Selecting the Best Column for Your Analysis

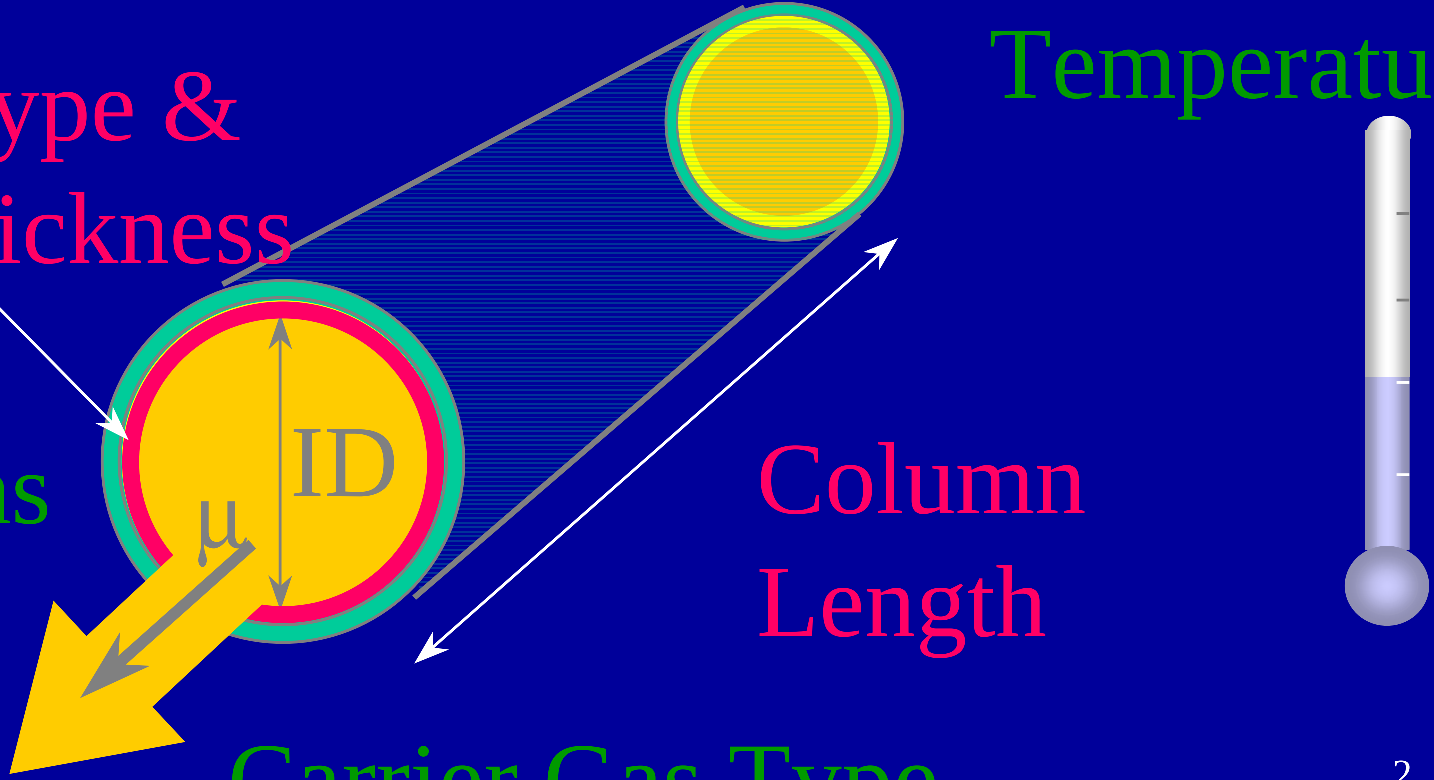
1. Factors Influencing Separation
2. Selectivity
3. Film Thickness
4. ID
5. Length
6. Capacity Issues

Column Selection

Factors Affecting Separation

Seven Main Factors Affect Separation

(note: other minor factors exist)



Phase Type &
Film Thickness

Temperature

Carrier Gas
Velocity

Column
Length

Carrier Gas Type

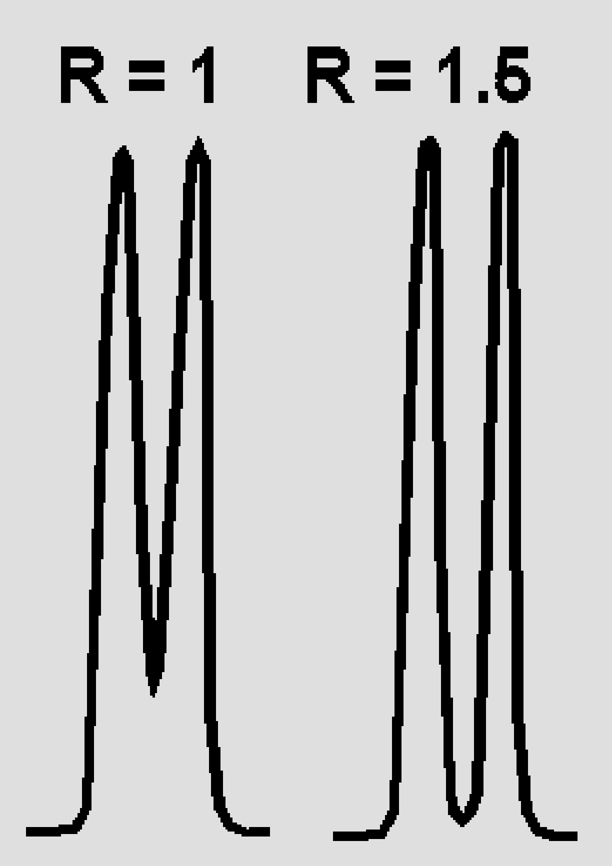
RESTEK

Effects of Column Length, ID, Film Thickness and Phase Type

General Resolution Equation

$$R = \frac{1}{4}\sqrt{\frac{L}{h}} \times \frac{k}{k+1} \times \frac{\alpha-1}{\alpha}$$

L = column length
h = HETP
k = capacity factor
α = selectivity



NOTE: Baseline resolution = 1.5

Column Selection

Variables to Consider

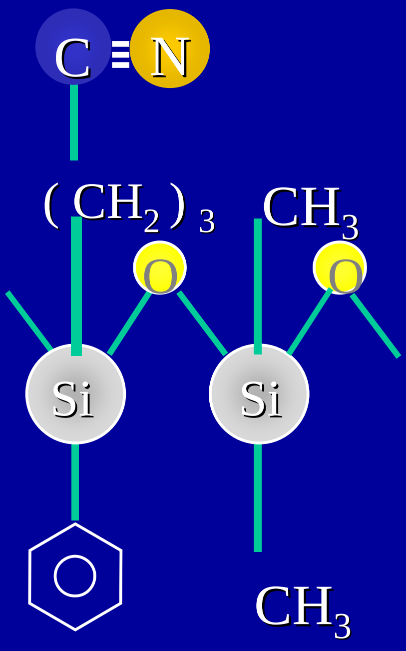
Variable:	Controls:
Stationary phase	• solubility, capacity, efficiency, resolution (R), retention time (t_R), analysis temperature, bleed
Film Thickness	• capacity, efficiency, R, t_R , T°, bleed
ID	• capacity, efficiency, t_R
Length	• total efficiency (total plates), R, t_R , Co$t

Stationary Phase Selectivity

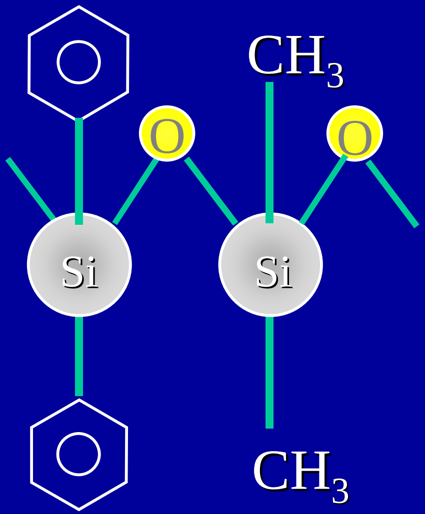
- Chemistry of Stationary Phases
- Effect of Selectivity on Separation
- Effect of Selectivity on Analysis Time
- Special Purpose Columns (Application Specific)

Stationary Phase Selectivity

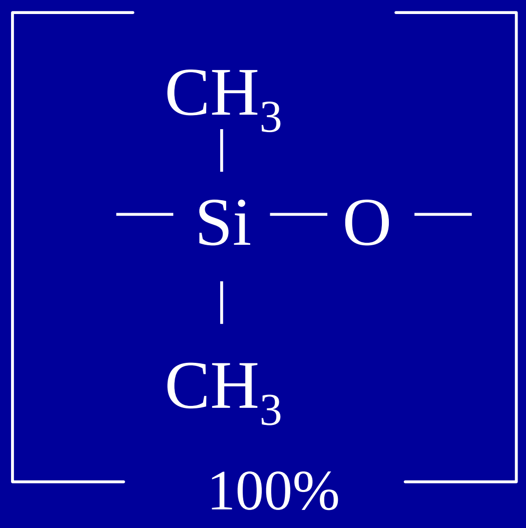
Determinants of Stationary Phase Selectivity



Type and amount of substituted functional groups



Rtx®-1

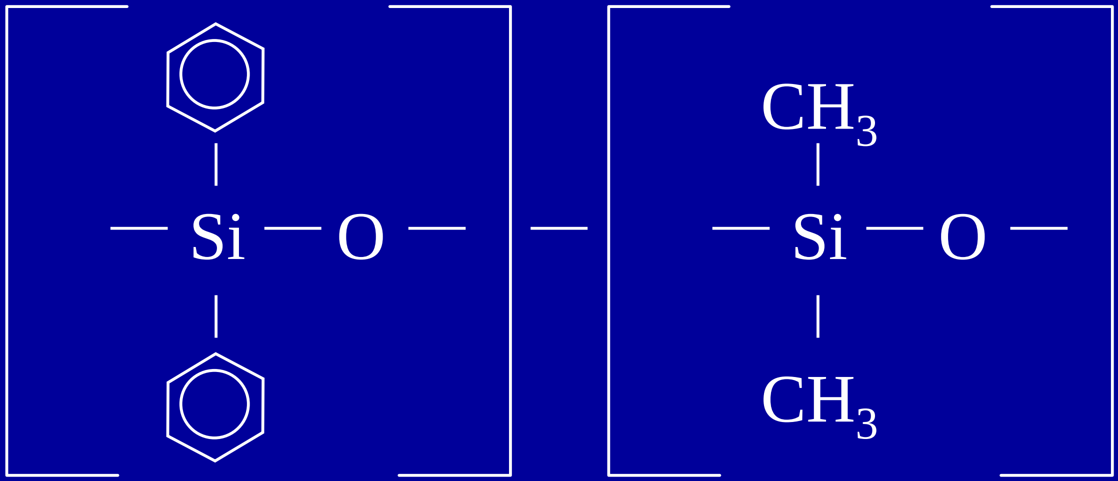


$$\left[\, -\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}- \,\right]_{100\%}$$

Dimethylpolysiloxane

Polarity:	least polar bonded phase
Uses:	boiling point separations (solvents, petroleum products, and pharmaceuticals)
Properties:	min. temp. (-60°C), max. temp. (360°C to 430°C)

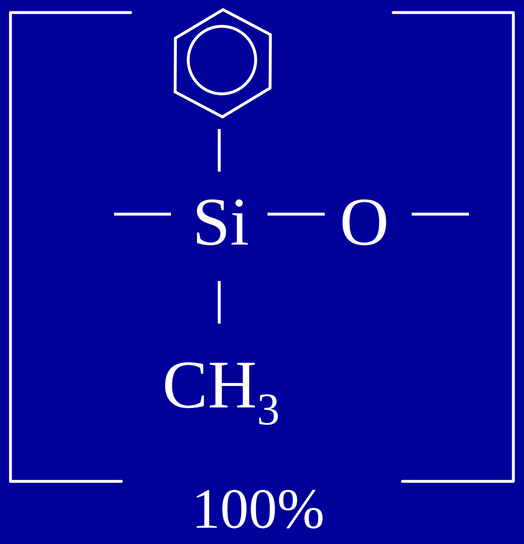
Rtx®-5, 20, 35, 65



e.g., Rtx-5: 5% diphenyl 95% dimethyl

Polarity:	non-polar
Uses:	boiling point separations (aromatics, flavors, environmental samples, and aromatic hydrocarbons
Properties:	min. temp. (-60°C), max. temp. (340°C to 360°C)

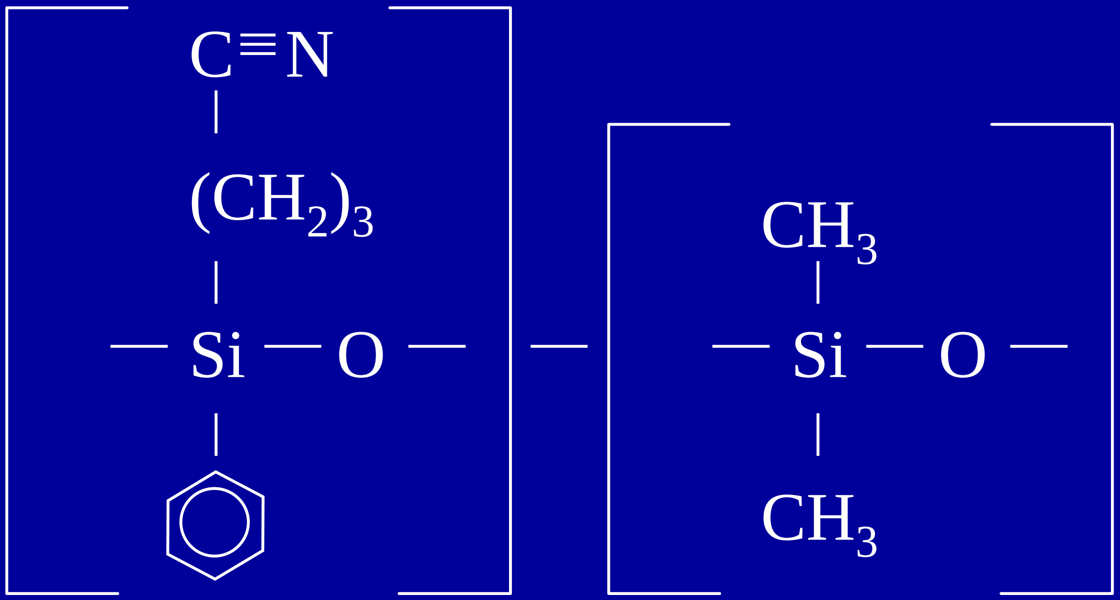
Rtx®-50



Phenylmethyl polysiloxane

Polarity: intermediate polarity
Uses: triglycerides and phthalate esters
Properties: min. temp. (0°C), max. temp. (340°C)

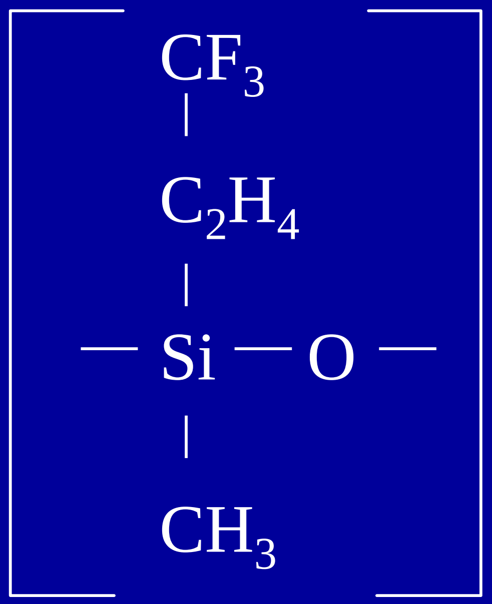
Rtx®-1301, 624, 1701



Cyanopropylphenylpolysiloxane Dimethylpolysiloxane

Polarity:	intermediate polarity
Uses:	pesticides, Aroclor®, alcohols, and oxygenates
Properties:	min. temp. (-20°C), max. temp. (280°C)

Rtx®-200

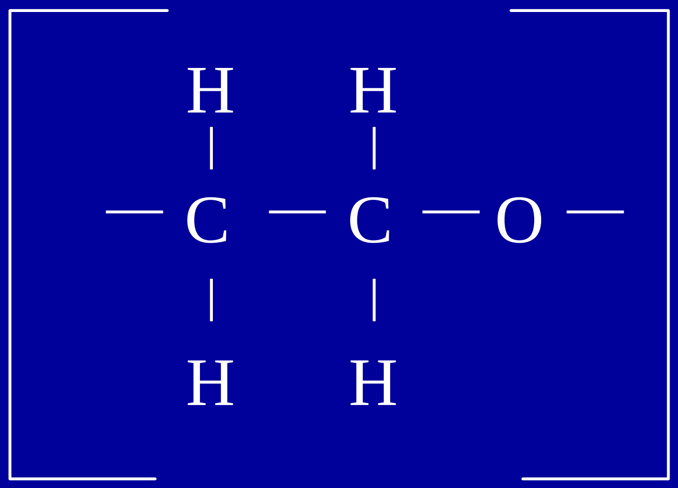


$$\left[\begin{array}{l} \quad\;\;\mathrm{CF_3} \\ \quad\;\;\; | \\ \quad\;\;\mathrm{C_2H_4} \\ \quad\;\;\; | \\ -\,\mathrm{Si}\,-\,\mathrm{O}\,- \\ \quad\;\;\; | \\ \quad\;\;\mathrm{CH_3} \end{array}\right]$$

Trifluoropropylmethyl polysiloxane

Polarity: selective for lone pair electrons
Uses: environmental samples, solvents, and Freon®
Properties: min. temp. (-20°C), max. temp. (360°C)

Stabilwax®

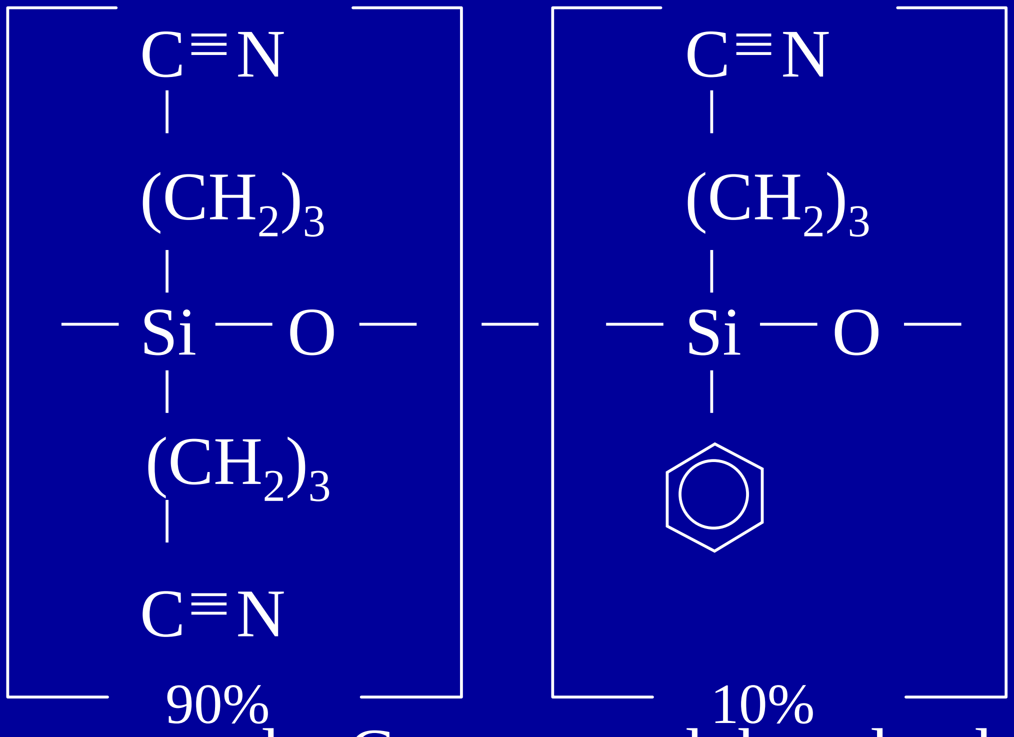


$$\left[\; -\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - O - \;\right]$$

Carbowax PEG

Polarity:	polar
Uses:	fames, flavors, acids, amines, and solvents
Properties:	min. temp. (40°C), max. temp. (250°C)

Rtx®-2330



Biscyanopropyl – Cyanopropylphenyl polysiloxane

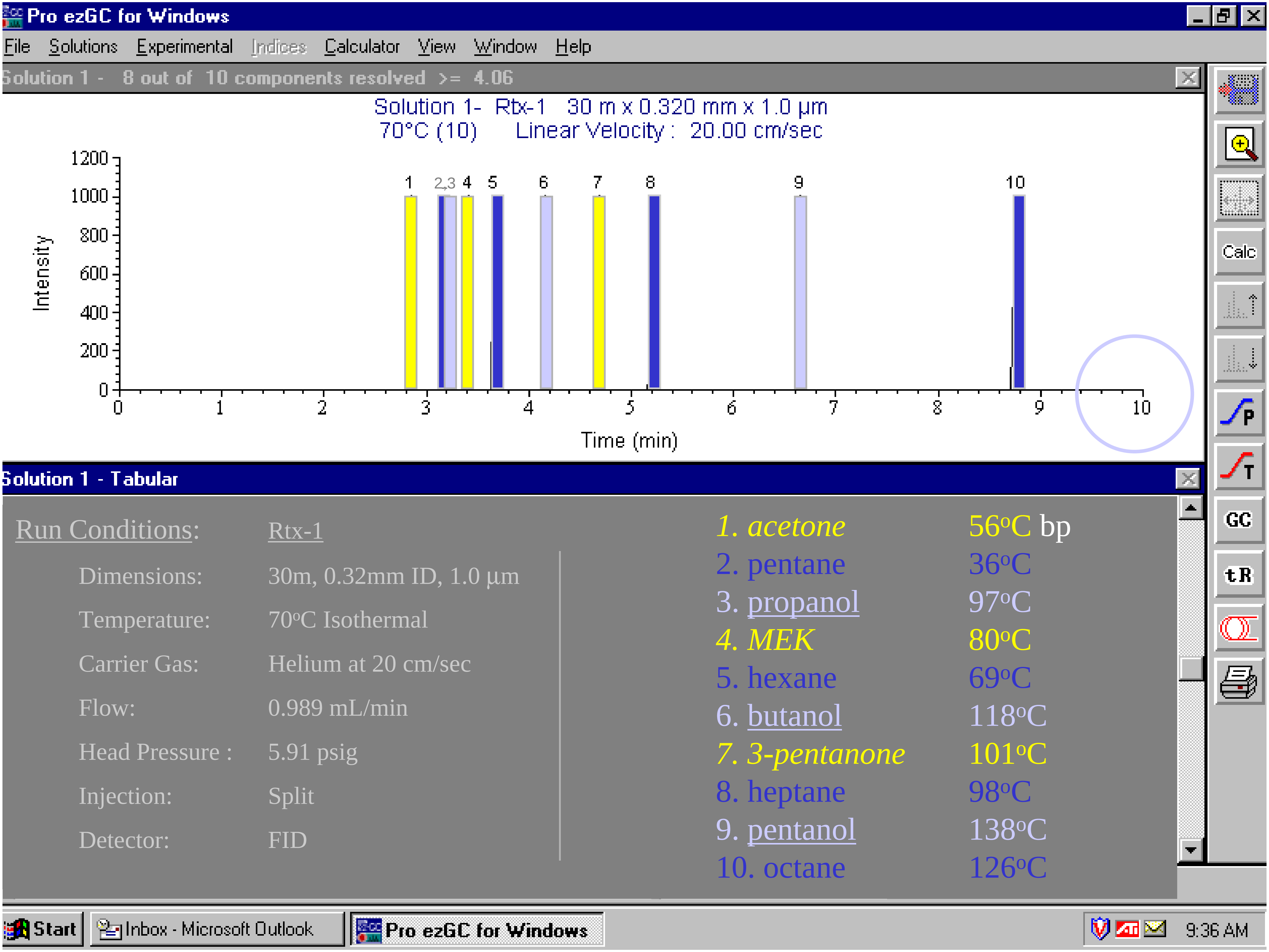
Polarity:	very polar
Uses:	cis/trans isomers
Properties:	min. temp. (0°C), max. temp. (275°C)

Stationary Phase Selectivity

Boiling Point vs. Solubility

- All columns are “boiling point” columns <u>within</u> a homologous class of compounds

- However, the solubility of a compound in the stationary phase is a better predictor of t_R than boiling point



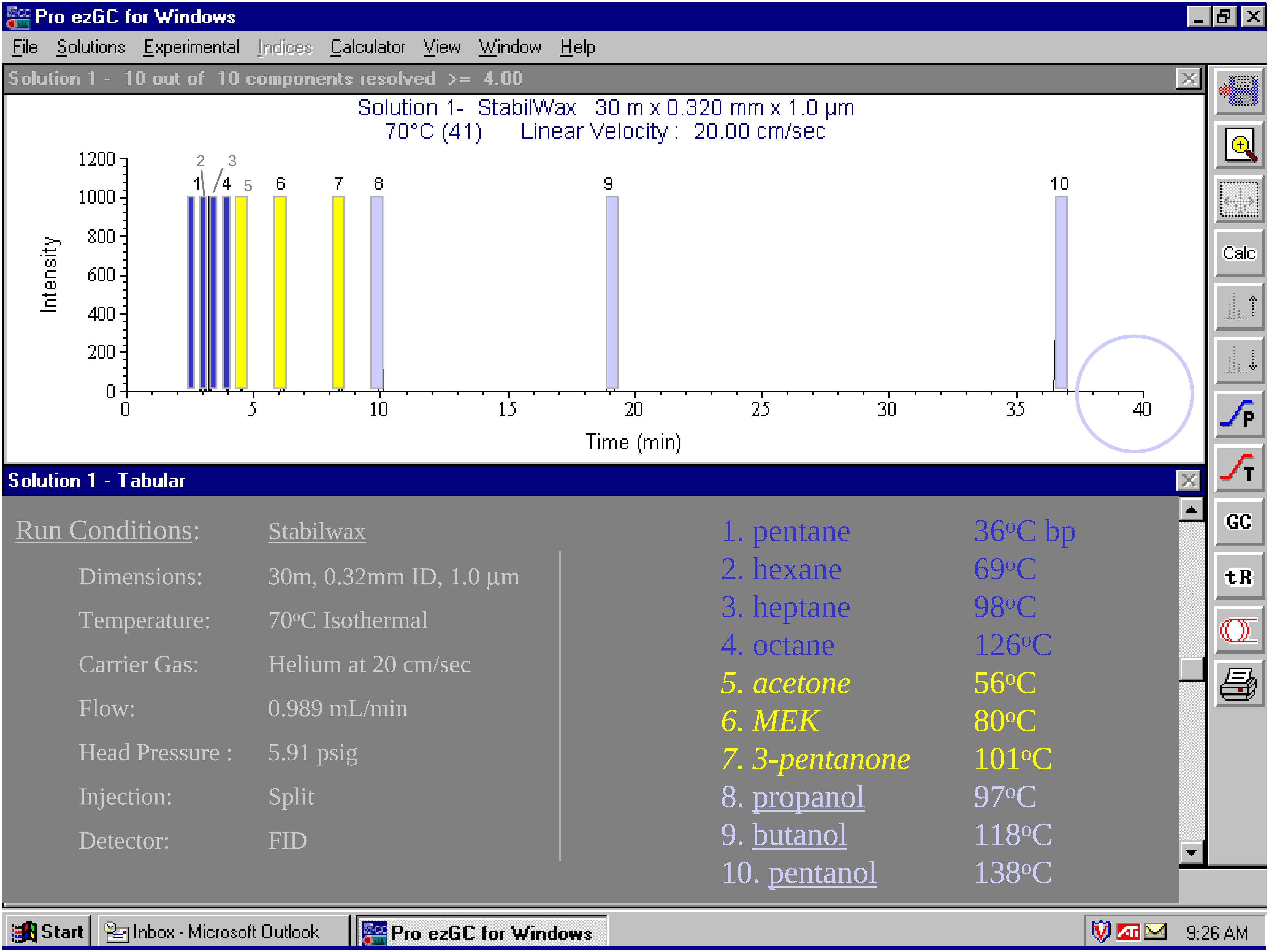
Solution 1 - 8 out of 10 components resolved >= 4.06

Solution 1- Rtx-1 30 m x 0.320 mm x 1.0 µm
70°C (10) Linear Velocity : 20.00 cm/sec

Solution 1 - Tabular

Run Conditions:	Rtx-1
Dimensions:	30m, 0.32mm ID, 1.0 µm
Temperature:	70°C Isothermal
Carrier Gas:	Helium at 20 cm/sec
Flow:	0.989 mL/min
Head Pressure :	5.91 psig
Injection:	Split
Detector:	FID

1. acetone	56°C bp
2. pentane	36°C
3. propanol	97°C
4. MEK	80°C
5. hexane	69°C
6. butanol	118°C
7. 3-pentanone	101°C
8. heptane	98°C
9. pentanol	138°C
10. octane	126°C



Solution 1 - 10 out of 10 components resolved >= 4.00

Solution 1 - Tabular

Run Conditions:	Stabilwax
Dimensions:	30m, 0.32mm ID, 1.0 µm
Temperature:	70°C Isothermal
Carrier Gas:	Helium at 20 cm/sec
Flow:	0.989 mL/min
Head Pressure :	5.91 psig
Injection:	Split
Detector:	FID

1. pentane	36°C bp
2. hexane	69°C
3. heptane	98°C
4. octane	126°C
5. acetone	56°C
6. MEK	80°C
7. 3-pentanone	101°C
8. propanol	97°C
9. butanol	118°C
10. pentanol	138°C

Special Purpose Columns

- Rtx-CLPesticides / CLPesticides2
- Rtx-OPPesticides / OPPesticides2
- Rtx-TNT / TNT2
- Rtx-BAC1 / BAC2
- Rtx-VMS, Rtx-VGC, Rtx-502.2, Rtx-VRX
- Rtx-5 Amine, Rtx-35 Amine
- Stabilwax-DA, Stabilwax-DB
- Chiral columns
- Rtx-500

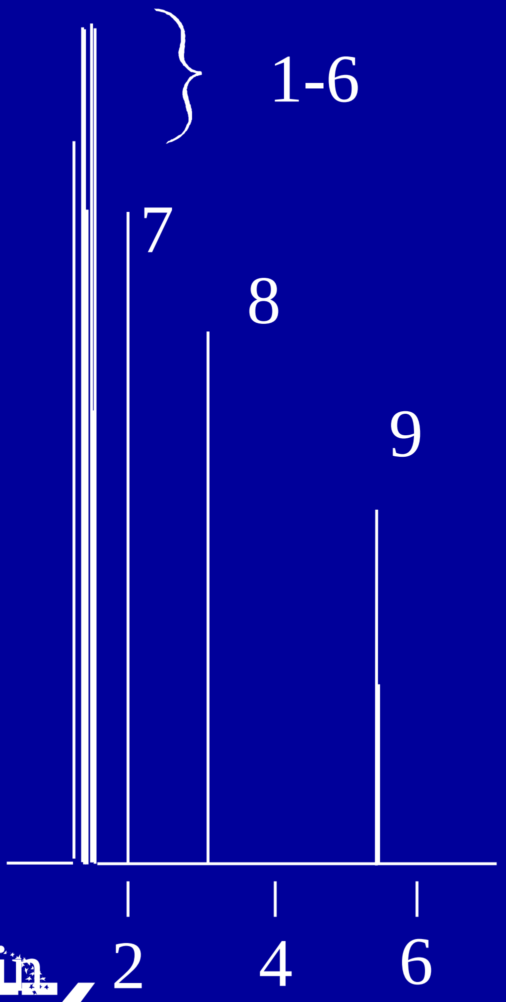
Film Thickness

- Effect of Film Thickness on Analysis Time
- Effect of Film Thickness on Separation
- Thin Films
- Thick Films

Film Thickness Effects

0.25µm Rtx®-1

30m, 0.32mm ID, 0.25µm



McReynolds probes

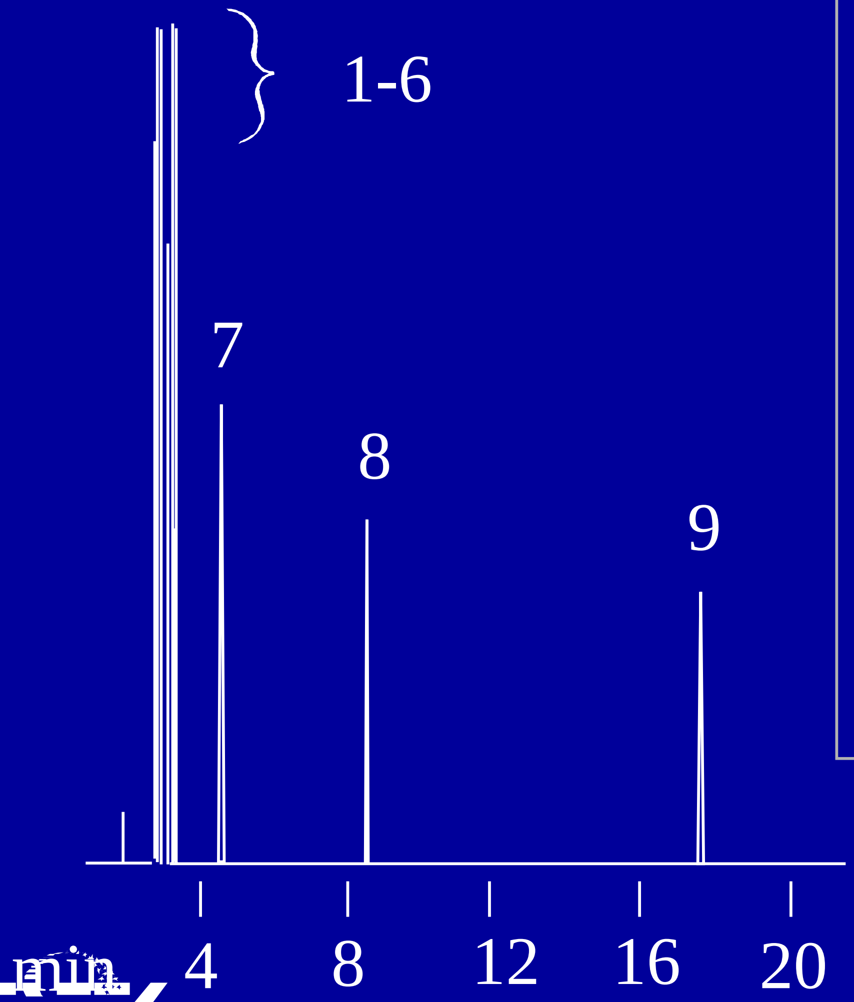
1. 1-butanol
2. benzene
3. 2-pentanone
4. C_7
5. 1-nitropropane
6. pyridine
7. C_8
8. C_9
9. C_{10} 5.5 min

70°C isothermal

Film Thickness Effects

1.0µm Rtx®-1

30m, 0.32mm ID, 1.0µm



McReynolds probes

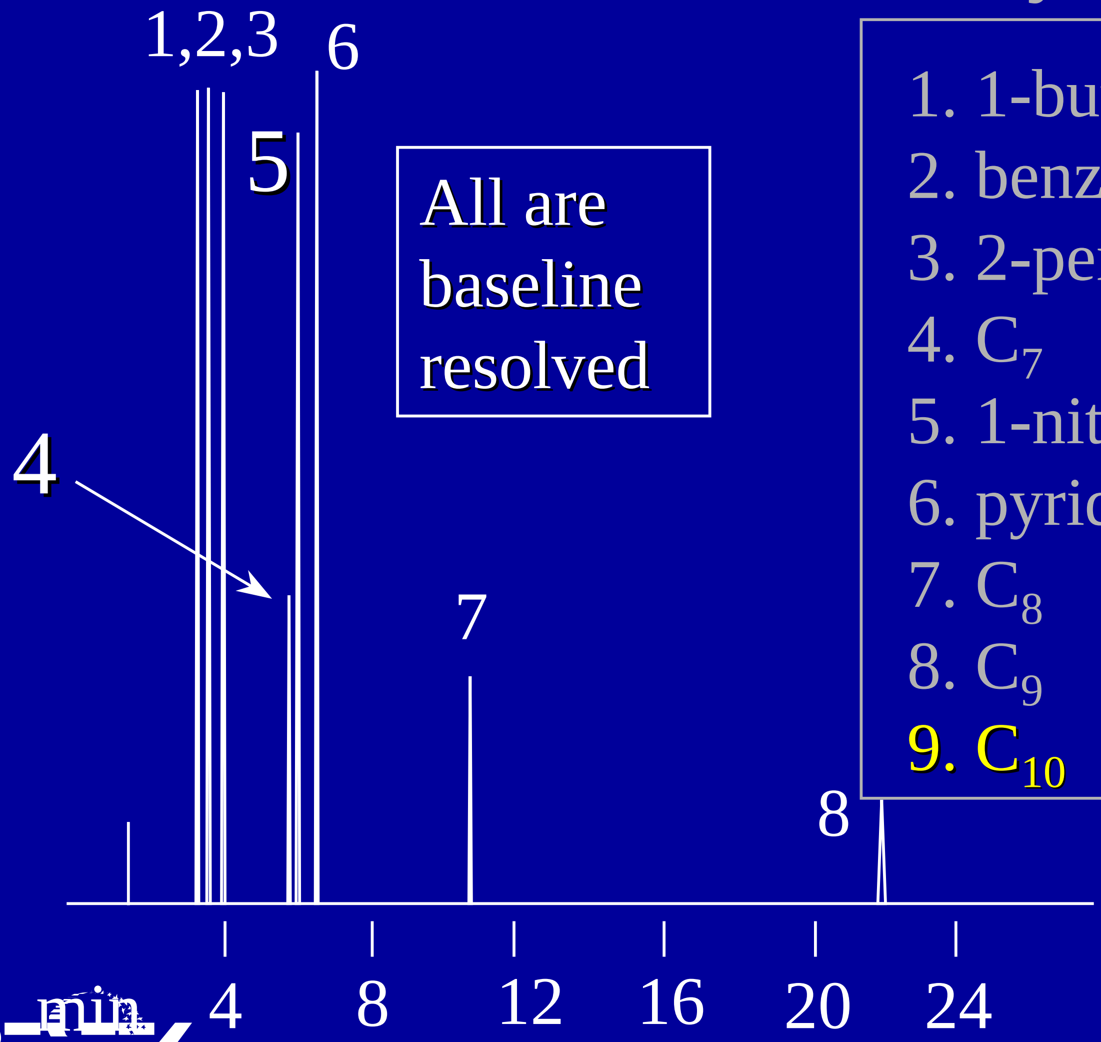
1. 1-butanol
2. benzene
3. 2-pentanone
4. C_7
5. 1-nitropropane
6. pyridine
7. C_8
8. C_9
9. C_{10} 18 min.

70^{o}C isothermal

Film Thickness Effects

3.0µm Rtx®-1

30m, 0.32mm ID, 3.0µm



All are baseline resolved

McReynolds probes

1. 1-butanol
2. benzene
3. 2-pentanone
4. C_7
5. 1-nitropropane
6. pyridine
7. C_8
8. C_9
9. C_{10} 68 min.

70°C isothermal

Film Thickness Effects

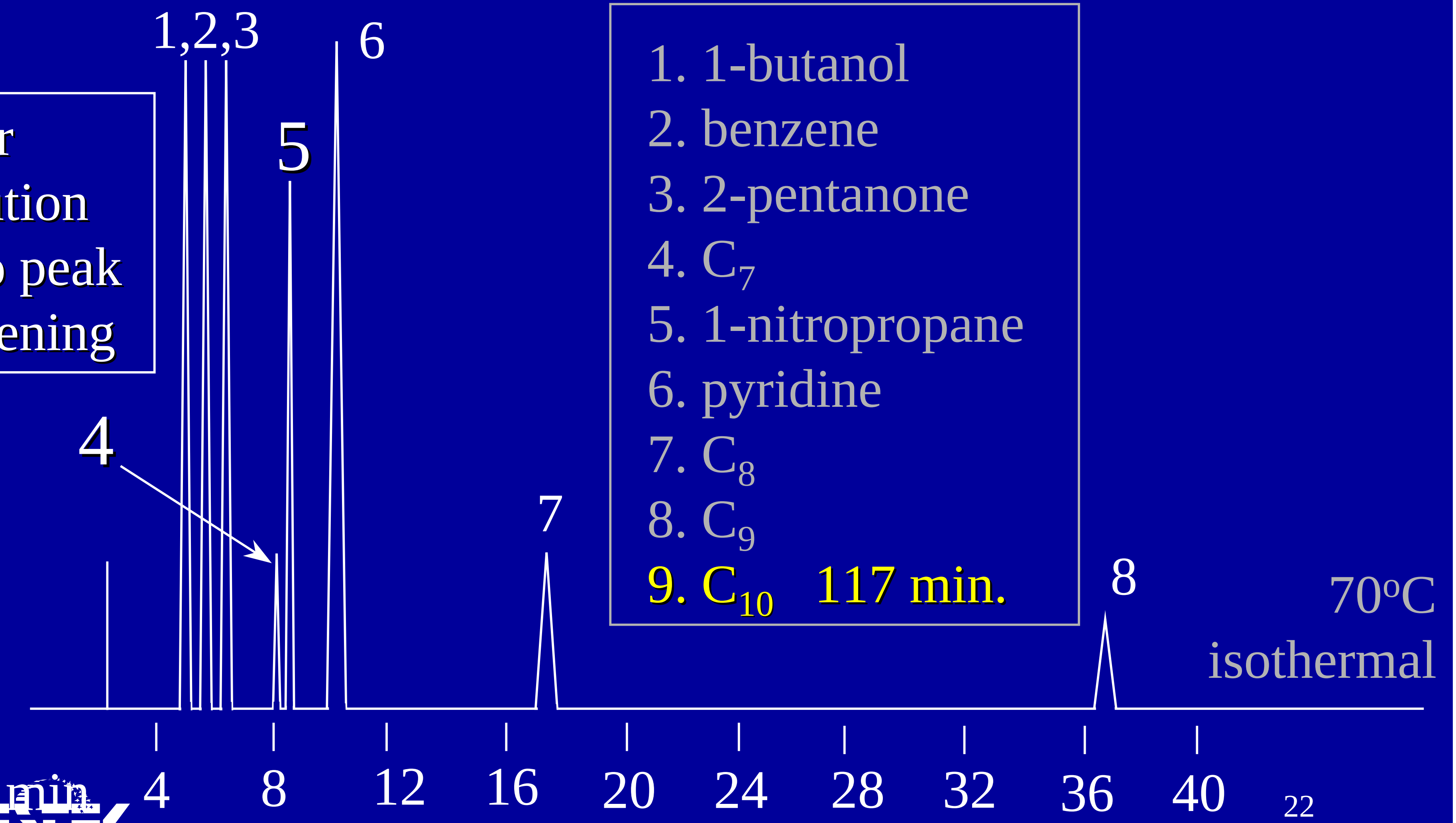
5.0µm Rtx®-1

30m, 0.32mm ID, 5.0µm

McReynolds probes

1. 1-butanol
2. benzene
3. 2-pentanone
4. C_7
5. 1-nitropropane
6. pyridine
7. C_8
8. C_9
9. C_{10} 117 min.

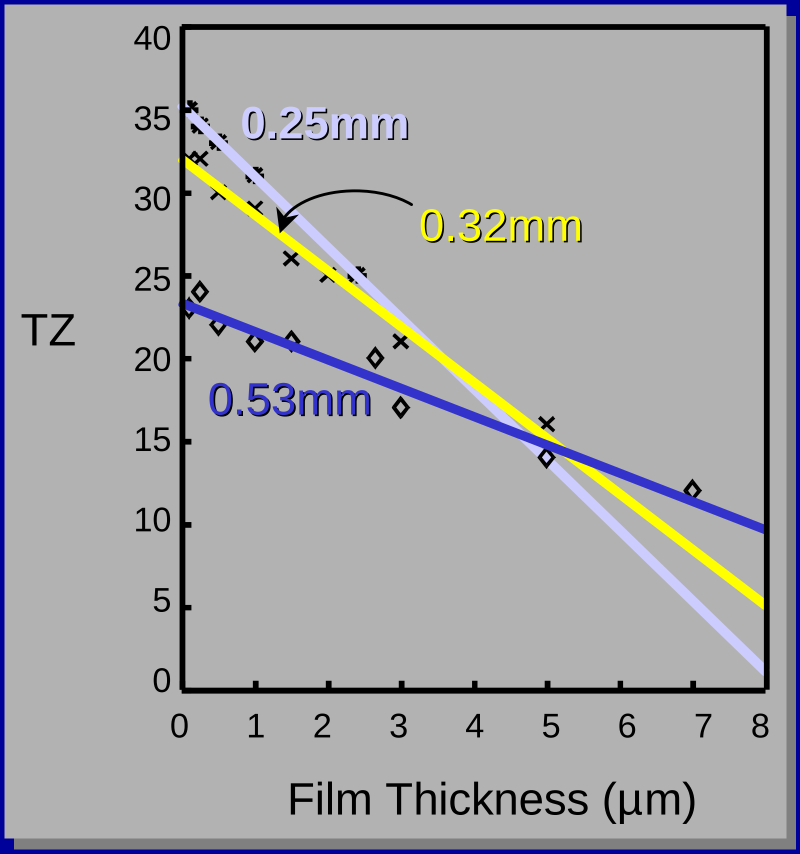
Lower resolution due to peak broadening



70°C isothermal

Film Thickness Effects

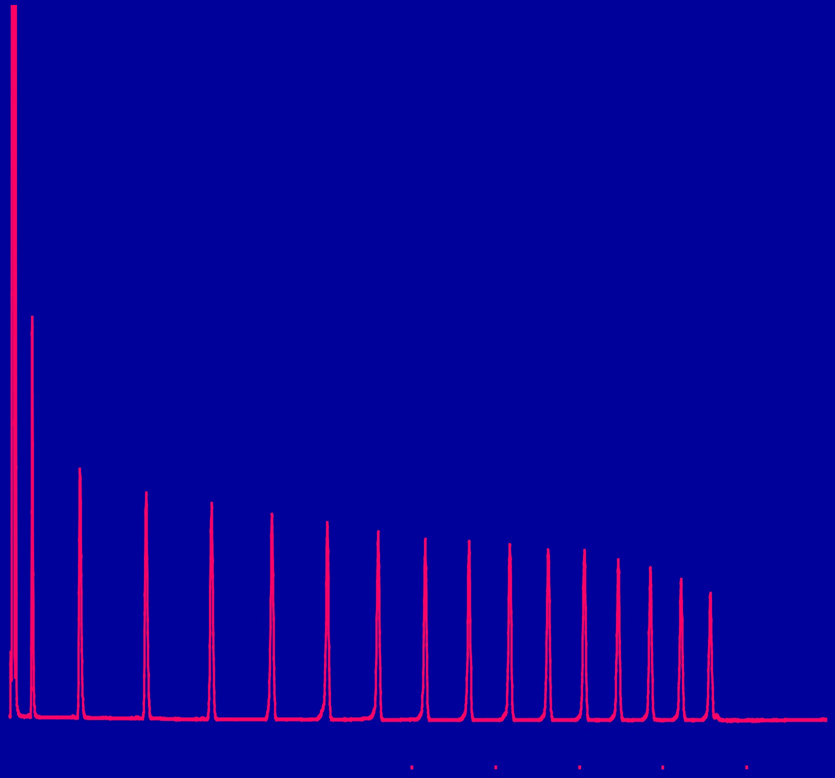
Efficiency (TZ)



Thin Films

Compatible with Wide Boiling Range Samples

Provide low stationary phase bleed necessary for analyzing high MW compounds



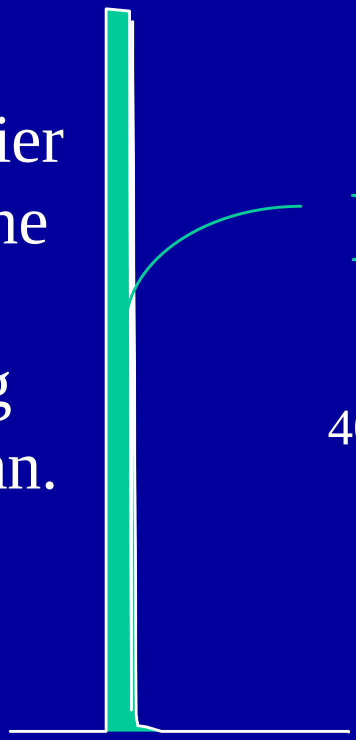
Thick Films

Good for Low MW Analyses: e.g., Solvent Purity

Rtx-1: 30m, 0.53mm ID, 0.25µm

Rtx-1: 30m, 0.53mm ID, **5.0**µm

The supplier reported the purity as 99% using this column.



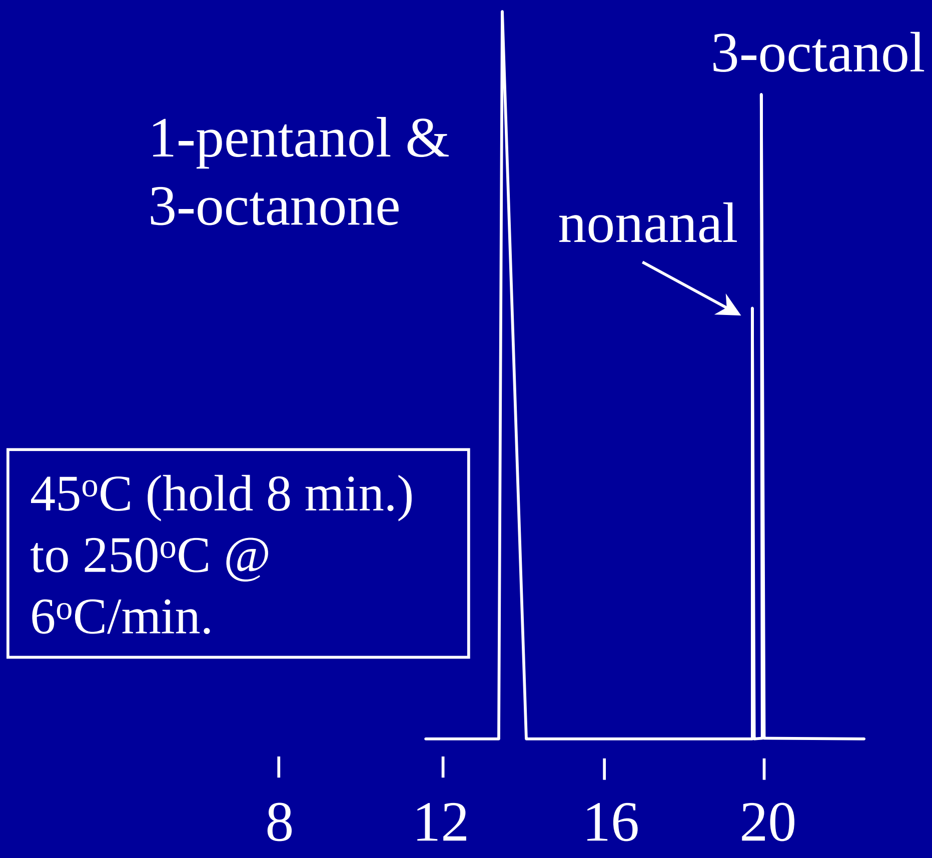
Pentane

40^{o}C isothermal

A closer look on a thick film column revealed that it was not.

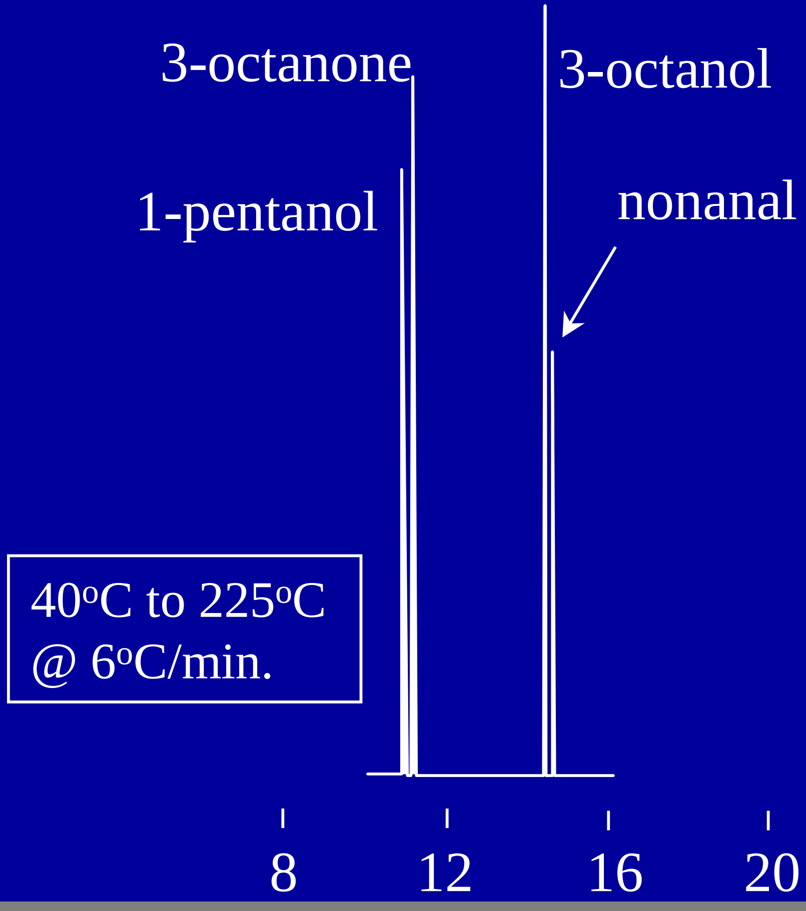
1µL direct injection

Film Thickness & Temperature Program - When Changing Both, Reconfirm Peak Identity



45^{o}C (hold 8 min.)
to 250^{o}C @
6^{o}C/min.

Stabilwax: 30m, 0.32mm ID, **0.25µm**



40^{o}C to 225^{o}C
@ 6^{o}C/min.

Stabilwax: 30m, 0.32mm ID, **1.0µm**

Inside Diameter (ID)

- Effect on Resolution
- Effect on Analysis Time
- Effect on Capacity

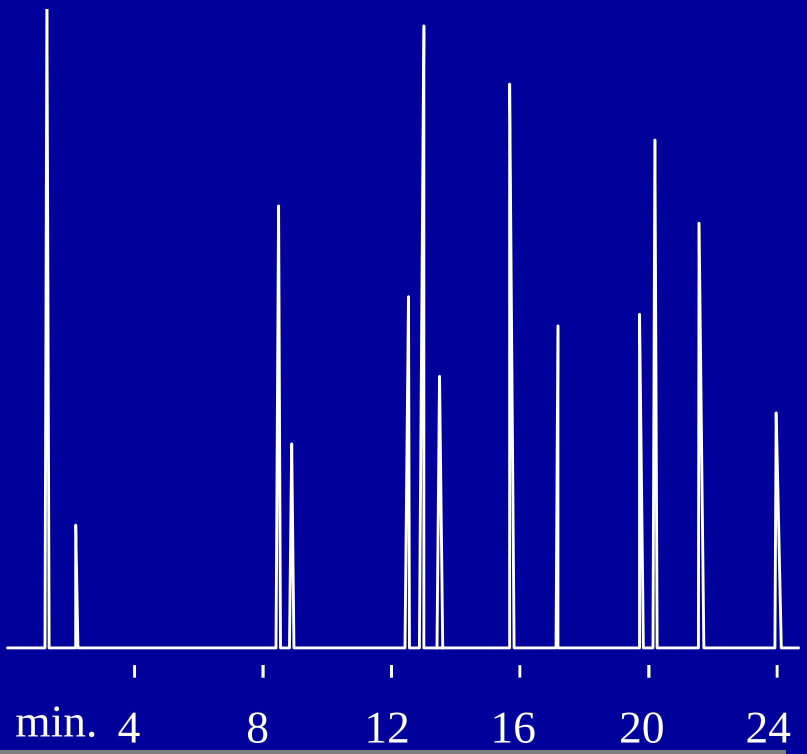
Effect of ID on Resolution and Analysis Time

- Smaller IDs
  - More resolution of early-eluting compounds
  - Longer analysis times
  - Limited dynamic range
- Larger IDs
  - Less resolution for early eluting compounds
  - Shorter analysis times
  - Greater dynamic range

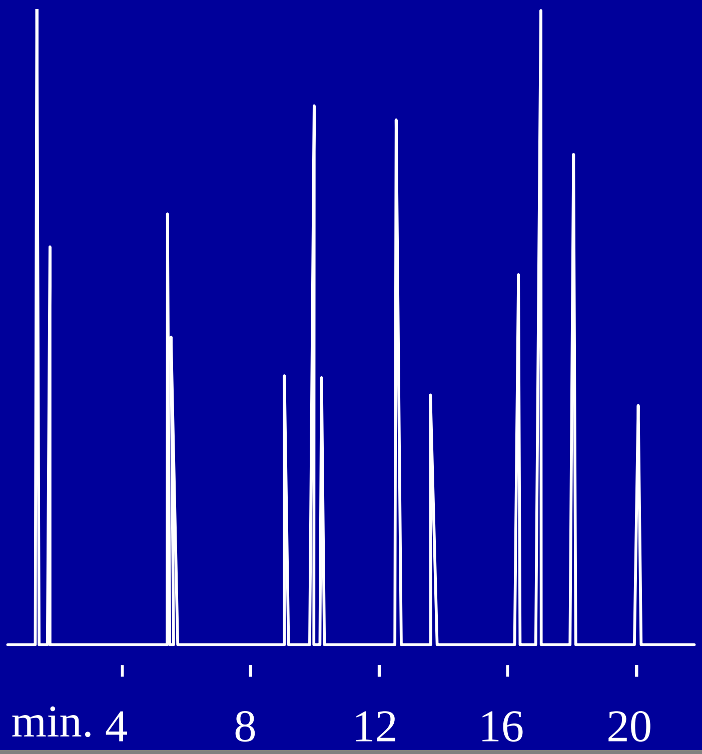
Effect of ID on Resolution and Analysis Time

Given the same d_f , a larger ID acts like a thinner film
(except that it will have more capacity than the smaller ID)

EPA 604
Phenols



Rtx-5: 30m, **0.25mm ID**, 0.25µm



Rtx-5: 30m, **0.53mm ID**, 0.25µm

Combining Film Thickness & ID Effects
Distribution Coefficient (K_D)

$$K_D = \frac{\text{wt. in liquid phase}}{\text{wt. in gas phase}} \text{ x } \frac{\text{volume of liquid phase}}{\text{volume of gas}} = k\beta$$

$$k \text{ (capacity factor)} = \frac{[t_R - t_M]}{t_M} = \frac{\text{time in stationary phase}}{\text{time in carrier gas}}$$

$$\beta \text{ (phase ratio)} = \frac{\text{radius}}{2d_f} = \frac{\text{radius}}{\text{2 x film thickness (cm)}}$$

RESTEK

Combining Film Thickness & ID Effects
β Values

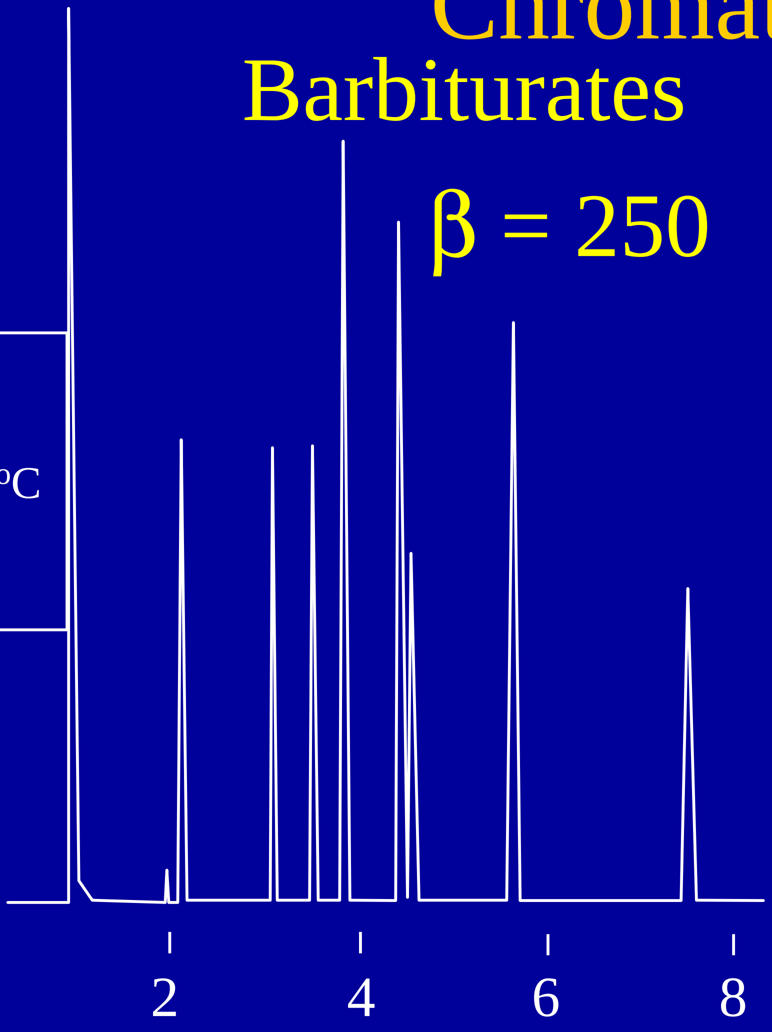
ID (mm)	Film (µm) 0.25	0.50	1.0	1.50	5.0
0.18	180	90	45	30	9
0.25	250	125	63	42	13
0.32	320	160	80	53	16
0.53	530	265	128	88	27

$$\beta = \text{phase ratio} = \frac{\text{radius}}{2d_f}$$

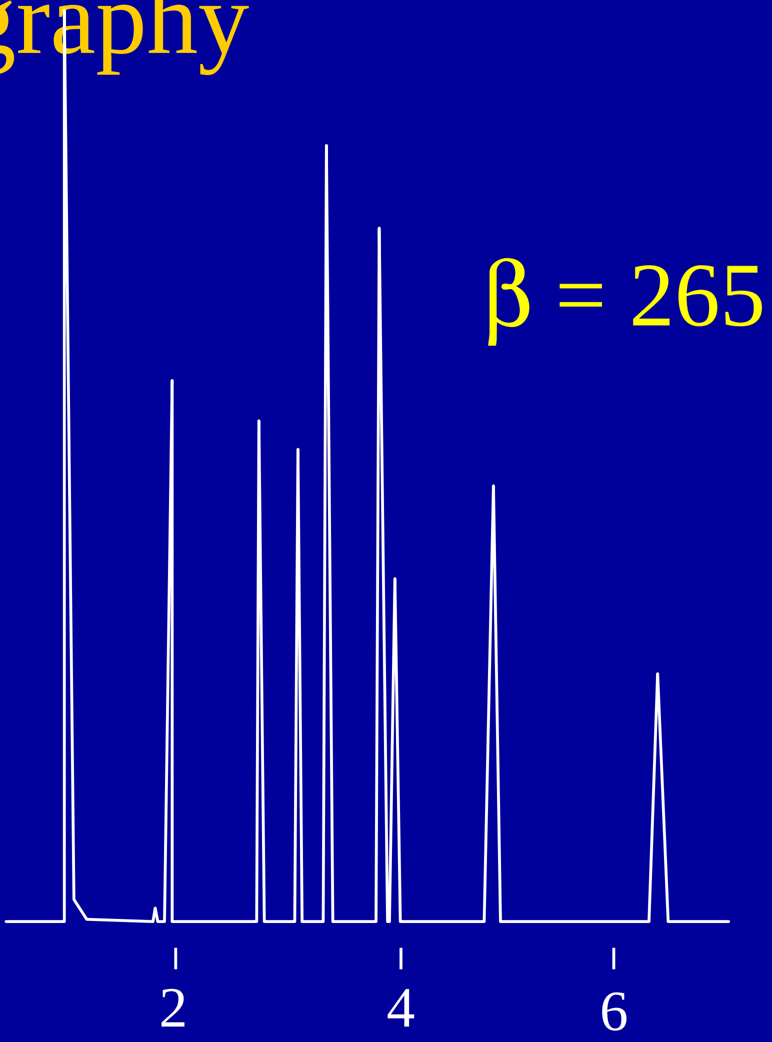
Combining Film Thickness & ID Effects

Similar β Values = Similar Chromatography

1.0µL split;
190°C (hold
5min.) to 280°C
@ 5°C/min.
(hold 15min.)



Rtx-5 : 30m, **0.25mm ID, 0.25µm**



Rtx-5 : 30m, **0.53mm ID, 0.5µm**

Column Length

- Effects on resolution
- Effects on Analysis Time

$$R = \frac{1}{4}\sqrt{\frac{L}{h}} \text{ X } \frac{k}{k+1} \text{ X } \frac{\alpha-1}{\alpha}$$

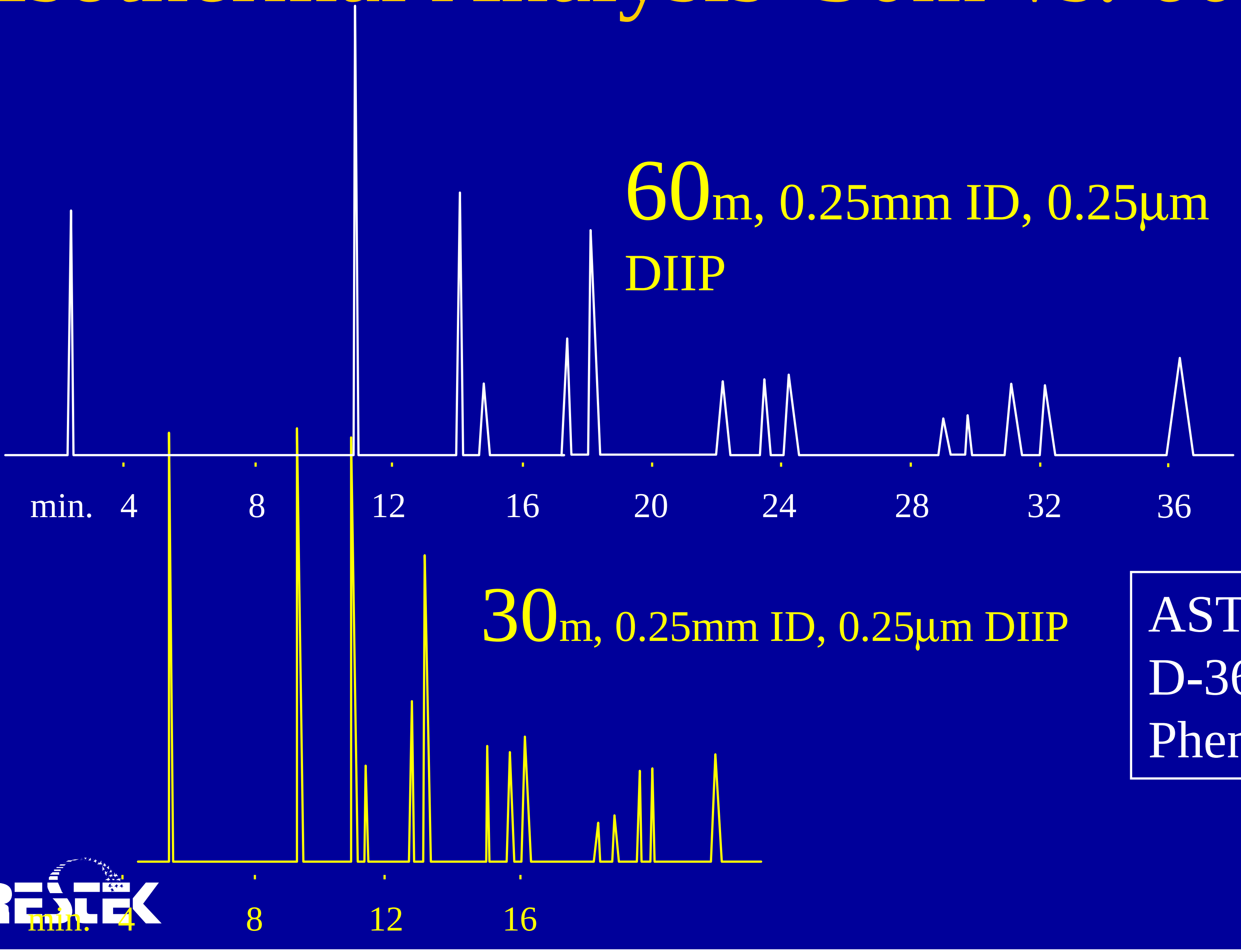
R = resolution
L = length
h = HETP
α = selectivity

Length Effects
Isothermal Conditions

- Retention is dependent on length
- Doubling column length doubles analysis times
- Doubling column length increases resolution by 41% (quadrupling L = doubling R)
- Is doubling the column length worth the extra analysis time?

Length Effects

Isothermal Analysis 30m vs. 60m



60m, 0.25mm ID, 0.25µm DIIP

30m, 0.25mm ID, 0.25µm DIIP

ASTM
D-3626
Phenols

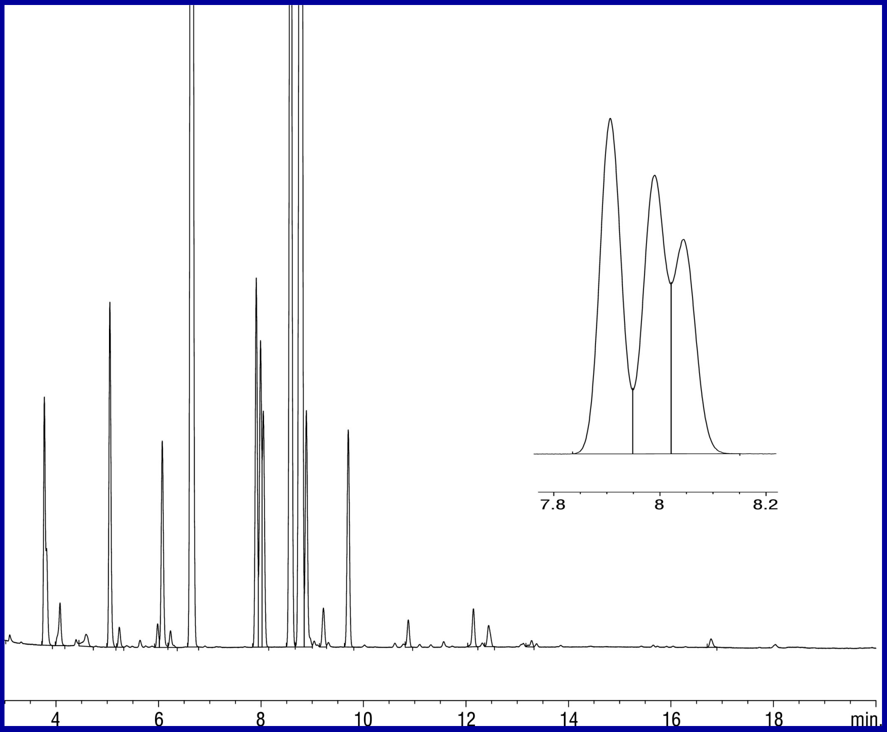
Length Effects
Temperature Programmed Conditions

- Retention more dependent upon temperature
- Doubling the length marginally increases analysis times
- Run conditions should be optimized

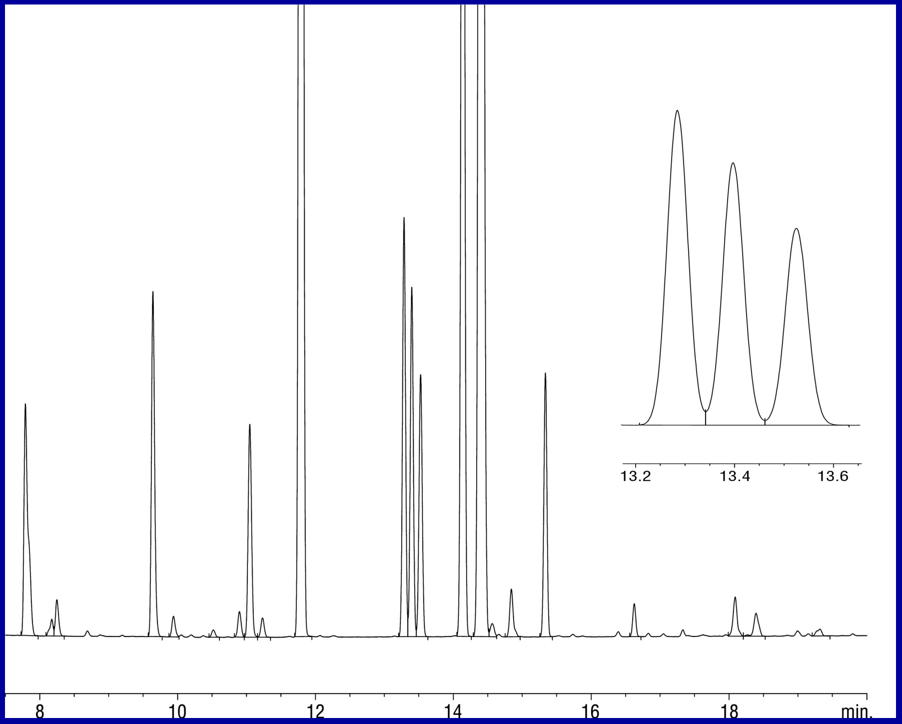
Length Effects

Temperature Programmed Analysis

Rtx-1, 30m x 0.25mm x 1µm



Rtx-1, 60m x 0.25mm x 1µm



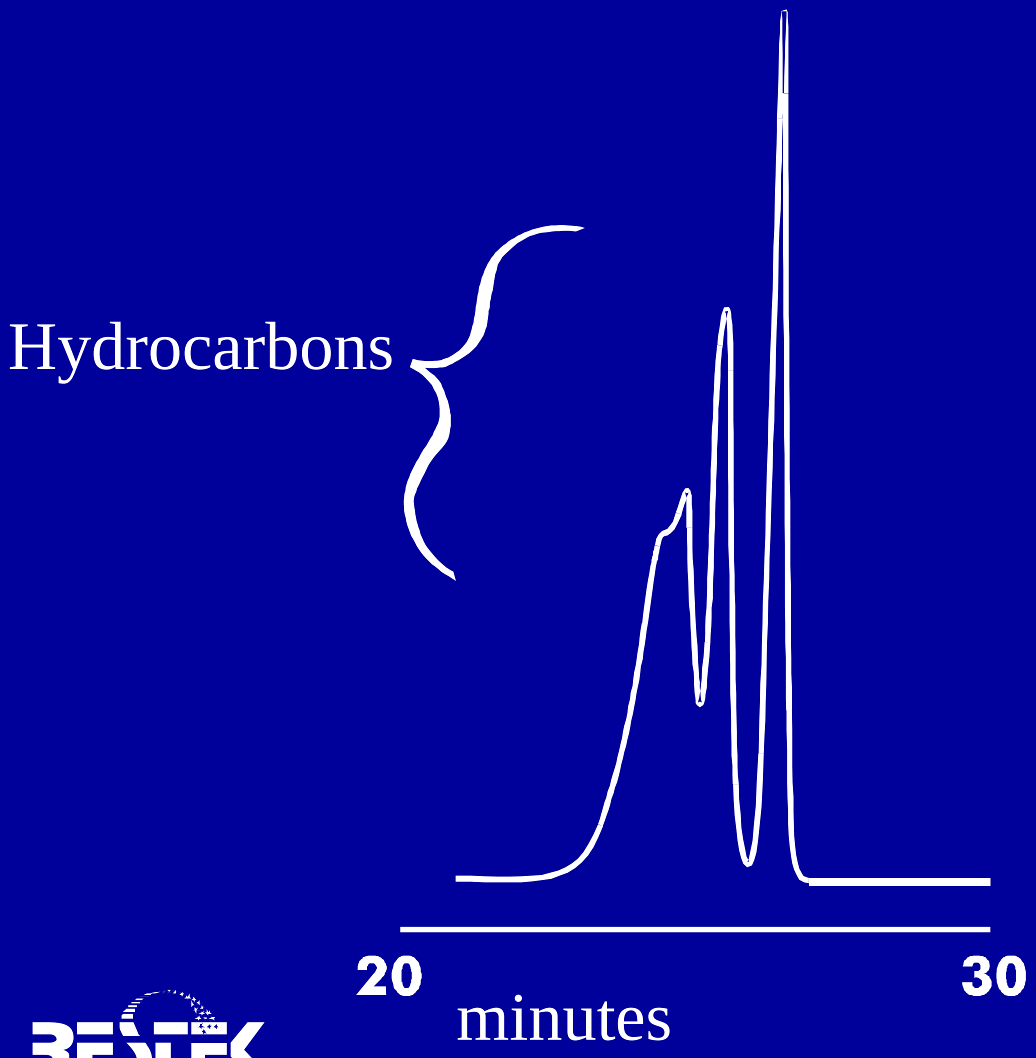
Sample: 500µg/mL Aviation Gas Standard in methanol

Capacity Issues

- Problems with Overload
- Effect of ID, Film Thickness, k’, & Solubilty

Column Capacity Effects

Overloading



Problems with:

Resolution

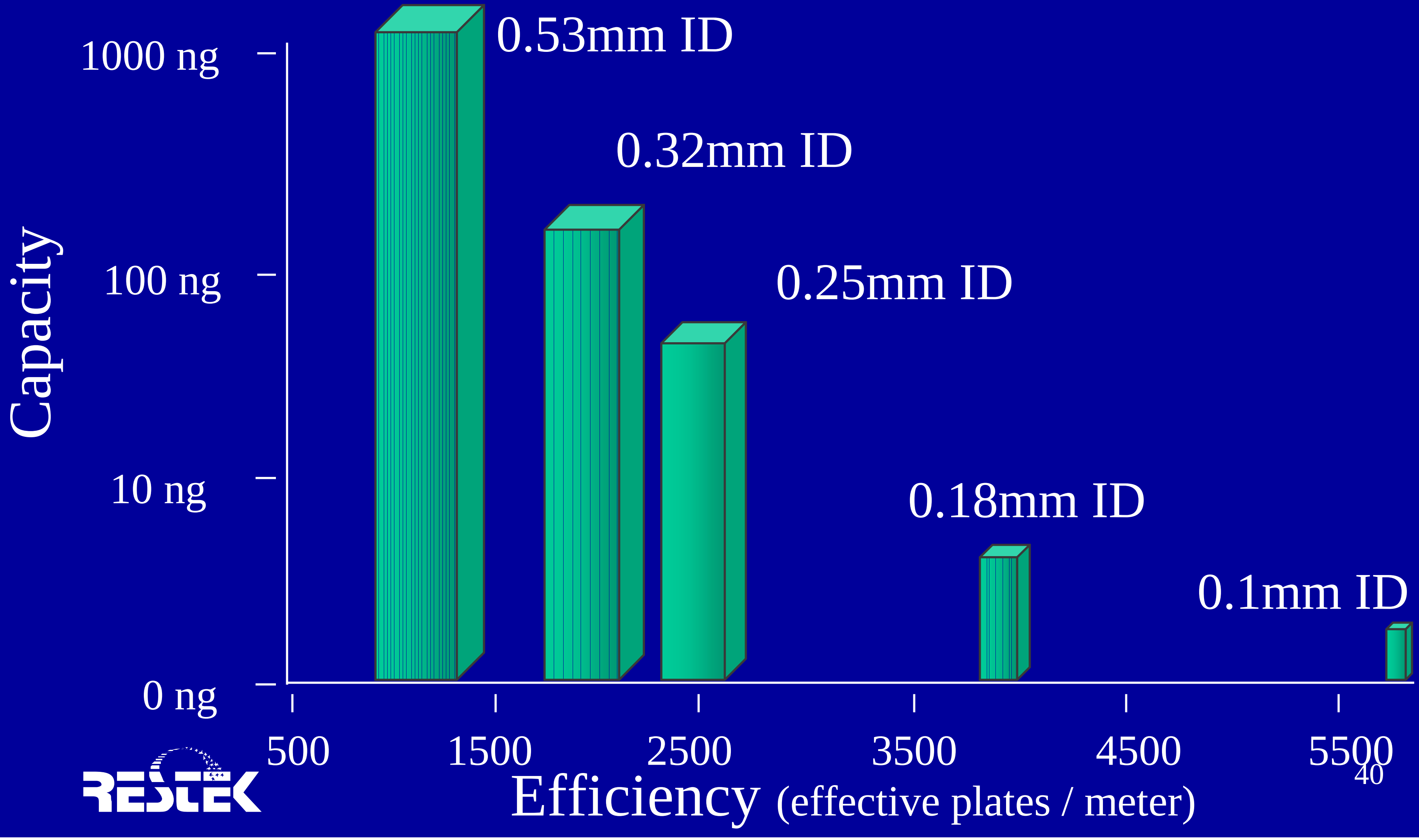
Integration

Retention Times

Linearity

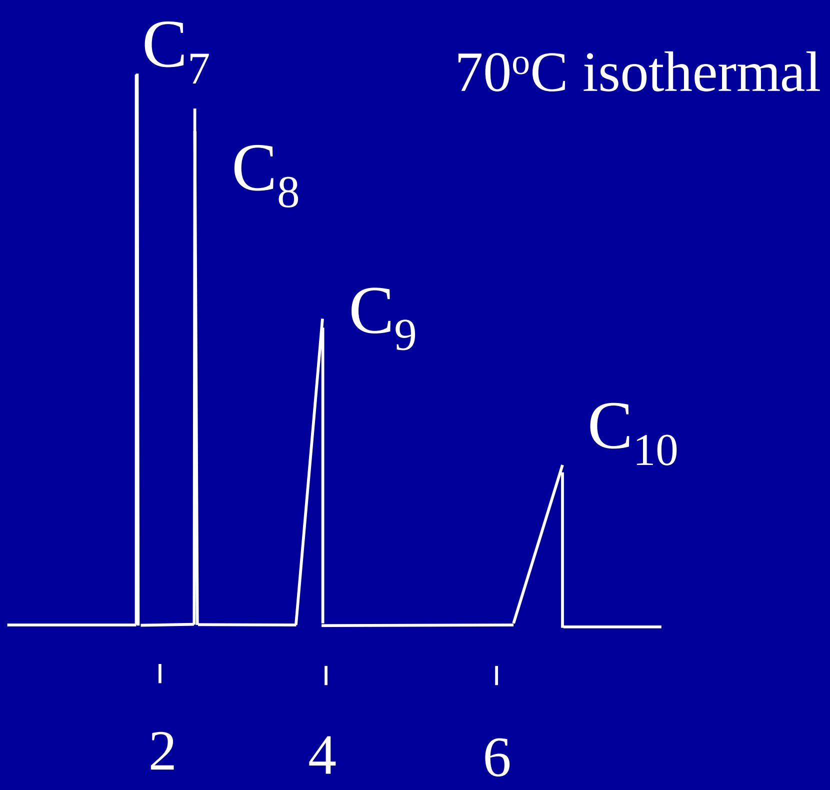
Column Selection

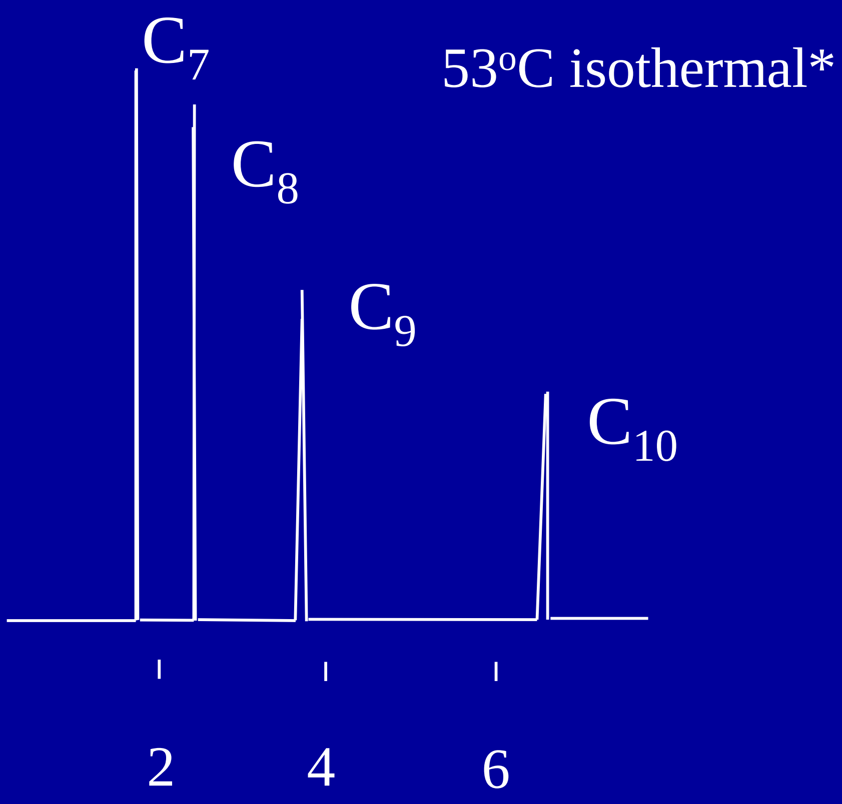
Typical Column Capacity vs. Efficiency



Effect of ID on Capacity

Rtx-1: 15m, 0.25mm ID, 0.25µm   15m, 0.53mm ID, 0.25µm



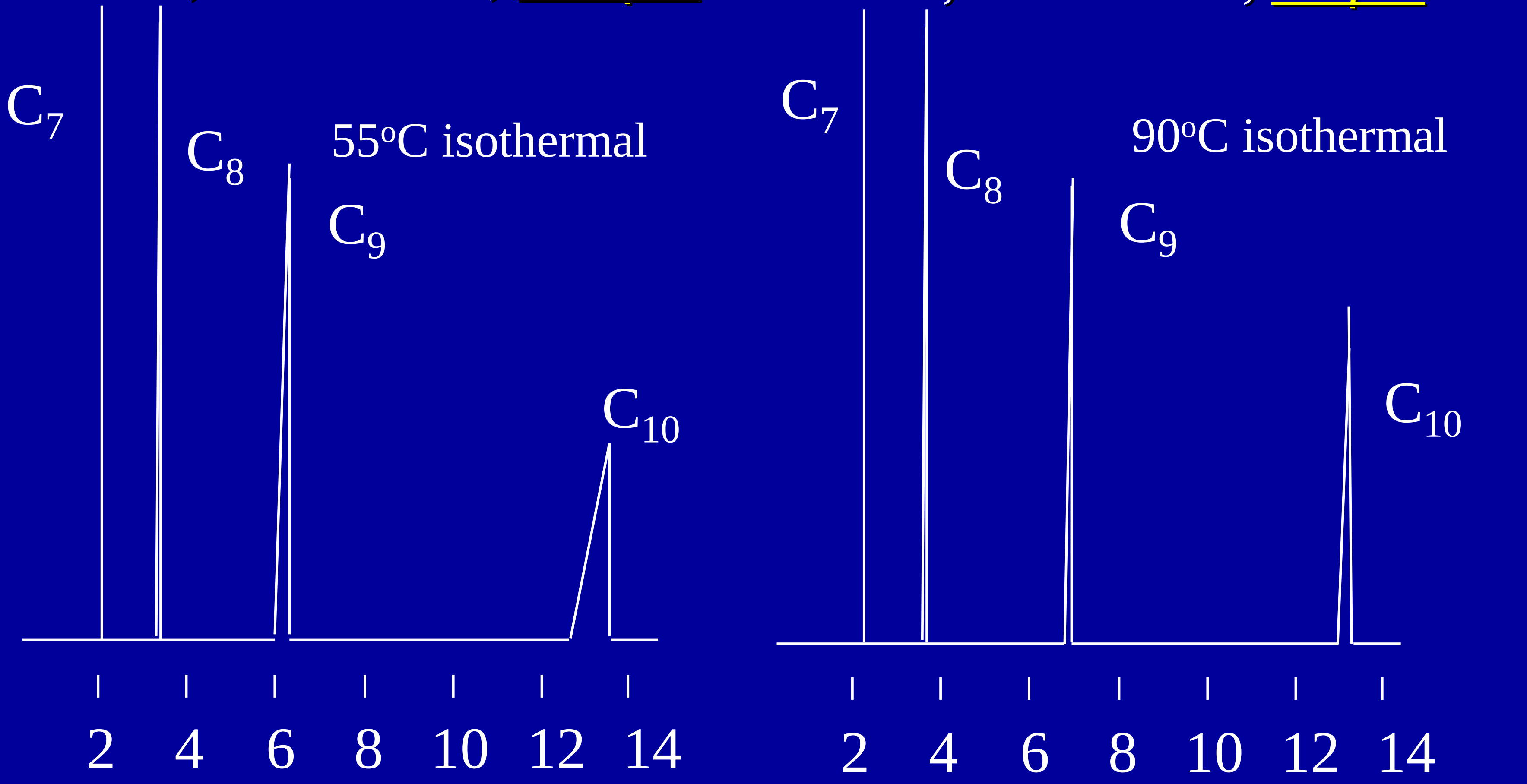


* run at different temperatures to keep k values similar

Effect of Film Thickness on Capacity

Rtx-1: 30m, 0.25mm ID, 0.25µm

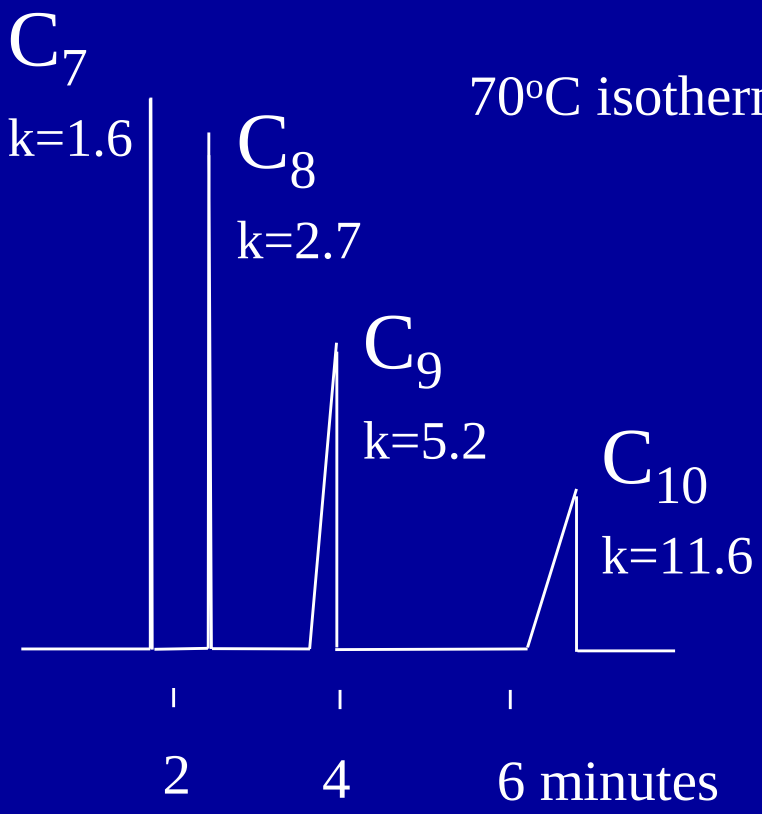
30m, 0.25mm ID, 1.0µm



* run at different temperatures to keep k values similar

Effect of k on Capacity

Rtx-1   15m, 0.25mm ID, 0.25µm



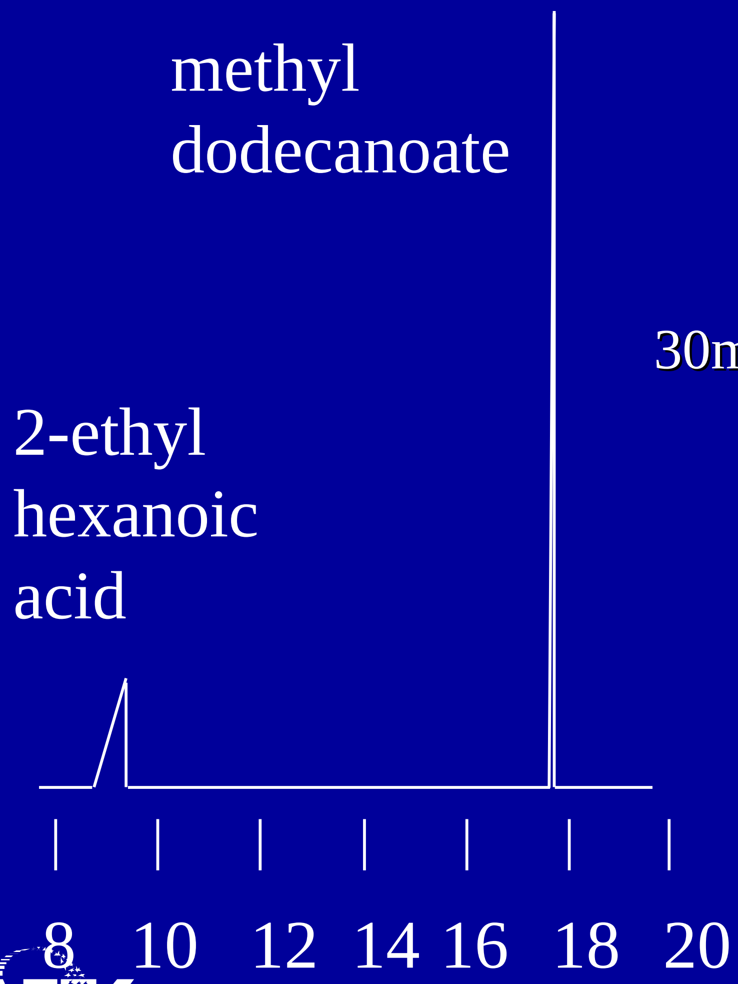
70°C isothermal

$$k = \frac{t'_R}{t_m}$$

1000ng/component

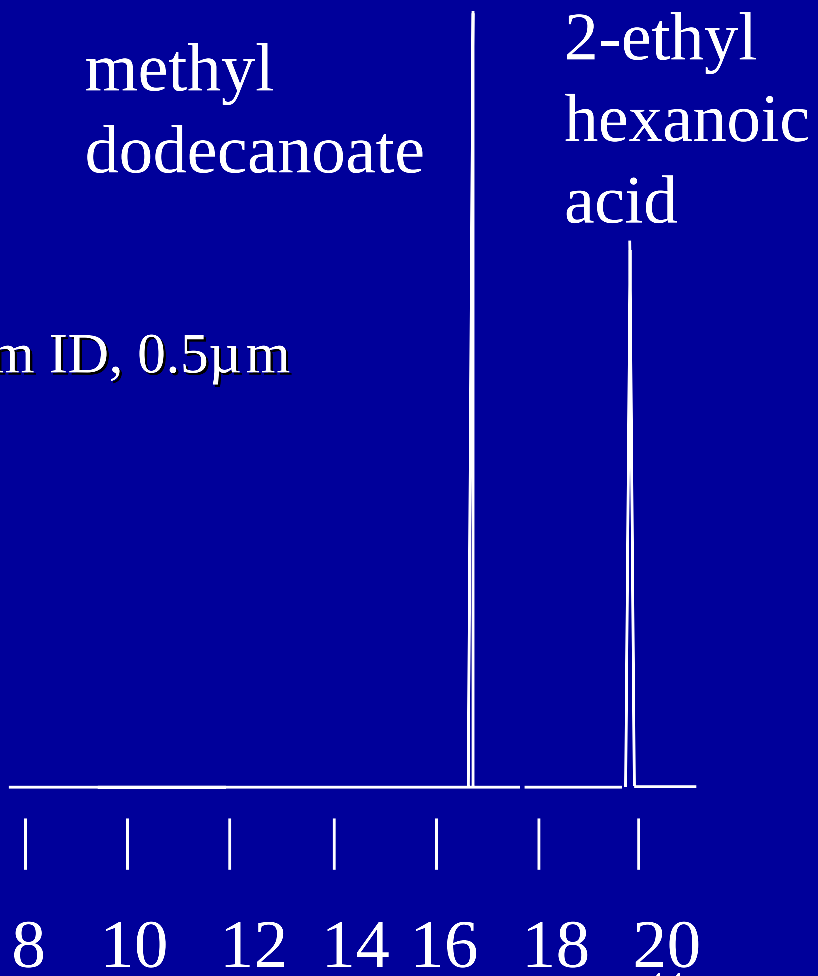
Effect of Solubility on Capacity

Rtx®-1



Stabilwax-DA

30m, 0.53mm ID, 0.5µm



Factors Affecting Separation

Temperature

Strongly affects amount of time analytes spend in stationary phase

$$k = \frac{\text{time spent in stationary phase}}{\text{time spent in the carrier gas}}$$

- The more time analytes spend in the stationary phase, the more retention differences are expressed
- Inversely,

higher temperature = less time in the phase
= less selectivity expression

$$t_R = \frac{L}{\bar{\mu}}(k+1)$$

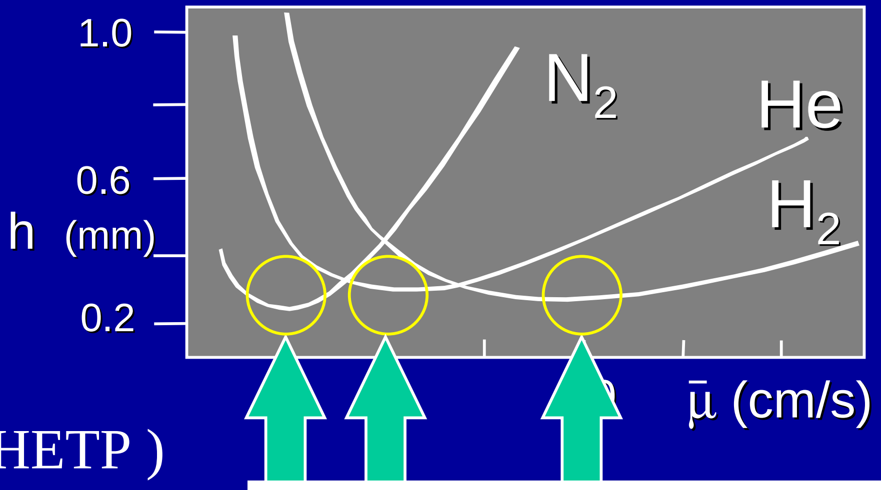
$$R = \frac{1}{4}\sqrt{\frac{L}{h}} \times \frac{k}{k+1} \times \frac{\alpha-1}{\alpha}$$

Factors Affecting Separation

Carrier Gas Type & Speed

van Deemter Equation

$$\boxed{h = \frac{B}{\bar{\mu}} + C_g \bar{\mu}}$$



$\bar{\mu}_{optimum}$ = 40cm/s H_2

h = height equivalent theoretical plate (HETP)

B = Band broadening

C_g = Resistence to mass transfer in the carrier gas

$\bar{\mu}$ = average linear velocity

$$R = \frac{1}{4} \sqrt{\frac{L}{h}} \times \frac{k}{k+1} \times \frac{\alpha - 1}{\alpha}$$

Column Selection Summary

- How selectivity affects resolution (R) and analysis time (T)
- How film thickness affects R & T
- How column ID affects R & T
- How column length affects R & T
- Column capacity