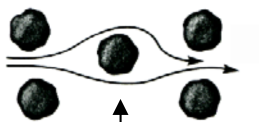
Capillary GC has much higher separation efficiency than packed-bed GC!

Rate theory-- Van Deemter Equation

1. Packed-bed system



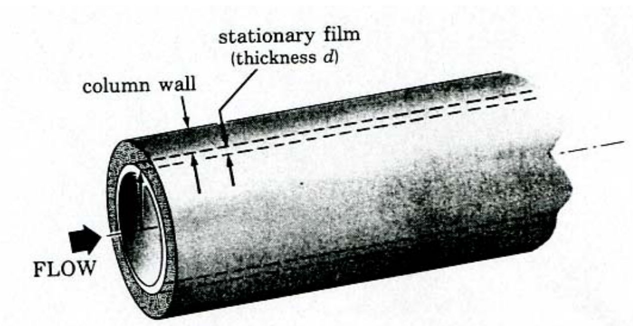
$$H = A + B/u + (C_S + C_M)u$$



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

λ:column packing factor (0.5~1.5)
d_p: average size of the filling particles
ε_p: intraparticle porosity
ε_e: interparticle porosity
D_m: solute diffusion coefficient in mobile phase.
k: capacity factor → $k = K (V_s/V_m)$
D_s: solute diffusion coefficient in stationary phase.
q_s:shape factor for the stationary phase coating coating (2/3 for a thin layer).
d_f: thickness of stationary phase

2. Capillary system—open tubular system



No eddy diffusion!

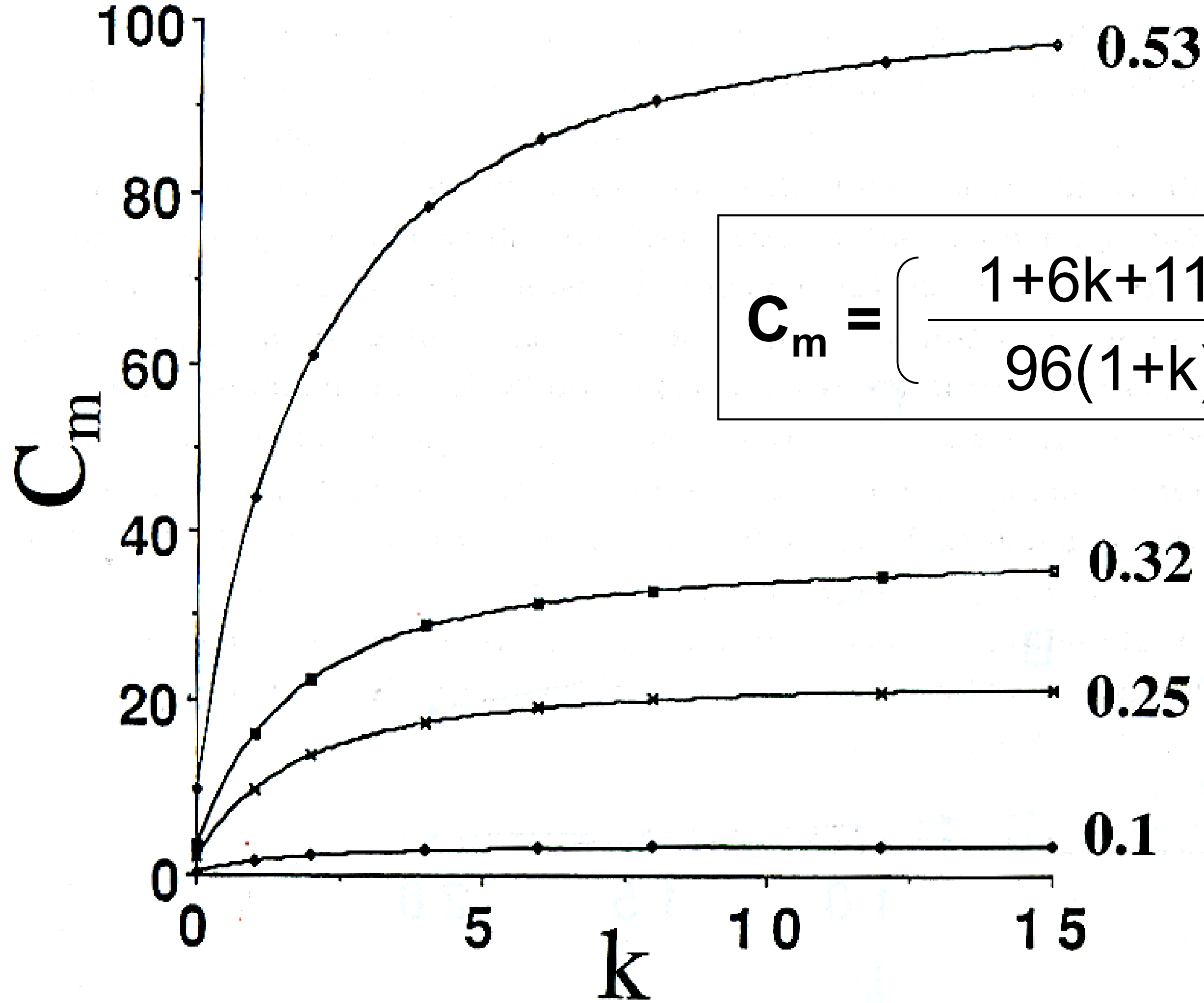
$$H = B/u + Cu$$

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

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

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

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



$$C_m = \left(\frac{1+6k+11k^2}{96(1+k)^2}\right)\left(\frac{d^2}{D_m}\right)$$

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).

Table 1.6
Relative contribution (%) of resistance to mass transfer in the mobile and stationary phases to the column plate height for undecane at 130°C for a 0.32 mm internal diameter open tubular columns in gas chromatography

Film thickness (μm)	Retention factor	Phase ratio	Mass transfer term (%)	
			C_M	C_S
0.25	0.56	320	95.2	4.8
0.5	1.12	160	87.2	12.8
1.00	2.24	80	73.4	26.6
5.00	11.2	16	31.5	68.5

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

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

The ratio of C_S and C_m contributions to the term of resistance to mass transfer is determined by the phase ration.

$$(V_m/V_s) = d/4d_f\text{, when, } d \gg d_f$$

The Effect of Carrier Gas

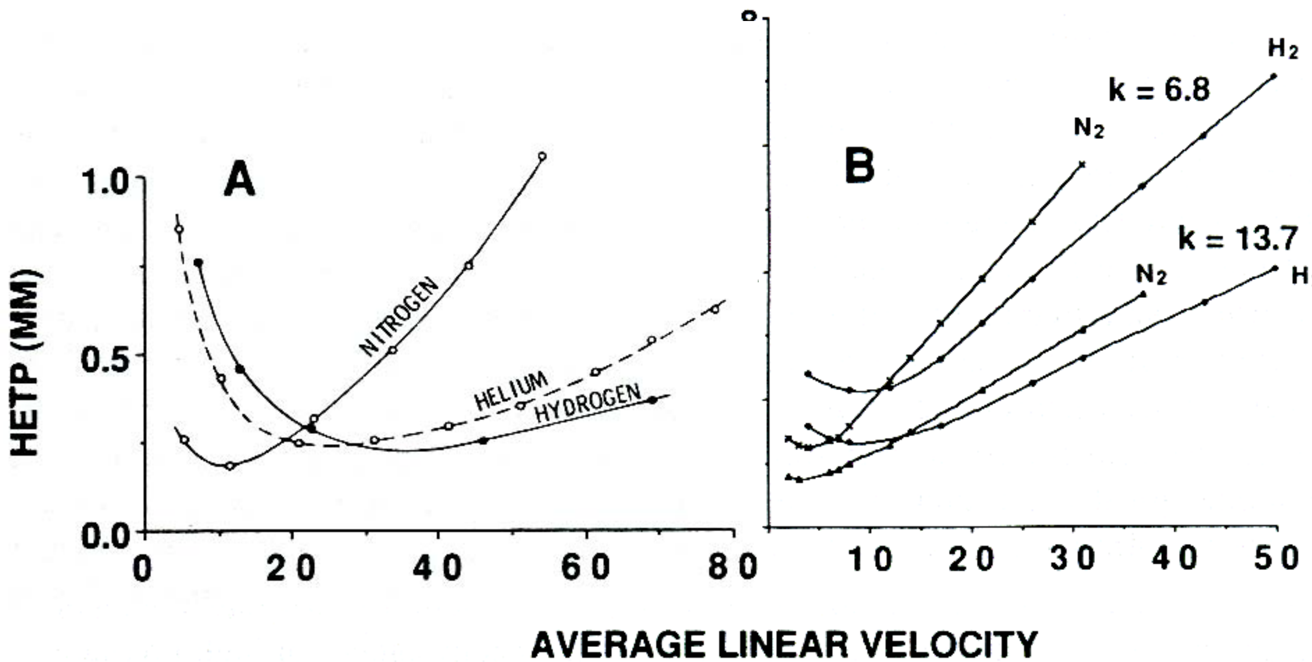


Figure 2.1. Van Deemter plots indicating the influence of the choice of carrier gas on column efficiency for thin-film (A) and thick-film (B) open tubular columns for solutes with different retention factors.

gas

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

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

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

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

$$\boxed{D_{AB} = kT/(6\pi\eta_B r_A)}$$ liquid

Parameters affecting plate height

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

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

	$\frac{2D_m}{u}$	$\frac{2k}{3(1+k)^2}\frac{d_f^2}{D_s}u$	$\frac{1+6k+11k^2}{96(1+k)^2}\frac{d^2}{D_m}u$
T	↑	↓	↓
u	↓	↑	↑
d_f	—	↑	—
d	—	—	↑
k	—	↓	↑

Preparation of Capillary Column

1. Materials

a. glass: soda-lime (soft) ***alkaline***

SiO_2 67.7%, Na_2O 15.6%, CaO 5.7%, MgO 3.9%, Al_2O_3 2.8%, BaO 0.8%, and K_2O 0.6%

borosilicate (hard), ***acidic***

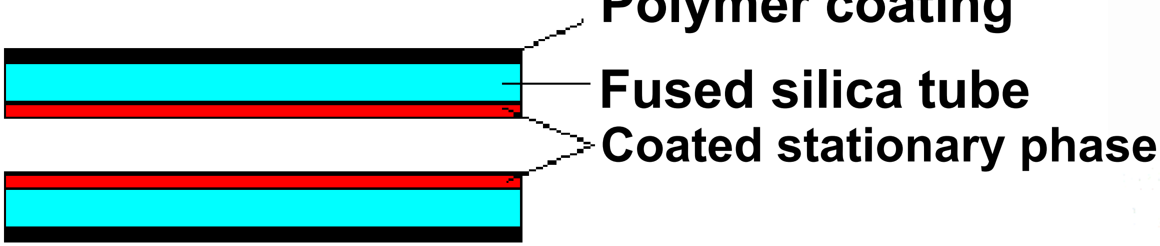
SiO_2 67.7%, B_2O_3 13 %, Na_2O 3.0%, Al_2O_3 2.0%, and K_2O 1.%

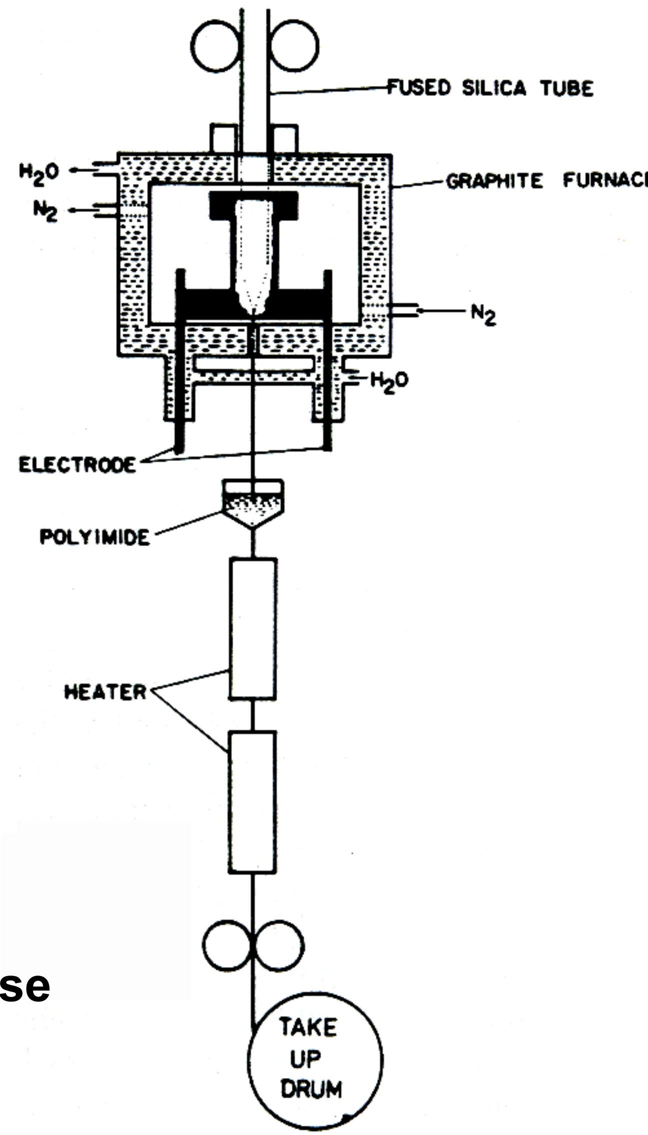
b. fused silica

$$SiCl_4 + O_2 \longrightarrow SiO_2$$

Surface: Si—OH, O--SiH-O

Silanol Siloxane





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

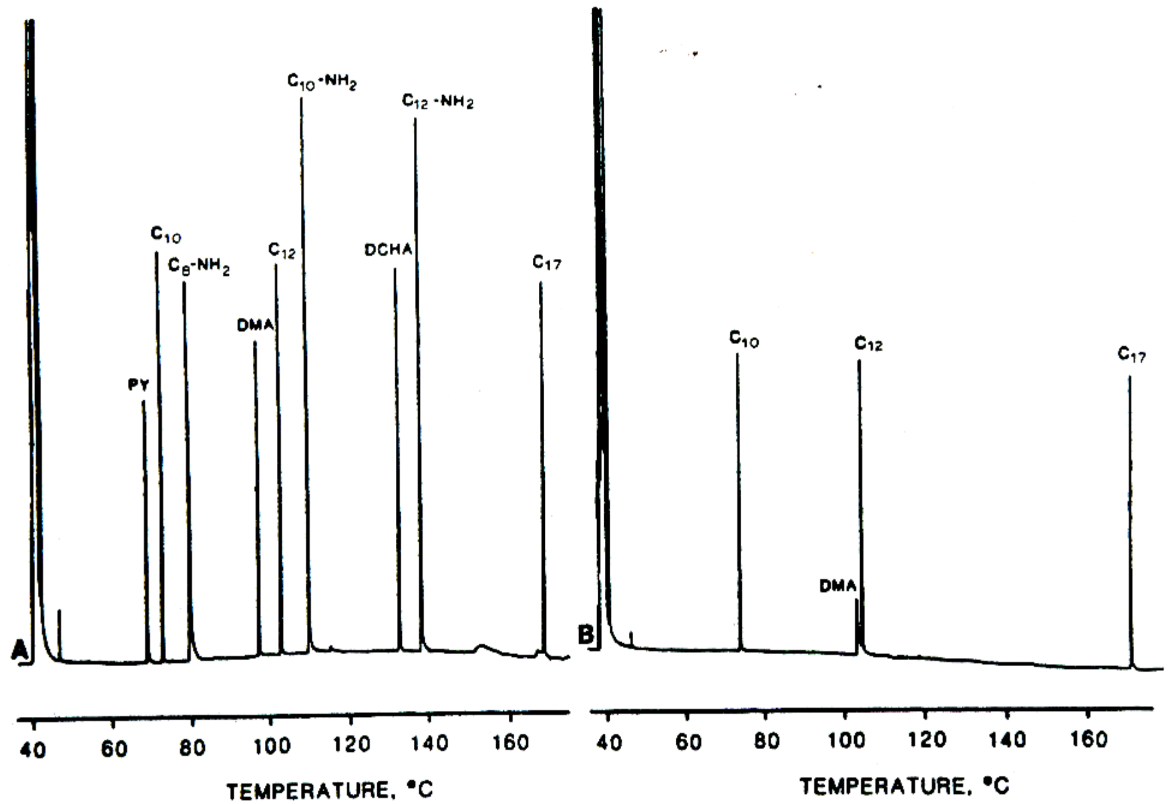


Figure 2.15. Activity test for an uncoated fused silica capillary column after (A) deactivation with poly(phenylmethylhydrosiloxane) and (B) before deactivation. Precolumn: 15 m x 0.20 mm I.D. coated with SE-54. Test columns 10 m x 0.20 mm I.D. The column tandem was programmed from 40 to 180°C at 4°C/min 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-aminooctane, PY = 3,5-dimethylpyrimidine, 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.

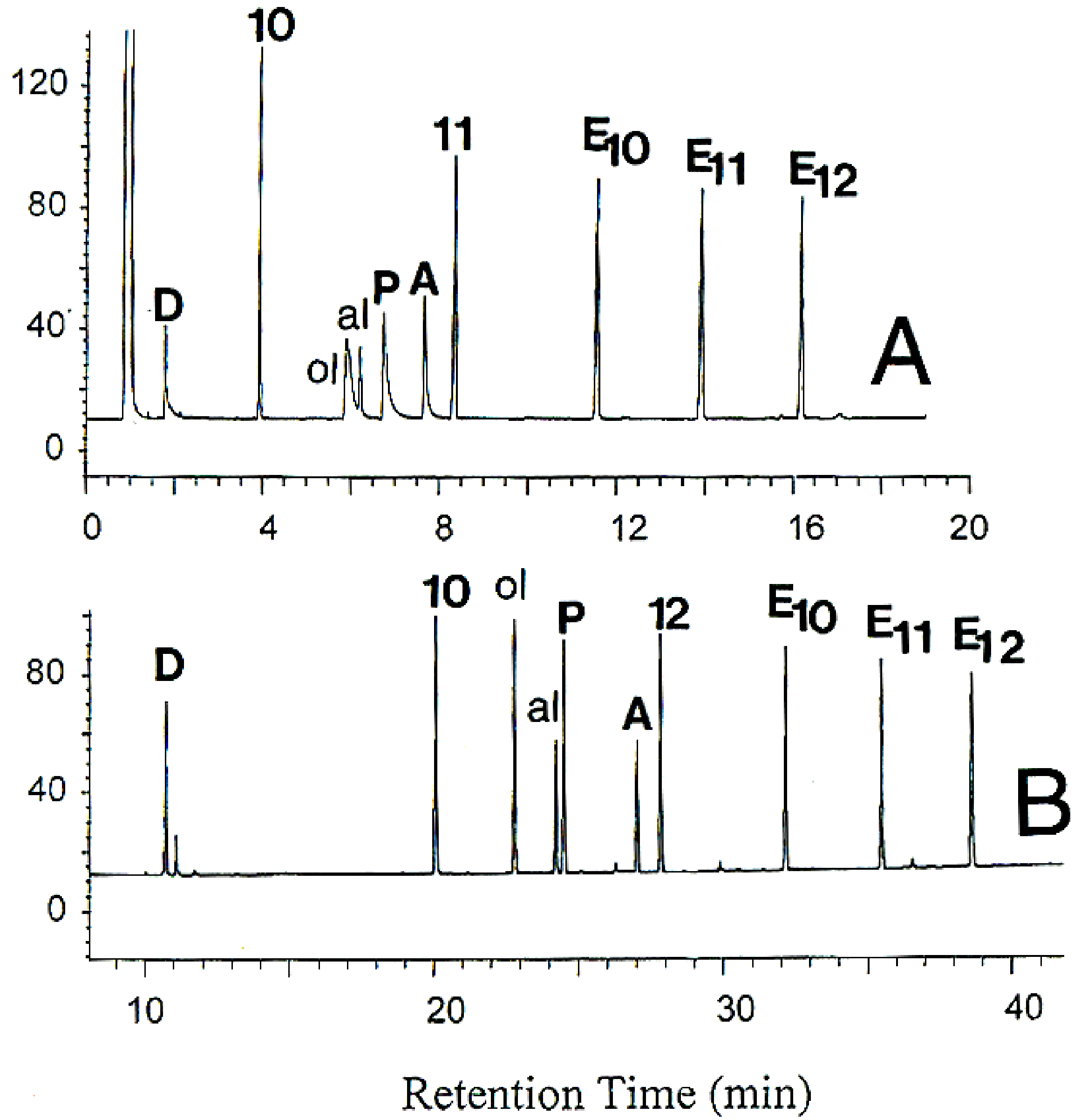
Composition of concentrated test mixture

Substance	Abbrev-ation	Amount (mg)	Substance	Abbrev-ation	Amount (mg)
Methyl decanoate	E_{10}	242	1-Octanol	ol	222
Methyl undecanoate	E_{11}	236	Nonanal	al	250
Methyl dodecanoate	E_{12}	230	2,3-Butanediol	D	380
n-Decane	10	172	2,6-Dimethylaniline	A	205
n-Undecane	11	174	2,6-Dimethylphenol	P	194
n-Dodecane	12	176	Dicyclohexylamine	am	204
			2-Ethylhexanoic Acid	S	242

Optimized experimental conditions

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

Column	Hydrogen		Helium	
length (m)	Methane elution (s)	Temperature program (°C/min)	Methane elution (s)	Temperature program (°C/min)
10	20	5.0	35	2.5
15	30	3.3	53	1.65
20	40	2.5	70	1.25
30	60	1.67	105	0.84
40	80	1.25	140	0.63
50	100	1.0	175	0.5



Old column

New column

(1) The height of the peaks

(2) The shape of the peaks

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3. Columns Thermal Stability

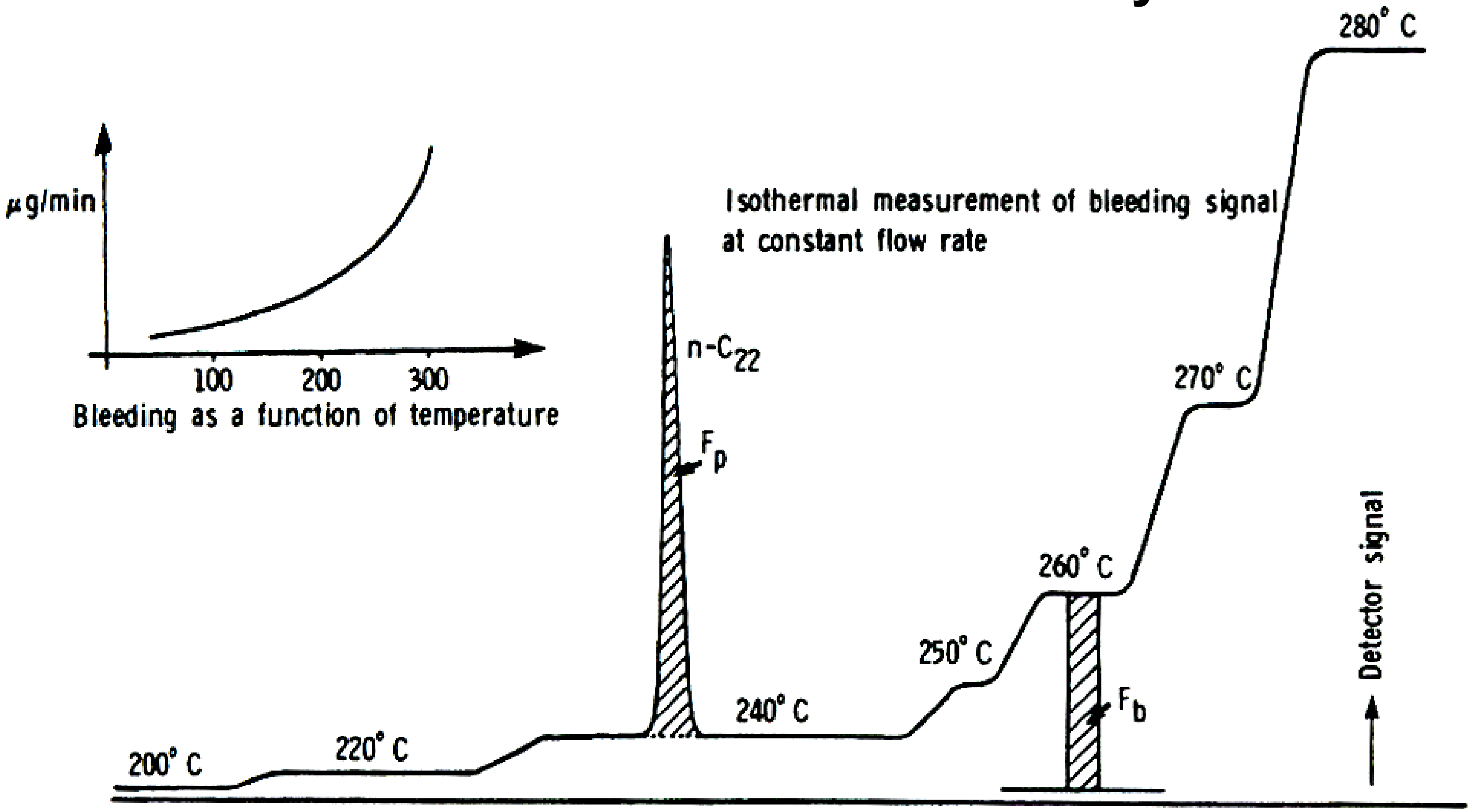

Figure 2.17. Standardized column bleed test. (From ref. [369]. ©Elsevier)

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

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