Research Proposal

0 . Abstract

1. **Introduction (with or without)**
2. **Specific aims (a few sentences: what do you want to do?)**
3. **Significance (one paragraph): How important is this research)**
4. **Background (what has been done?)**
5. **Proposed research (methods: how will you plan to do?)**
6. **Conclusions**

Length of the proposal: ~1800 words

Due dates:
The title is due on Mar. 23
(3 points)
The outline is due on Apr. 3
(3 points)
The draft is due on Apr. 15 (4 points)
The final proposal is due on Apr. 27 (40 points)

Gas Chromatography

1. Introduction

2. Stationary phases

3. Retention in Gas-Liquid Chromatography

4. Capillary gas-chromatography

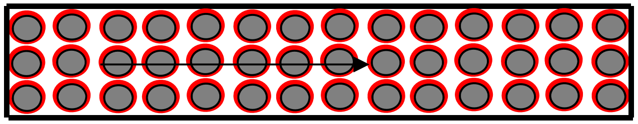
5. Sample preparation and injection

6. Detectors

(Chapter 2 and 3 in The essence of chromatography)

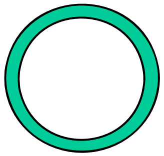
A. Types of Columns in GC

1. Packed-bed column (d > 2 mm, packing particle from 100 to 250 micron)



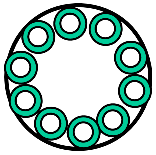
2. Micro-packed column (d < 1 mm, d_p/d_c less than 0.3)

3. Packed capillary column (d < 0.6 mm, packing particle 5-20 micron)

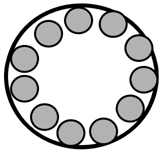


4. Wall coated open tubular columns (WCOT)
Thin layer of stationary phase coated directly on the wall of the tube.

5. Support coated open tubular (SCOT)
Liquid phase + glass powder or particle support



6. Porous layer open tubular column (PLOT)
Particle support

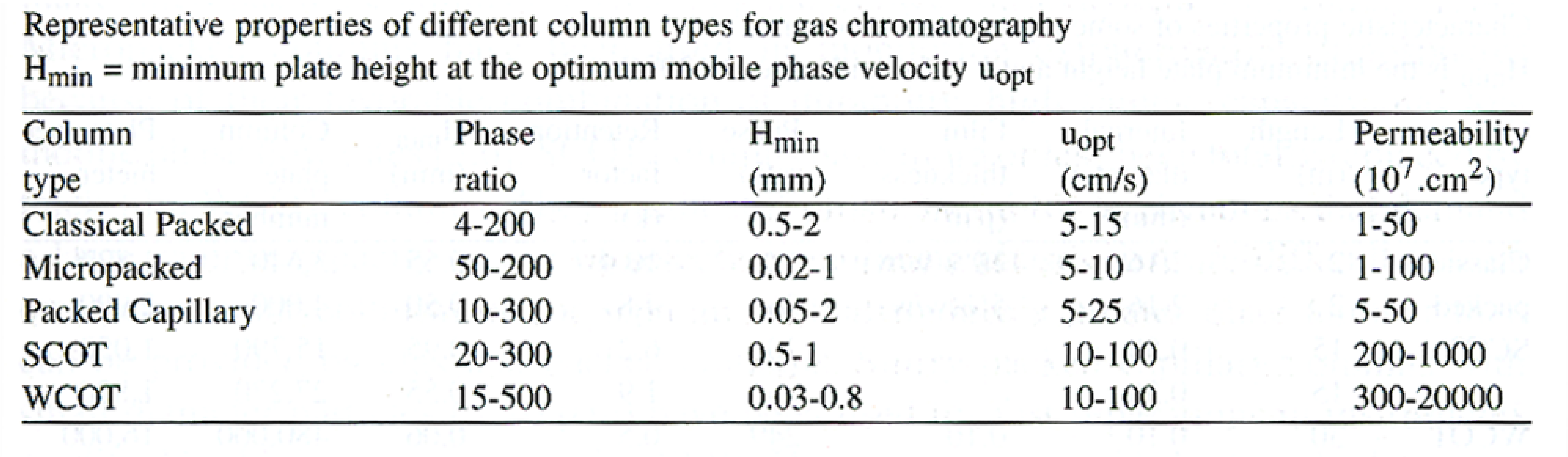


Gas-liquid Chromatography: Classical packed column, and WCOT

Partition mechanism

Gas-Solid Chromatography: Classical packed column, and PLOT

Adsorption mechanism



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

Question. **In a WCOT GC, two component, each with plate height H = 0.0064 cm, are observed have a resolution of 0.5 when the length of column is 1 m. How long should the column to be achieve baseline resolution?**

B. Stationary phase in Gas-liquid Chromatography

1. General Considerations for liquid stationary phase materials:

a. un-reactive with carrier gas and solutes

b. low vapor pressure

c. good coating characteristics (i.e. wet the materials used in the column fabrication)

d. Have reasonable solubility in some common volatile organic solvent.

e. Wide temperature operating range.
The low limit: melting point, or glass point for polymers
The maximum temperature is determined by thermal stability and vapor pressure. In practice, the higher T is that can be maintained without breakup of the liquid film into droplets.

2. Types of liquid stationary phases

a. Hydrocarbon and Perfluorocarbon stationary phases (non-polar)

Squalane ($C_{30}H_{62}$); Apiezon; Apolane-87 ($C_{87}H_{167}$)

b. Ether and ester stationary phases

Poly-ethers (e.g., poly-phenyl ethers), phthalate esters

c. Liquid organic-salts stationary phases

Alkylammonium or alkylphosphonium
with nucleophilic anions (such as BF_4^-)

d. poly(siloxane) stationary phases

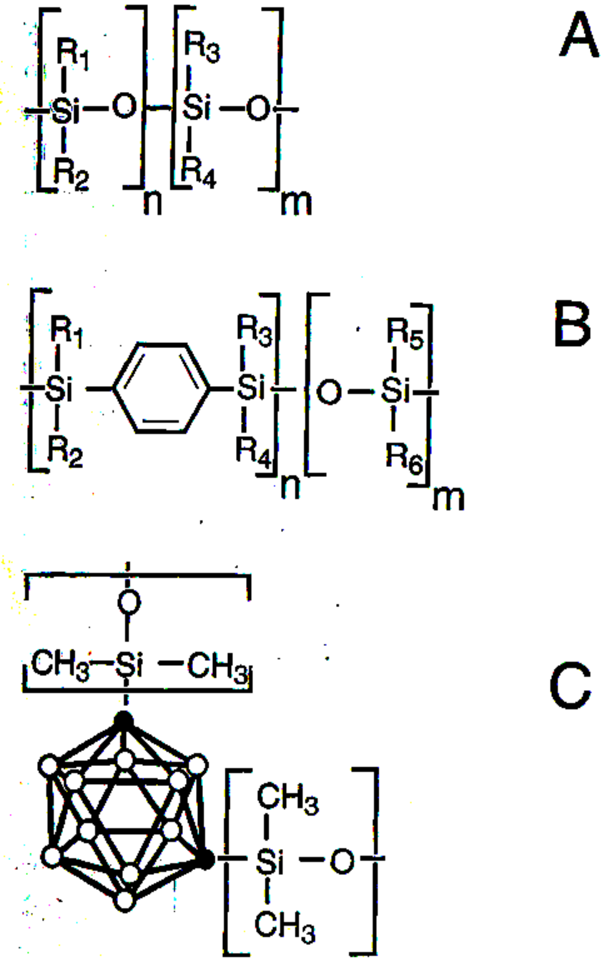


Figure 2.2. General structures of poly(siloxane) liquid phases. A, poly(siloxane) polymer; B, poly(silarylene-siloxane) copolymer; and C, a poly(carborane-siloxane) copolymer (● = carbon and ○ = BH).

Table 2.4

Characteristic properties of some poly(siloxane) liquid phases used for packed column gas chromatography

Name	Structure	Viscosity (cP)	Average molecular weight	Temperature operating range (°C) Minimum	Maximum
OV-1	Dimethylsiloxane	gum	$> 10^6$	100	350
OV-101	Dimethylsiloxane	1500	30,000	<20	350
OV-7	Phenylmethyldimethylsiloxane 80 % methyl and 20 % phenyl	500	10,000	<20	350
OV-17	Phenylmethylsiloxane 50 % methyl and 50 % phenyl	1300	40,000	<20	350
OV-25	Phenylmethyldiphenylsiloxane 25 % methyl and 75 % phenyl	>100,000	10,000	<20	300
OV-210	Trifluoropropylmethylsiloxane 50 % methyl and 50 % 3,3,3-trifluoropropyl	10,000	200,000	<20	275
OV-225	Cyanopropylmethylphenylmethylsiloxane 50 % methyl, 25 % phenyl and 25 % 3-cyanopropyl	9000	8,000	<20	250
Silar 7CP	Cyanopropylphenylsiloxane 75 % 3-cyanopropyl and 25 % phenyl			50	250
OV-275	Di(cyanoalkyl)siloxane 70 % 3-cyanopropyl and 30 % 2-cyanoethyl	20,000	5,000		250
Silar 10CP	Di(3-Cyanopropyl)siloxane			50	250

State of the art GC performance

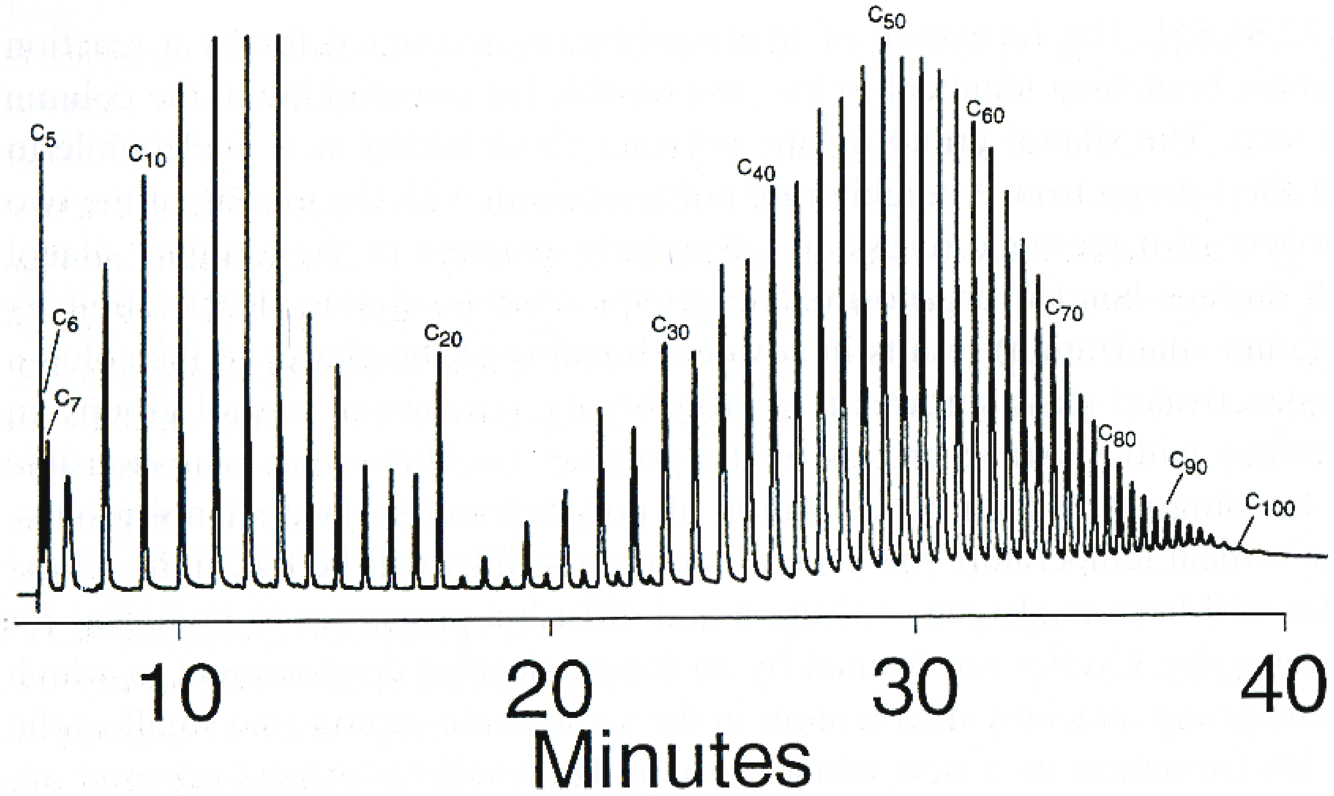


Figure 2.3. Separation of polywax 655 by high temperature gas chromatography on a 6 m x 0.53 mm I. D. open tubular column coated with a 0.1 µm film of a poly(carborane-siloxane) copolymer (equivalent to 5 % phenyl). Initial column temperature -20°C for 1 min, programmed at 10°C/min to 430°C, and final hold 5 min at 430°C. The helium carrier gas flow rate was 20 ml/min. (©SGE, Inc.)

3. How to choose liquid stationary phases.

$$\log k = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\,\Sigma\,\beta_2^H + l\log L^{16}$$ (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.

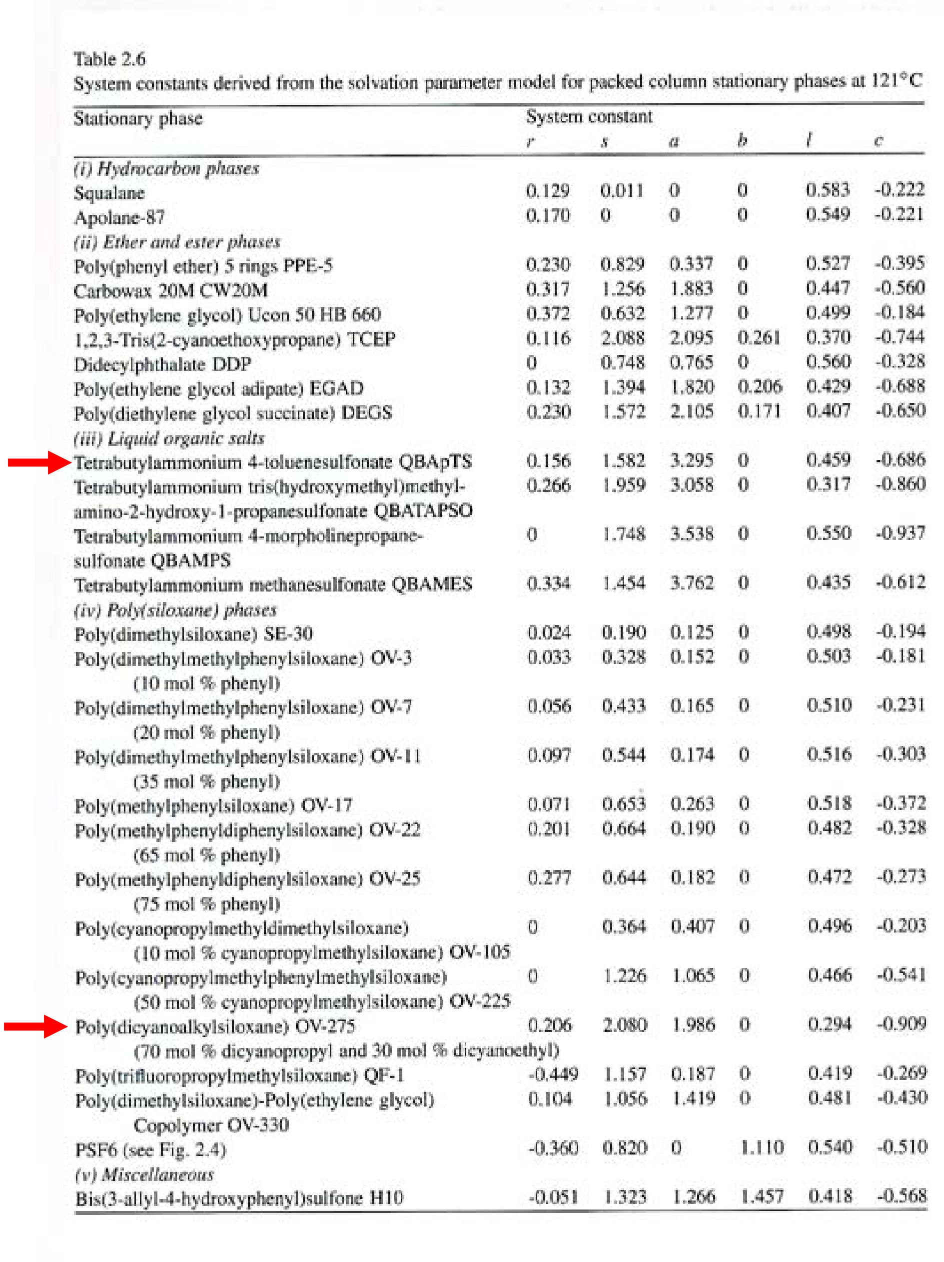
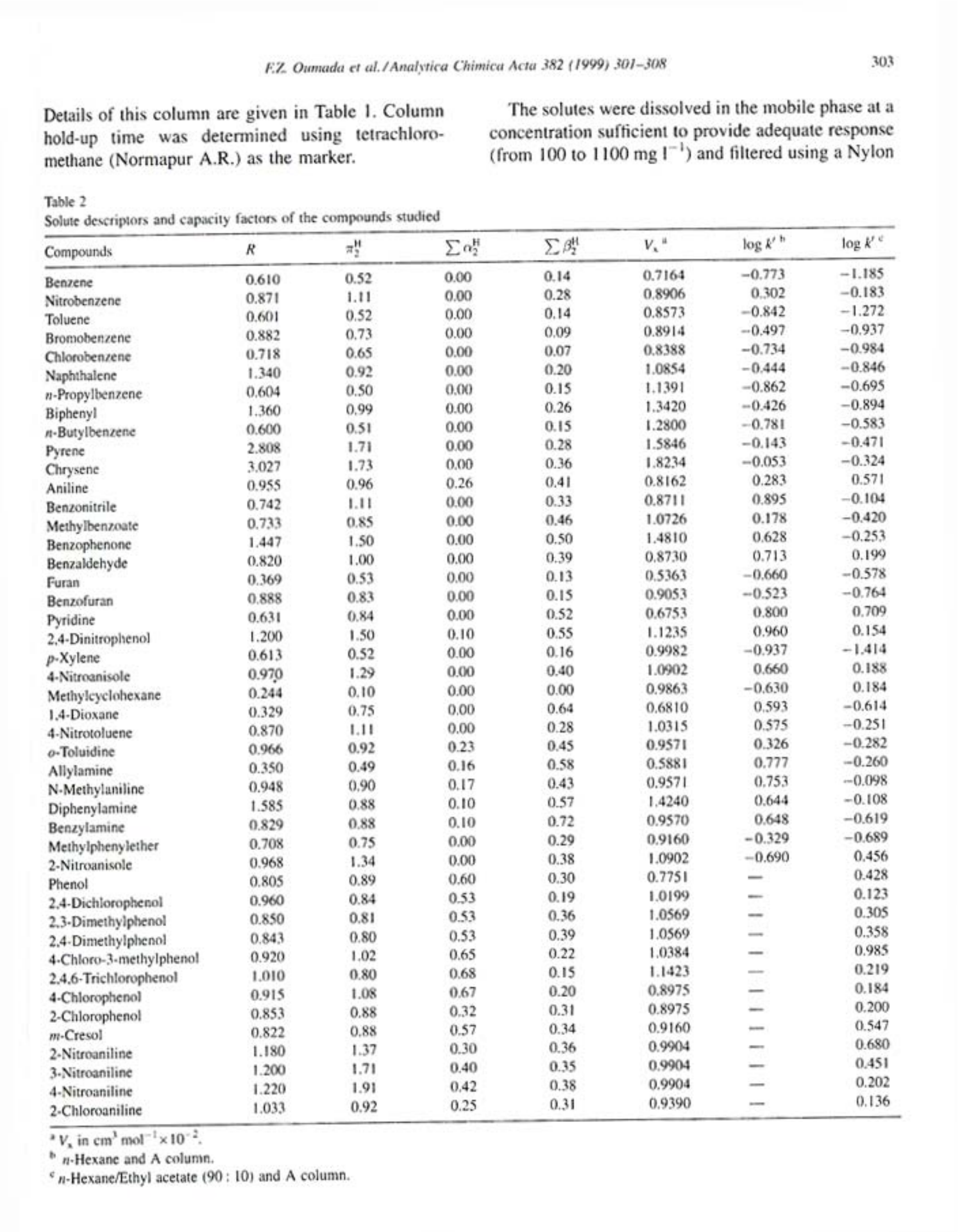


Table 2.6
System constants derived from the solvation parameter model for packed column stationary phases at 121°C

Stationary phase	System constant *r*	*s*	*a*	*b*	*l*	*c*
(i) Hydrocarbon phases						
Squalane	0.129	0.011	0	0	0.583	-0.222
Apolane-87	0.170	0	0	0	0.549	-0.221
(ii) Ether and ester phases						
Poly(phenyl ether) 5 rings PPE-5	0.230	0.829	0.337	0	0.527	-0.395
Carbowax 20M CW20M	0.317	1.256	1.883	0	0.447	-0.560
Poly(ethylene glycol) Ucon 50 HB 660	0.372	0.632	1.277	0	0.499	-0.184
1,2,3-Tris(2-cyanoethoxypropane) TCEP	0.116	2.088	2.095	0.261	0.370	-0.744
Didecylphthalate DDP	0	0.748	0.765	0	0.560	-0.328
Poly(ethylene glycol adipate) EGAD	0.132	1.394	1.820	0.206	0.429	-0.688
Poly(diethylene glycol succinate) DEGS	0.230	1.572	2.105	0.171	0.407	-0.650
(iii) Liquid organic salts						
Tetrabutylammonium 4-toluenesulfonate QBApTS	0.156	1.582	3.295	0	0.459	-0.686
Tetrabutylammonium tris(hydroxymethyl)methyl-amino-2-hydroxy-1-propanesulfonate QBATAPSO	0.266	1.959	3.058	0	0.317	-0.860
Tetrabutylammonium 4-morpholinepropane-sulfonate QBAMPS	0	1.748	3.538	0	0.550	-0.937
Tetrabutylammonium methanesulfonate QBAMES	0.334	1.454	3.762	0	0.435	-0.612
(iv) Poly(siloxane) phases						
Poly(dimethylsiloxane) SE-30	0.024	0.190	0.125	0	0.498	-0.194
Poly(dimethylmethylphenylsiloxane) OV-3 (10 mol % phenyl)	0.033	0.328	0.152	0	0.503	-0.181
Poly(dimethylmethylphenylsiloxane) OV-7 (20 mol % phenyl)	0.056	0.433	0.165	0	0.510	-0.231
Poly(dimethylmethylphenylsiloxane) OV-11 (35 mol % phenyl)	0.097	0.544	0.174	0	0.516	-0.303
Poly(methylphenylsiloxane) OV-17	0.071	0.653	0.263	0	0.518	-0.372
Poly(methylphenyldiphenylsiloxane) OV-22 (65 mol % phenyl)	0.201	0.664	0.190	0	0.482	-0.328
Poly(methylphenyldiphenylsiloxane) OV-25 (75 mol % phenyl)	0.277	0.644	0.182	0	0.472	-0.273
Poly(cyanopropylmethyldimethylsiloxane) (10 mol % cyanopropylmethylsiloxane) OV-105	0	0.364	0.407	0	0.496	-0.203
Poly(cyanopropylmethylphenylmethylsiloxane) (50 mol % cyanopropylmethylsiloxane) OV-225	0	1.226	1.065	0	0.466	-0.541
Poly(dicyanoalkylsiloxane) OV-275 (70 mol % dicyanopropyl and 30 mol % dicyanoethyl)	0.206	2.080	1.986	0	0.294	-0.909
Poly(trifluoropropylmethylsiloxane) QF-1	-0.449	1.157	0.187	0	0.419	-0.269
Poly(dimethylsiloxane)-Poly(ethylene glycol) Copolymer OV-330	0.104	1.056	1.419	0	0.481	-0.430
PSF6 (see Fig. 2.4)	-0.360	0.820	0	1.110	0.540	-0.510
(v) Miscellaneous						
Bis(3-allyl-4-hydroxyphenyl)sulfone H10	-0.051	1.323	1.266	1.457	0.418	-0.568

Systems



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Details of this column are given in Table 1. Column hold-up time was determined using tetrachloromethane (Normapur A.R.) as the marker.

The solutes were dissolved in the mobile phase at a concentration sufficient to provide adequate response (from 100 to 1100 mg l^{-1}) and filtered using a Nylon

Table 2
Solute descriptors and capacity factors of the compounds studied

Compounds	*R*	π_2^H	$\sum \alpha_2^H$	$\sum \beta_2^H$	V_x [a]	log *k'* [b]	log *k'* [c]
Benzene	0.610	0.52	0.00	0.14	0.7164	−0.773	−1.185
Nitrobenzene	0.871	1.11	0.00	0.28	0.8906	0.302	−0.183
Toluene	0.601	0.52	0.00	0.14	0.8573	−0.842	−1.272
Bromobenzene	0.882	0.73	0.00	0.09	0.8914	−0.497	−0.937
Chlorobenzene	0.718	0.65	0.00	0.07	0.8388	−0.734	−0.984
Naphthalene	1.340	0.92	0.00	0.20	1.0854	−0.444	−0.846
n-Propylbenzene	0.604	0.50	0.00	0.15	1.1391	−0.862	−0.695
Biphenyl	1.360	0.99	0.00	0.26	1.3420	−0.426	−0.894
n-Butylbenzene	0.600	0.51	0.00	0.15	1.2800	−0.781	−0.583
Pyrene	2.808	1.71	0.00	0.28	1.5846	−0.143	−0.471
Chrysene	3.027	1.73	0.00	0.36	1.8234	−0.053	−0.324
Aniline	0.955	0.96	0.26	0.41	0.8162	0.283	0.571
Benzonitrile	0.742	1.11	0.00	0.33	0.8711	0.895	−0.104
Methylbenzoate	0.733	0.85	0.00	0.46	1.0726	0.178	−0.420
Benzophenone	1.447	1.50	0.00	0.50	1.4810	0.628	−0.253
Benzaldehyde	0.820	1.00	0.00	0.39	0.8730	0.713	0.199
Furan	0.369	0.53	0.00	0.13	0.5363	−0.660	−0.578
Benzofuran	0.888	0.83	0.00	0.15	0.9053	−0.523	−0.764
Pyridine	0.631	0.84	0.00	0.52	0.6753	0.800	0.709
2,4-Dinitrophenol	1.200	1.50	0.10	0.55	1.1235	0.960	0.154
p-Xylene	0.613	0.52	0.00	0.16	0.9982	−0.937	−1.414
4-Nitroanisole	0.970	1.29	0.00	0.40	1.0902	0.660	0.188
Methylcyclohexane	0.244	0.10	0.00	0.00	0.9863	−0.630	0.184
1,4-Dioxane	0.329	0.75	0.00	0.64	0.6810	0.593	−0.614
4-Nitrotoluene	0.870	1.11	0.00	0.28	1.0315	0.575	−0.251
o-Toluidine	0.966	0.92	0.23	0.45	0.9571	0.326	−0.282
Allylamine	0.350	0.49	0.16	0.58	0.5881	0.777	−0.260
N-Methylaniline	0.948	0.90	0.17	0.43	0.9571	0.753	−0.098
Diphenylamine	1.585	0.88	0.10	0.57	1.4240	0.644	−0.108
Benzylamine	0.829	0.88	0.10	0.72	0.9570	0.648	−0.619
Methylphenylether	0.708	0.75	0.00	0.29	0.9160	−0.329	−0.689
2-Nitroanisole	0.968	1.34	0.00	0.38	1.0902	−0.690	0.456
Phenol	0.805	0.89	0.60	0.30	0.7751	—	0.428
2,4-Dichlorophenol	0.960	0.84	0.53	0.19	1.0199	—	0.123
2,3-Dimethylphenol	0.850	0.81	0.53	0.36	1.0569	—	0.305
2,4-Dimethylphenol	0.843	0.80	0.53	0.39	1.0569	—	0.358
4-Chloro-3-methylphenol	0.920	1.02	0.65	0.22	1.0384	—	0.985
2,4,6-Trichlorophenol	1.010	0.80	0.68	0.15	1.1423	—	0.219
4-Chlorophenol	0.915	1.08	0.67	0.20	0.8975	—	0.184
2-Chlorophenol	0.853	0.88	0.32	0.31	0.8975	—	0.200
m-Cresol	0.822	0.88	0.57	0.34	0.9160	—	0.547
2-Nitroaniline	1.180	1.37	0.30	0.36	0.9904	—	0.680
3-Nitroaniline	1.200	1.71	0.40	0.35	0.9904	—	0.451
4-Nitroaniline	1.220	1.91	0.42	0.38	0.9904	—	0.202
2-Chloroaniline	1.033	0.92	0.25	0.31	0.9390	—	0.136

[a] V_x in $cm^3\ mol^{-1} \times 10^{-2}$.
[b] *n*-Hexane and A column.
[c] *n*-Hexane/Ethyl acetate (90 : 10) and A column.

Solutes

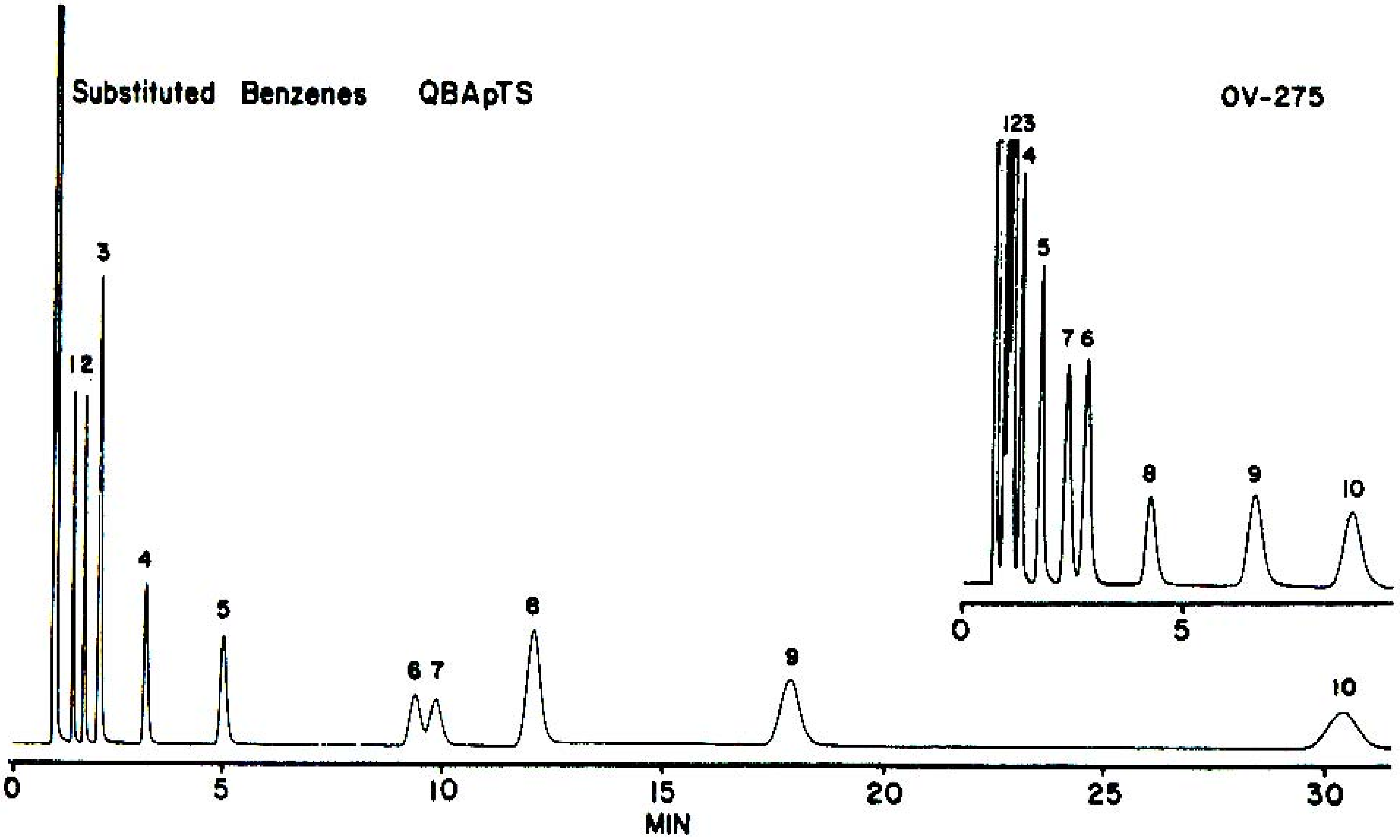
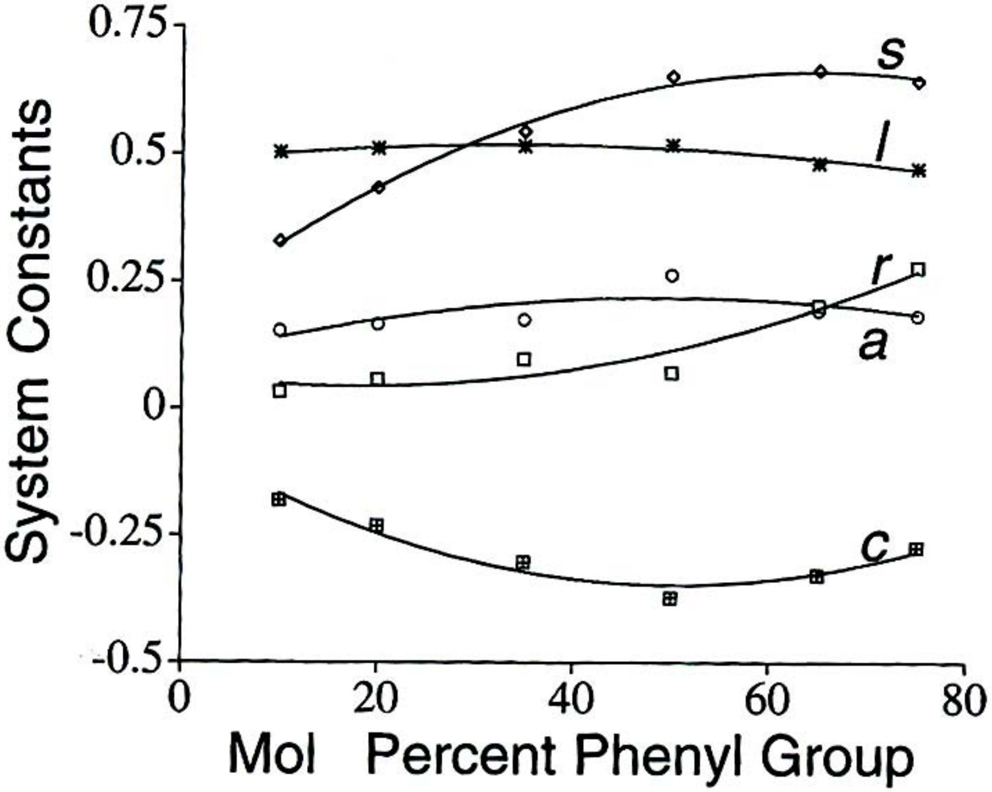


Figure 2.5. Separation of a mixture of polar compounds on matched packed columns coated with tetrabutylammonium 4-toluenesulfonate (QBApTS) and OV-275. Each column was 3.5 m x 2 mm I.D. containing 10% (w/w) of stationary phase on Chromosorb W-AW (100-120 mesh) with a carrier gas flow rate of 15 ml/min and column temperature 140°C. Peak assignments: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = chlorobenzene; 5 = bromobenzene; 6 = iodobenzene; 7 = 1,2-dichlorobenzene; 8 = benzaldehyde; 9 = acetophenone; and 10 = nitrobenzene.

Effects on system constants



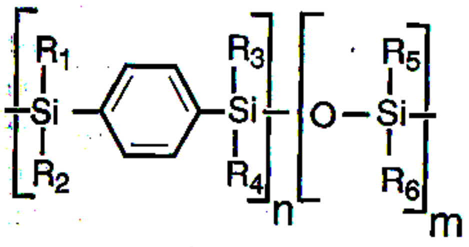


Figure 2.6. Plot of the system constants against the mol % phenyl composition for a series of poly(methylphenylsiloxane) and poly(methylphenyldiphenylsiloxane) phases.

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

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

Temperature Effects

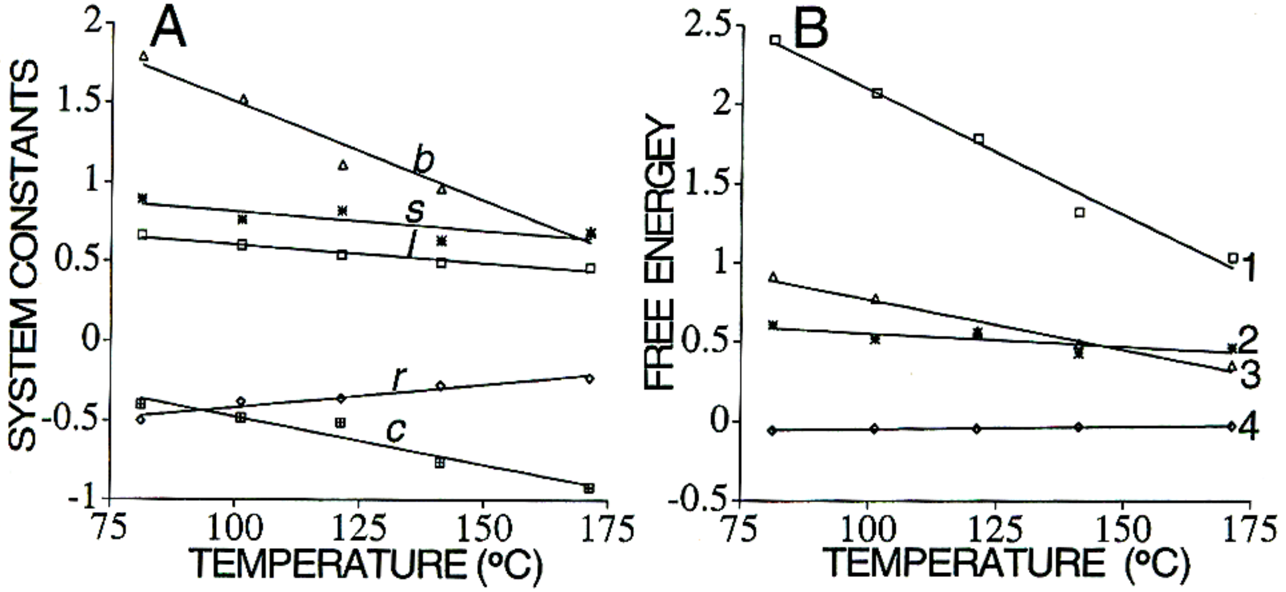


Figure 2.9. Influence of temperature on the system constants (A) and contributions of individual intermolecular interactions to the retention of octan-2-one (B) for the hydrogen-bond acid stationary phase PSF6. For (B) 1 = contribution from cavity formation and dispersion interactions; (2) contribution from dipole-type interactions; (3) contribution from solute hydrogen-bond base and stationary phase hydrogen-bond acid interactions; and (4) contribution from lone pair electron repulsion. Note for PSF6 there are no contributions from stationary phase hydrogen-bond base interactions since the *a* system constant is zero. (From ref. [81]; ©Elsevier)

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

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

C. Solid stationary phases in Gas-solid chromatography

G-S chromatography has a narrow range applications

Such as separation of volatile hydrocarbons and halocarbons solvents, sulfur gases.

Advantages: high stability.

Disadvantages: low capacity factor, irreversible-adsorption.

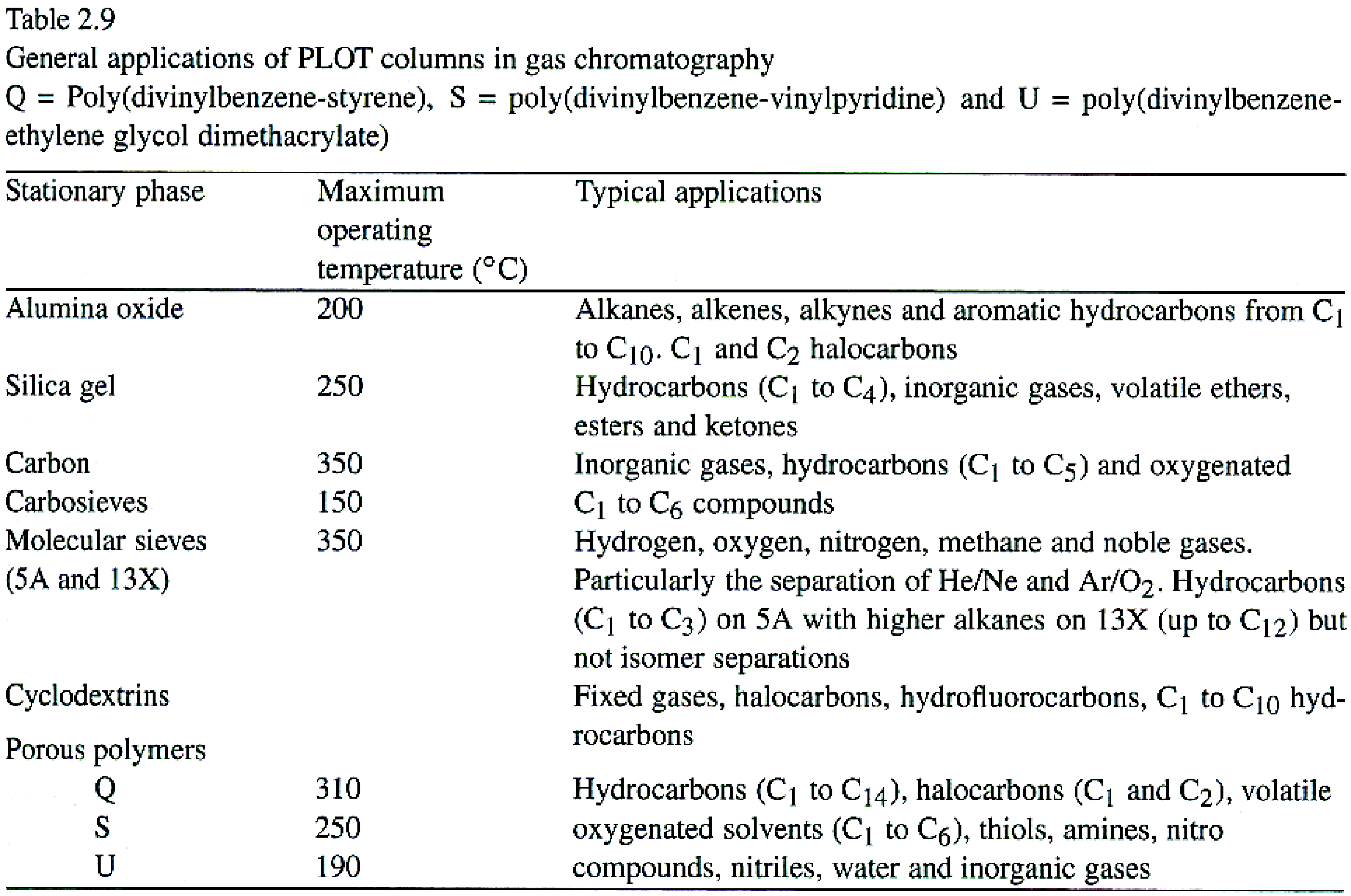
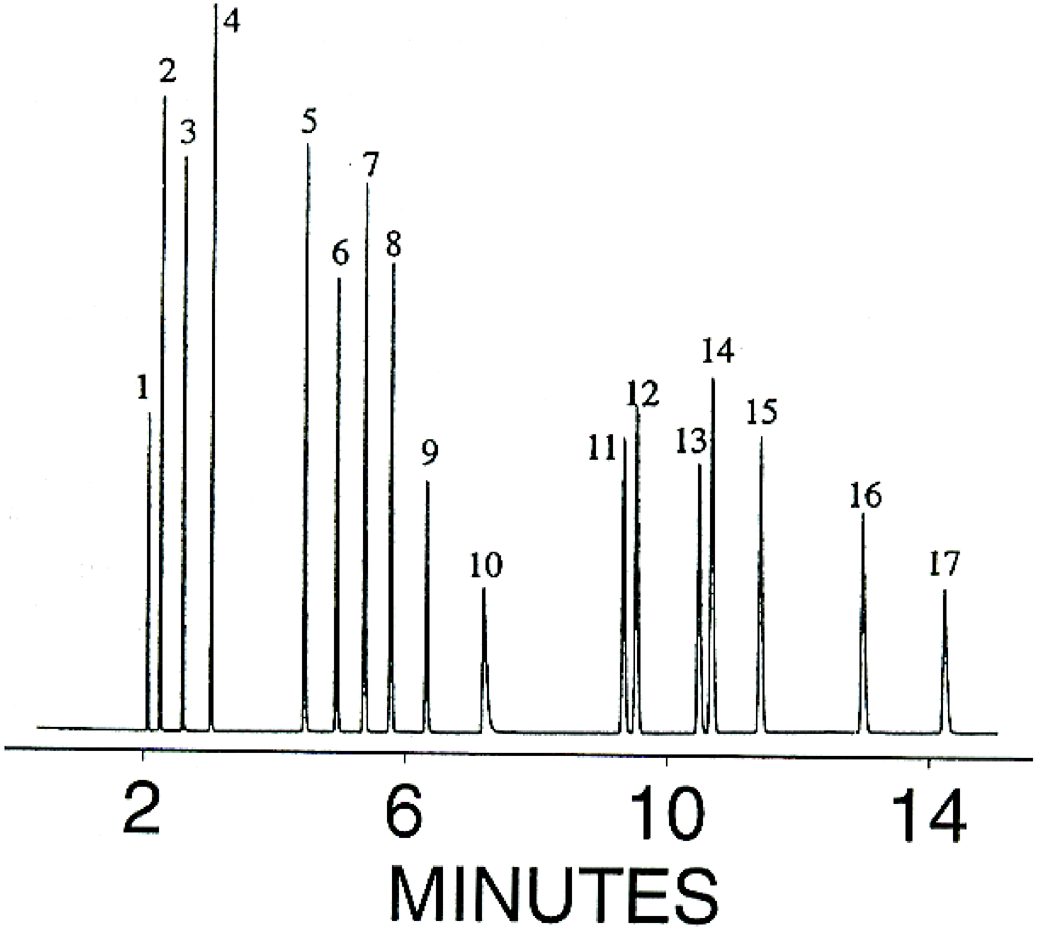


Table 2.9
General applications of PLOT columns in gas chromatography
Q = Poly(divinylbenzene-styrene), S = poly(divinylbenzene-vinylpyridine) and U = poly(divinylbenzene-ethylene glycol dimethacrylate)

Stationary phase	Maximum operating temperature (°C)	Typical applications
Alumina oxide	200	Alkanes, alkenes, alkynes and aromatic hydrocarbons from C_1 to C_{10}. C_1 and C_2 halocarbons
Silica gel	250	Hydrocarbons (C_1 to C_4), inorganic gases, volatile ethers, esters and ketones
Carbon	350	Inorganic gases, hydrocarbons (C_1 to C_5) and oxygenated
Carbosieves	150	C_1 to C_6 compounds
Molecular sieves (5A and 13X)	350	Hydrogen, oxygen, nitrogen, methane and noble gases. Particularly the separation of He/Ne and Ar/O_2. Hydrocarbons (C_1 to C_3) on 5A with higher alkanes on 13X (up to C_{12}) but not isomer separations
Cyclodextrins		Fixed gases, halocarbons, hydrofluorocarbons, C_1 to C_{10} hydrocarbons
Porous polymers		
Q	310	Hydrocarbons (C_1 to C_{14}), halocarbons (C_1 and C_2), volatile
S	250	oxygenated solvents (C_1 to C_6), thiols, amines, nitro
U	190	compounds, nitriles, water and inorganic gases

State of the art performance



1. methane
2. ethane
3. ethylene
4. propane
5. cyclopropane
6. propylene
7. isobutane
8. n-butane
9. propadiene
10. acetylene
11. *trans*-2-butene
12. 1-butene
13. *cis*-2-butene
14. isopentane
15. n-pentane
16. 1,3-butadiene
17. propyne

Figure 2.11. Separation of saturated and unsaturated volatile hydrocarbons on a 50 m x 0.53 mm internal diameter sodium sulfate deactivated alumina PLOT column. Carrier gas was helium at 5.0 ml/min and the temperature program 40 to 120°C at 5°C/min with a 5 min hold at 120°C. (©Restek Corporation).

Question. **In a WCOT GC, two component, each with plate height H = 0.0064 cm, are observed have a resolution of 0.5 when the length of column is 1 m. How long should the column to be achieve baseline resolution?**

5. A graduate student performed a separation of a potential drug A and B in extraction of natural products. A mixture of component A and B were separated on a 30-cm long uniform LC column. The retention times of these two components were 16.40 and 18.63 min, and the base-widths were 1.11 and 1.21 min, respectively. A component that does not be retained by the stationary needs 1.30 min to pass the column. Please calculate (1) the resolution, plate number and plate height of these two components. (2) How long should the column be to achieve a baseline resolution of these two peaks? and what are the retention times for components A and B in this new column?