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CEE 772:
Instrumental Methods in Environmental Analysis

Lecture #24

Special Applications: Chromatographic Retention Time and Environmental Properties

(Skoog, nothing)

(Harris, Nothing)

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Stationary Phases:

Stationary phase in GC is the main factor determining the selectivity and retention of solutes.

There are three types of stationary phases used in GC:

Solid adsorbents
Liquids coated on solid supports
Bonded-phase supports

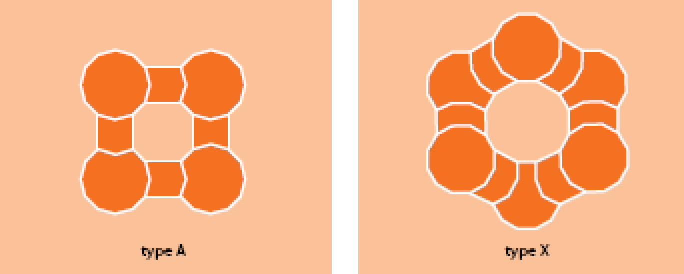
1.) *Gas-solid chromatography (GSC)*

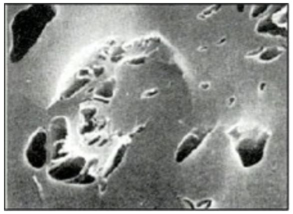
- same material is used as <u>both</u> the stationary phase and support material
- common adsorbents include:

② alumina
② molecular sieves (**crystalline aluminosilicates [zeolites]**

and c

② silica
② active carbon





Magnified Pores in activated carbon

2.) *Gas-liquid chromatography (GLC)*

- stationary phase is some liquid coated on a solid support
- over 400 liquid stationary phases available for GLC
  - ② many stationary phases are very similar in terms of their retention properties
- material range from polymers (polysiloxanes, polyesters, polyethylene glycols) to fluorocarbons, molten salts and liquid crystals

Based on polarity, of the 400 phases available only 6-12 are needed for most separations. The routinely recommended phases are listed below:

Name	Chemical nature of polysiloxane	Max. temp.	McReynolds' constants x'	y'	z'	μ'	s'
SE-30	Dimethyl	350	14	53	44	64	41
Dexsil300	Carborane-dimethyl	450	43	64	111	151	101
OV-17	50% Phenyl methyl	375	119	158	162	243	202
OV-210	50% Trifluoropropyl	270	146	238	358	468	310
OV-225	25% Cyanopropyl-25% phenyl	250	238	369	338	492	386
Silar-SCP	50% Cyanopropyl-50% phenyl	275	319	495	446	637	531
SP-2340	75% Cyanopropyl	275	520	757	659	942	804
OV-275	Dicyanoallyl	250	629	872	763	1106	849

Higher the number the higher the absorption.

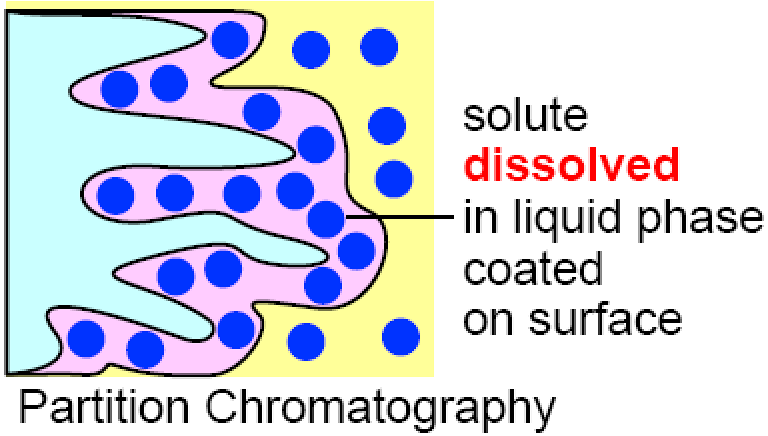
McReynolds' constants based on retention of 5 standard "probe" analytes
– Benzene, n-butanol, 2-pentanone, nitropropanone, pyridine

Preparing a stationary phase for GLC:

- slurry of the desired liquid phase and solvent is made with a solid support
  - ② solid support is usually diatomaceous earth (fossilized shells of ancient aquatic algae (diatoms), silica-based material)
- solvent is evaporated off, coating the liquid stationary phase on the support
- the resulting material is then packed into the column

disadvantage:

- liquid may slowly *bleed* off with time
  - ② especially if high temperatures are used
  - ② contribute to background
  - ② change characteristics of the column with time



Partition Chromatography

3.) *Bonded-Phase Gas chromatography*

- covalently attach stationary phase to the solid support material
- avoids column bleeding in GLC
- bonded phases are prepared by reacting the desired phase with the surface of a silica-based support

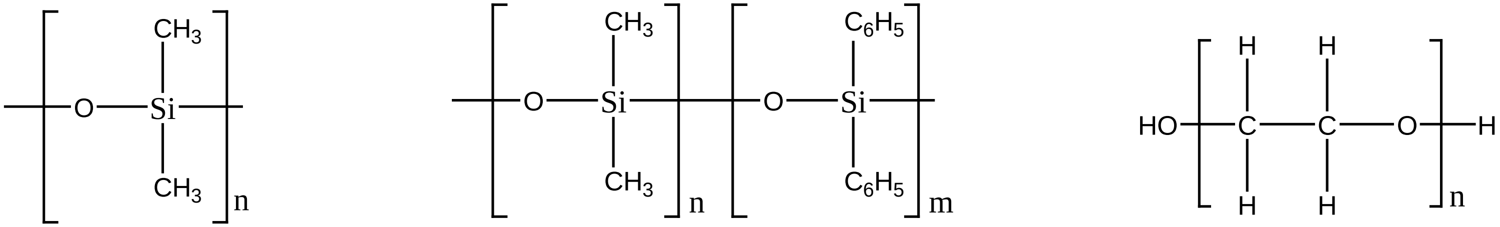
reactions form an Si-O-Si bond between the stationary phase and support

or

reactions form an Si-C-C-Si bond between the stationary phase and support

- many bonded phases exist, but most separations can be formed with the following commonly recommended bonded-phases:

② Dimethylpolysiloxane
② Methyl(phenyl)polysiloxane
② Polyethylene glycol (Carbowax 20M)
② Trifluoropropylpolysiloxane
② Cyanopropylpolysiloxane



advantages:

- more stable than coated liquid phases
- can be placed on support with thinner and more uniform thickness than liquid phases

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

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

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

Retention Index
(Kovats)

Based on n-alkanes

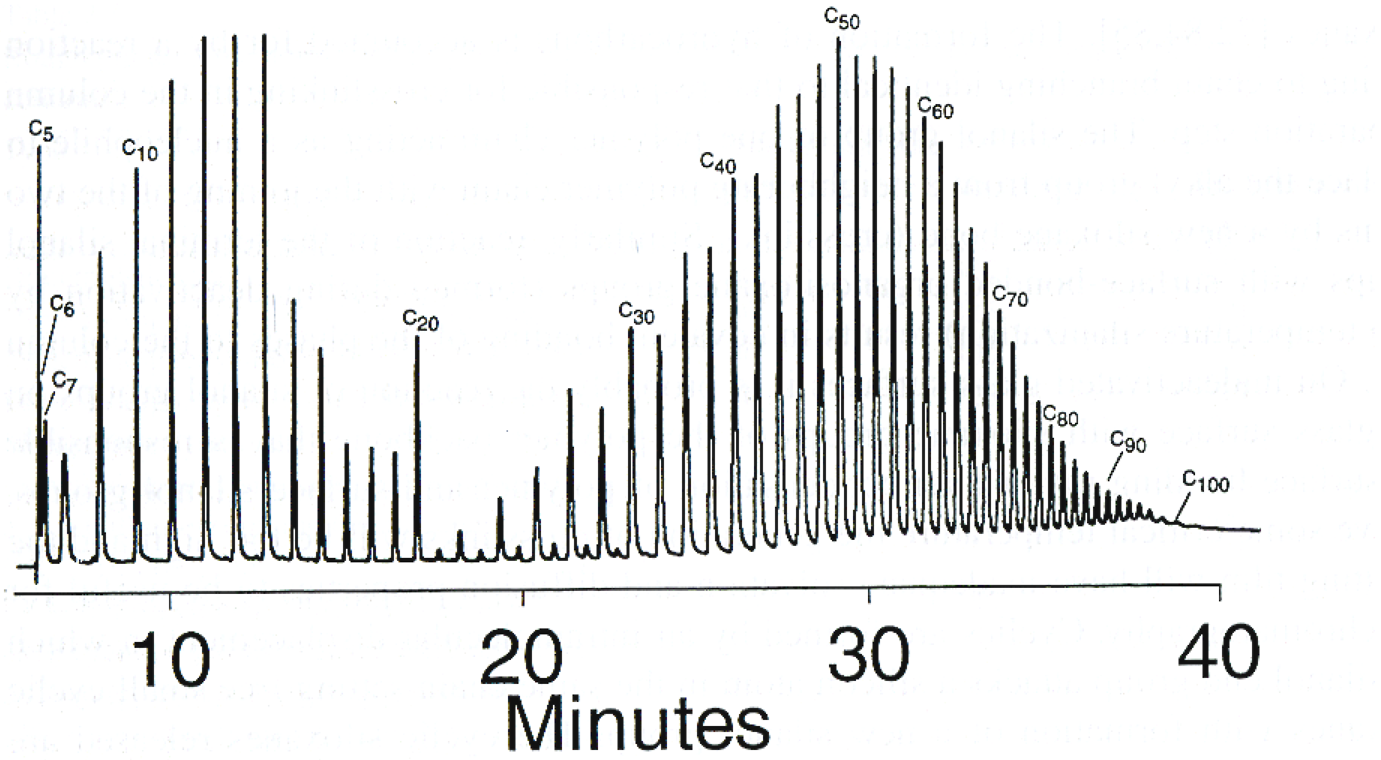
$$I = 100\left[n + \frac{\log t'_{NX} - \log t'_{Nn}}{\log t'_{N(n+1)} - \log t'_{Nn}} \right]$$

where:

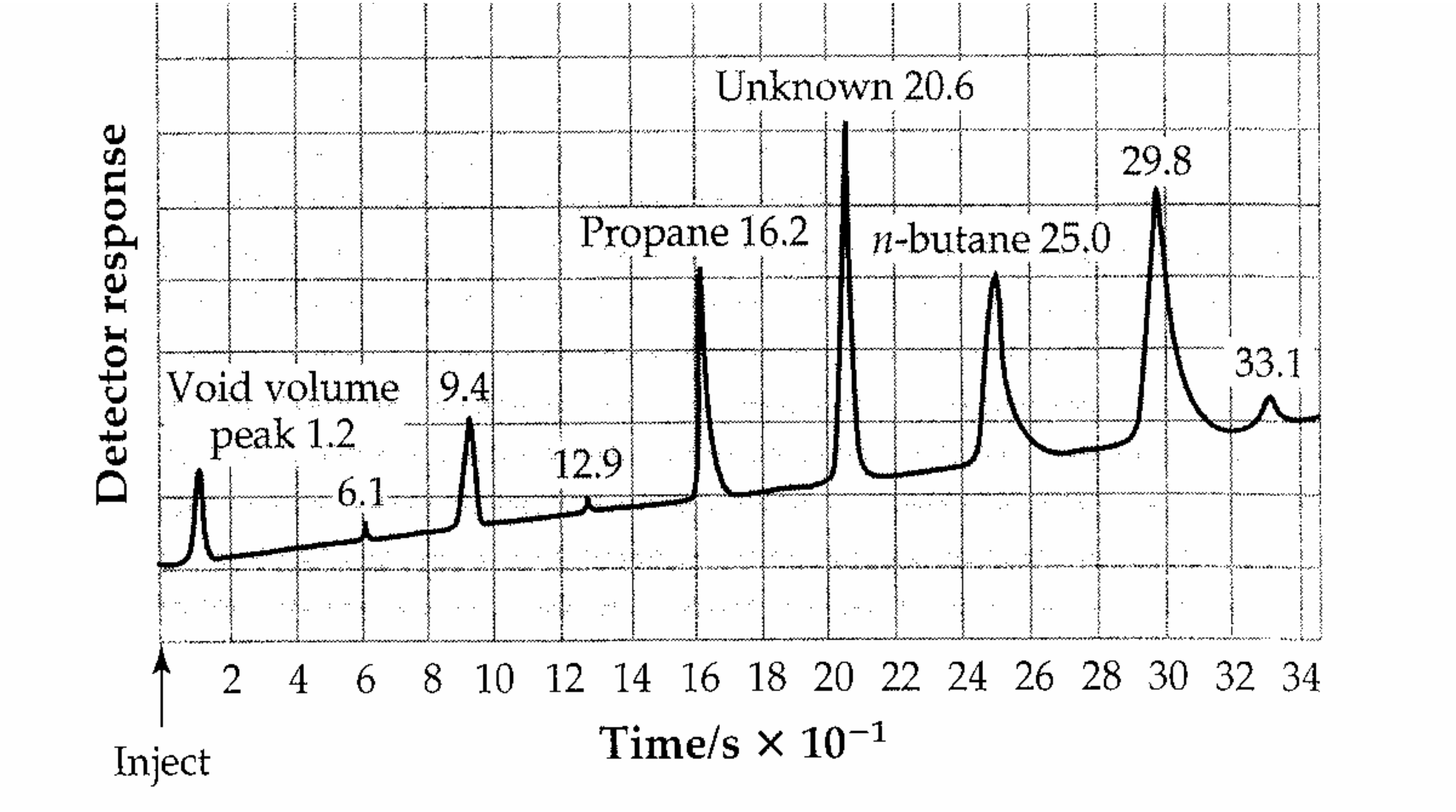
t'_N = Net retention time = $t_r - t_0$

and the analyte elutes between C_n and C_{n+1}

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



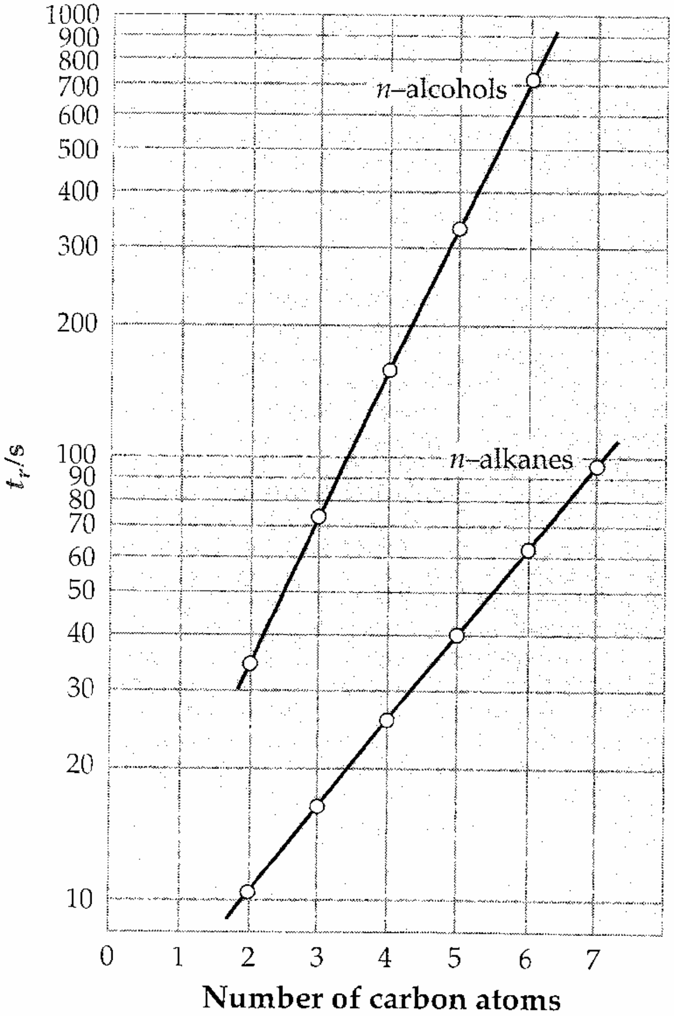
$$I = 100z + 100*[\log t_R'(x) - \log t_R'(z)]/[\log t_R'(z+1) - \log t_R'(z)]$$



$$I_{unk} = 100\left[3 + \frac{\log(20.6-1.2)-\log(16.2-1.2)}{\log(25.0-1.2)-\log(16.2-1.2)}\right]$$

$$I_{unk} = 356$$

Retention Index (Kovats)



Based on the log-linear relationship between number of carbons (n) in an n-alkane and retention time.

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.

Retention Index (McReynolds Constant)

Reports ΔI for a specific stationary phase (squalane), and 5 different reference compounds: benzene, n-butanol, 2-pentanone, nitropropane, pyridine

$$\Delta I = I_{sp} - I_{squalane.}$$

From a table of stationary phase ΔI values, one may choose the biggest ΔI value for the reference compound most like the solute of interest.

McReynolds Constants: Example

- Example:
  - Kovats index of toluene:
    - 773 on SP squalene (non-polar)
    - 860 on SP dioctylphatalate
  - Define McReynolds constant as:
    - $\Delta I = 860 - 773 = 87$
  - Results:
    - Dioctylphatalate is a more polar stationary phase
    - The larger the McReynolds constant, the greater the retention time than compared to the non-polar column.

Method by McReynolds

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.

Method by Kamlet, Taft, and Abraham

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

McReynolds Constants

From McNair

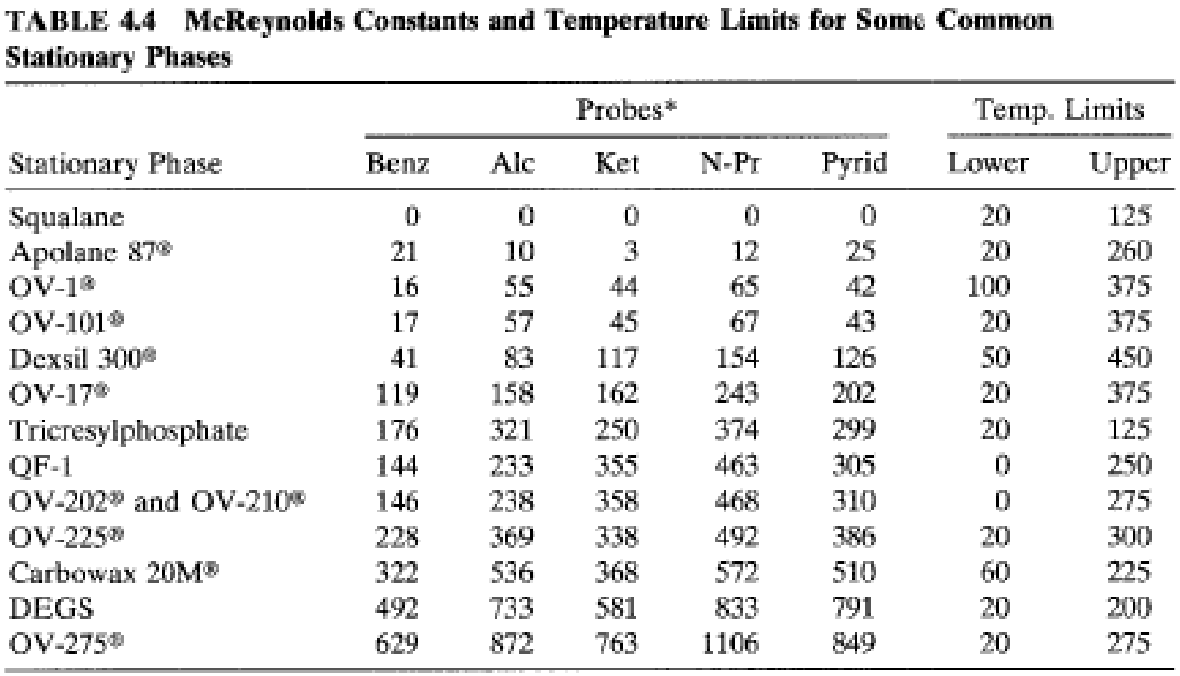


TABLE 4.4 McReynolds Constants and Temperature Limits for Some Common Stationary Phases

	Probes*					Temp. Limits		Sum of ΔI
Stationary Phase	Benz	Alc	Ket	N-Pr	Pyrid	Lower	Upper	
Squalane	0	0	0	0	0	20	125	0
Apolane 87®	21	10	3	12	25	20	260	
OV-1®	16	55	44	65	42	100	375	
OV-101®	17	57	45	67	43	20	375	
Dexsil 300®	41	83	117	154	126	50	450	
OV-17®	119	158	162	243	202	20	375	884
Tricresylphosphate	176	321	250	374	299	20	125	
QF-1	144	233	355	463	305	0	250	
OV-202® and OV-210®	146	238	358	468	310	0	275	
OV-225®	228	369	338	492	386	20	300	
Carbowax 20M®	322	536	368	572	510	60	225	
DEGS	492	733	581	833	791	20	200	
OV-275®	629	872	763	1106	849	20	275	4219

Each sum is a measure of the “polarity” of the liquid phase. The higher the sum, the higher the polarity, the higher the retention time.

Comparison to the method by Kamlet, Taft, and Abraham

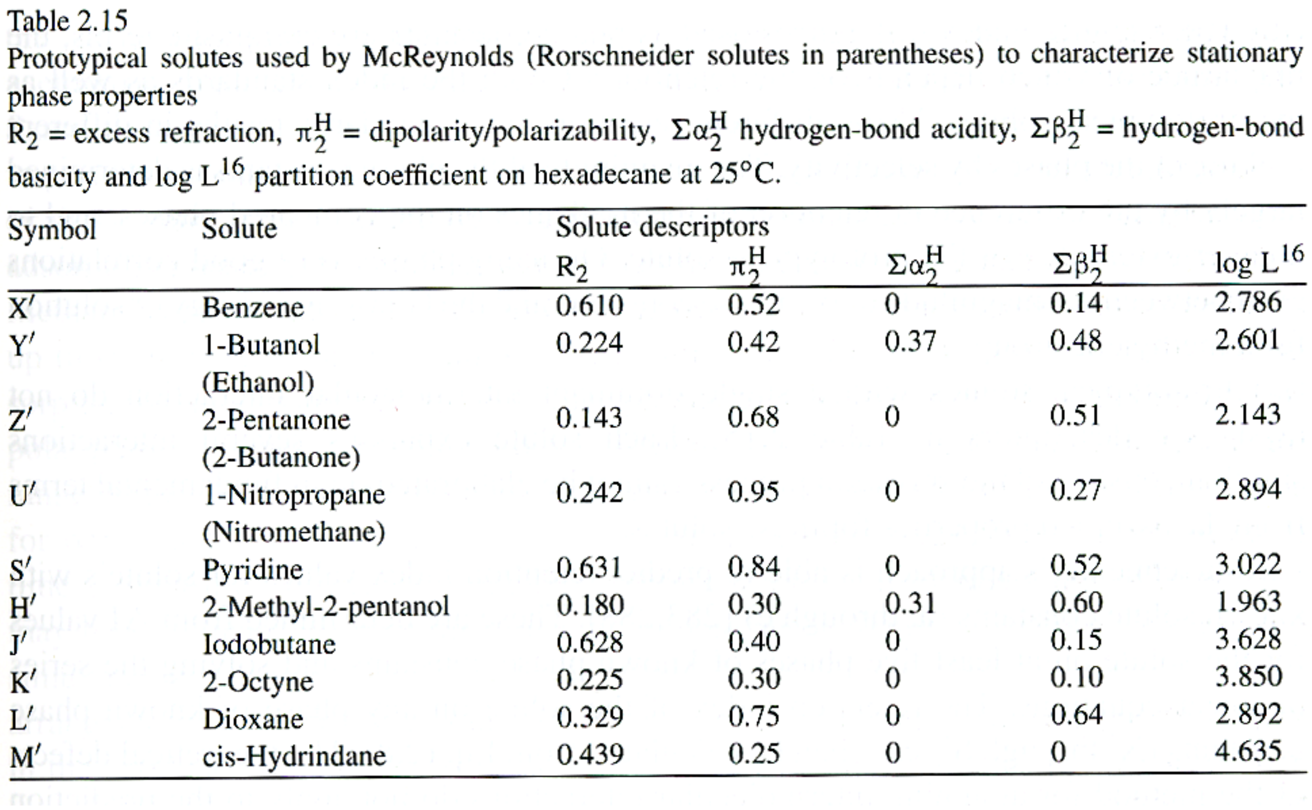


Table 2.15
Prototypical solutes used by McReynolds (Rorschneider solutes in parentheses) to characterize stationary phase properties
R_2 = excess refraction, π_2^H = dipolarity/polarizability, $\Sigma\alpha_2^H$ hydrogen-bond acidity, $\Sigma\beta_2^H$ = hydrogen-bond basicity and log L^{16} partition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

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Review

Estimation of the environmental properties of compounds from chromatographic measurements and the solvation parameter model

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ABSTRACT

This article provides an overview of chromatographic methods as surrogate models for environmental processes and for the determination of descriptors for compounds of environmental interest. The solvation parameter model is the link to the identification of suitable chromatographic models for the estimation of environmental properties using a set of tools that allow screening of chromatographic databases for the selection of candidate systems. As an alternative approach, many transport and distribution properties of environmental interest can be described directly by the solvation parameter model. Environmental properties for compounds with known descriptors can then be predicted through these models. The central role chromatographic methods, together with liquid–liquid partition coefficients, occupy in the determination of the six descriptors used in the solvation parameter model is detailed. There is a current need to accelerate efforts to expand the coverage of environmental process models by incorporating more complex molecules of contemporary environmental interest. For many of these molecules descriptor values are unavailable and their determination should be prioritized.

Standard model

- Log SP = c + eE + sS + aA + bB + lL
  - Where
    - SP = solute property
    - L = gas-hexadecane partition coefficient
      - Cavity formation and solute-solvent dispersion interactions
    - E = excess molar refraction descriptor
    - A, B = hydrogen bonding acidity and basicity descriptors

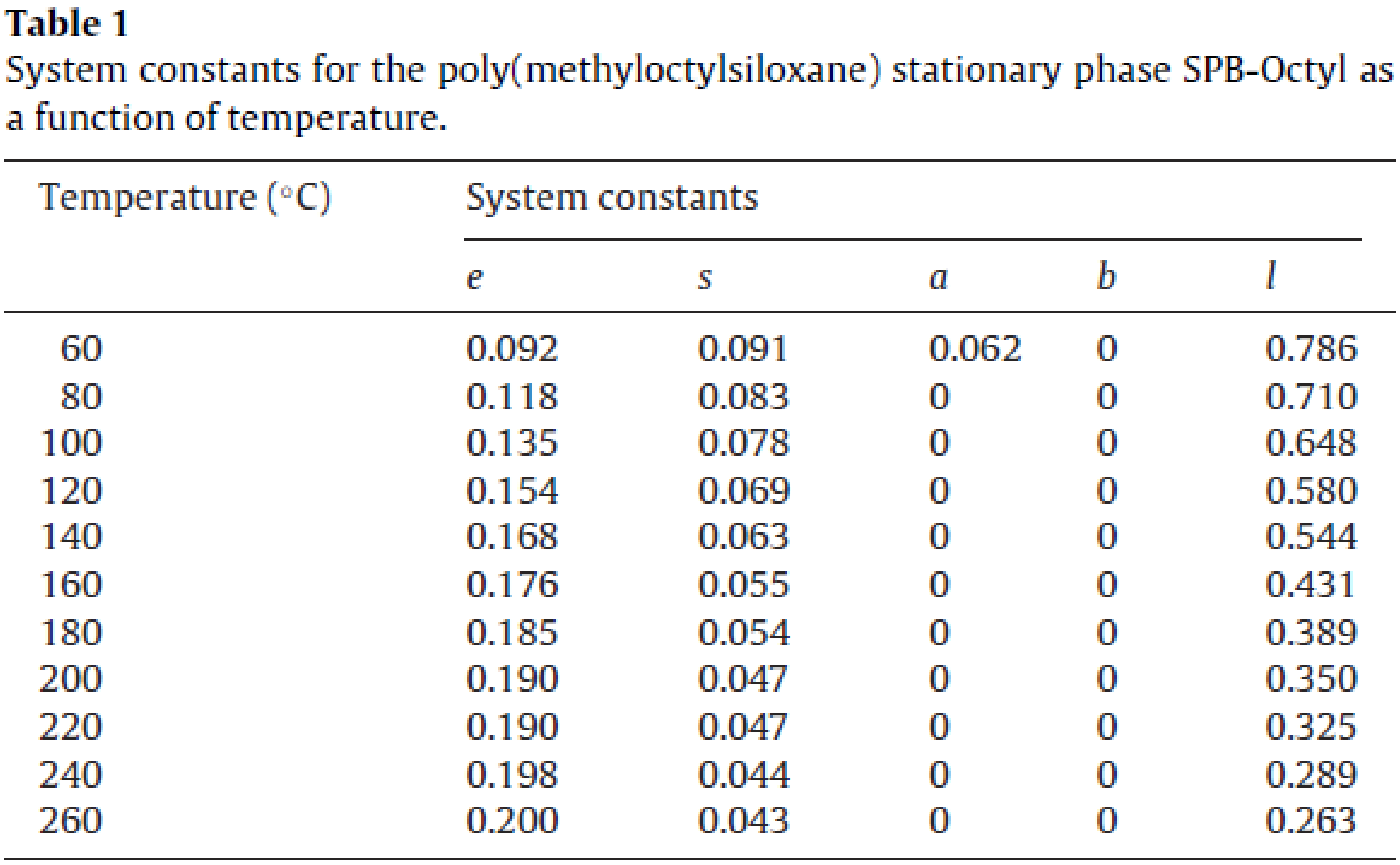

Table 1
System constants for the poly(methyloctylsiloxane) stationary phase SPB-Octyl as a function of temperature.

Temperature (°C)	System constants				
	e	*s*	*a*	*b*	*l*
60	0.092	0.091	0.062	0	0.786
80	0.118	0.083	0	0	0.710
100	0.135	0.078	0	0	0.648
120	0.154	0.069	0	0	0.580
140	0.168	0.063	0	0	0.544
160	0.176	0.055	0	0	0.431
180	0.185	0.054	0	0	0.389
200	0.190	0.047	0	0	0.350
220	0.190	0.047	0	0	0.325
240	0.198	0.044	0	0	0.289
260	0.200	0.043	0	0	0.263

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Review

Separation methods for estimating octanol–water partition coefficients

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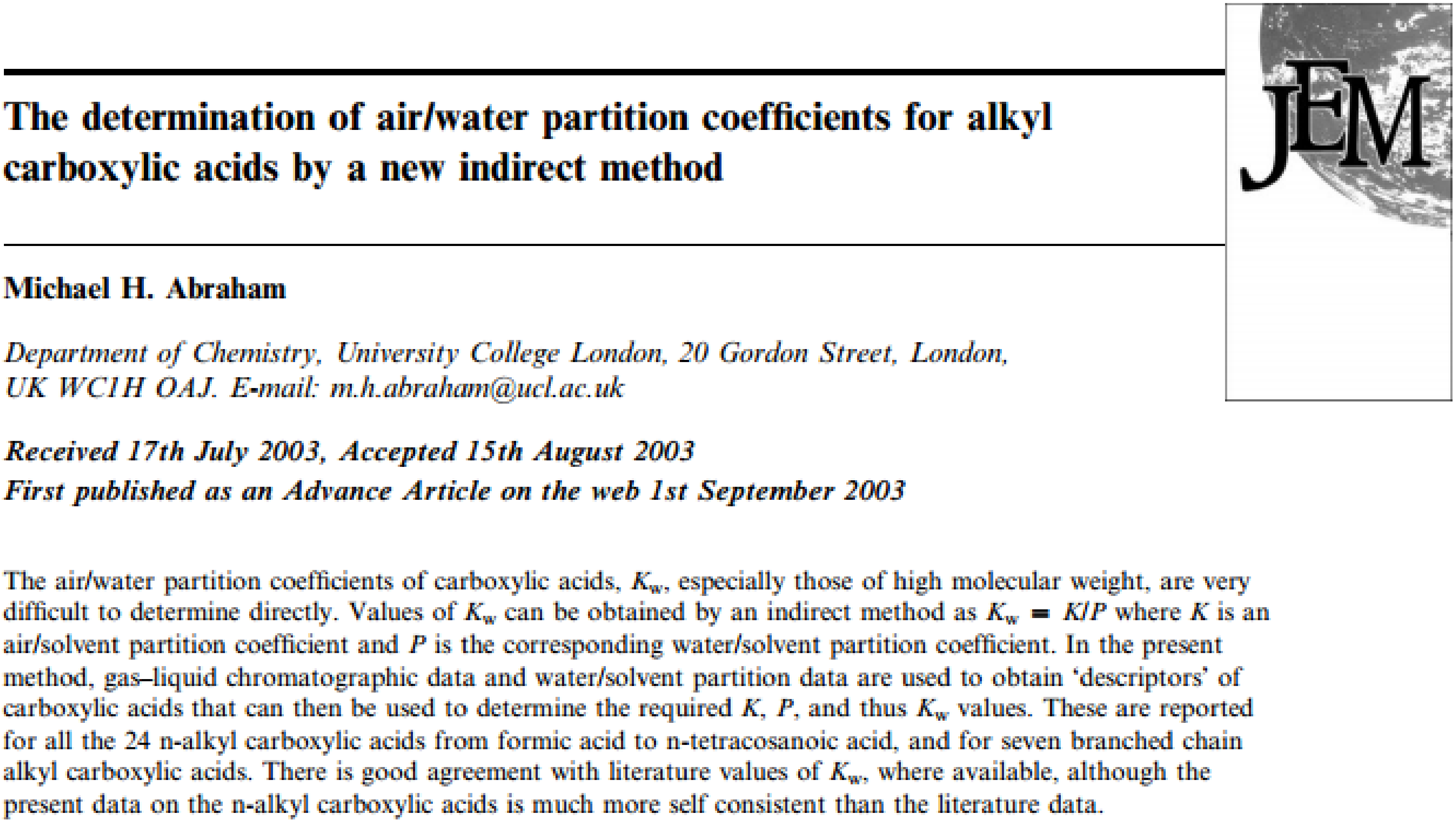
Abstract

Separation methods for the indirect estimation of the octanol–water partition coefficient (log *P*) are reviewed with an emphasis on high throughput methods with a wide application range. The solvation parameter model is used to identify suitable separation systems for estimating log *P* in an efficient manner that negates the need for empirical trial and error experiments. With a few exceptions, systems based on reversed-phase chromatography employing chemically bonded phases are shown to be unsuitable for estimating log *P* for compounds of diverse structure. This is because the fundamental properties responsible for chromatographic retention tend to be different to those responsible for partition between octanol and water, especially the contribution from hydrogen bonding interactions. On the other hand, retention in several micellar and microemulsion electrokinetic chromatography systems is shown to be highly correlated with the octanol–water partition coefficient. These systems are suitable for the rapid, high throughput determination of log *P* for neutral, weakly acidic, and weakly basic compounds. For compounds with a permanent charge, electrophoretic migration and electrostatic interactions with the stationary phase results in inaccurate estimation of partition coefficients. The experimental determination of solute descriptors offers an alternative approach for estimating log *P*, and other biopartitioning properties. A distinct advantage of this approach is that once the solute descriptors are known, solute properties can be estimated for any distribution or transport system for which a solvation parameter model has been established.

Keywords: Reviews; Octanol–water partition coefficient



The determination of air/water partition coefficients for alkyl carboxylic acids by a new indirect method

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The air/water partition coefficients of carboxylic acids, K_w, especially those of high molecular weight, are very difficult to determine directly. Values of K_w can be obtained by an indirect method as $K_w = K/P$ where K is an air/solvent partition coefficient and P is the corresponding water/solvent partition coefficient. In the present method, gas–liquid chromatographic data and water/solvent partition data are used to obtain 'descriptors' of carboxylic acids that can then be used to determine the required K, P, and thus K_w values. These are reported for all the 24 n-alkyl carboxylic acids from formic acid to n-tetracosanoic acid, and for seven branched chain alkyl carboxylic acids. There is good agreement with literature values of K_w, where available, although the present data on the n-alkyl carboxylic acids is much more self consistent than the literature data.

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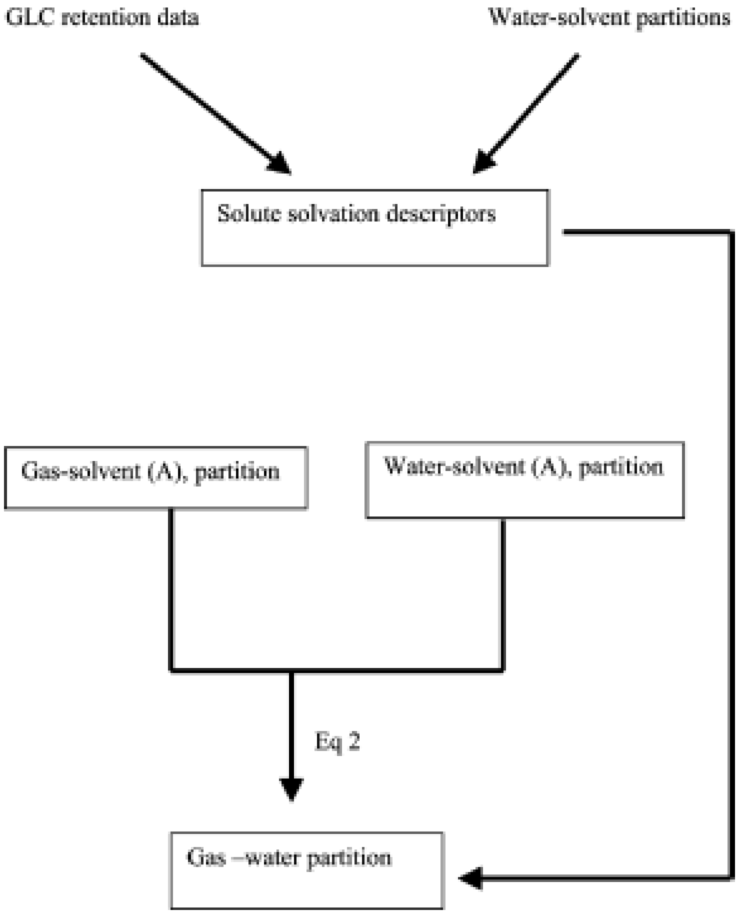

Fig. 2 Outline of the indirect method.

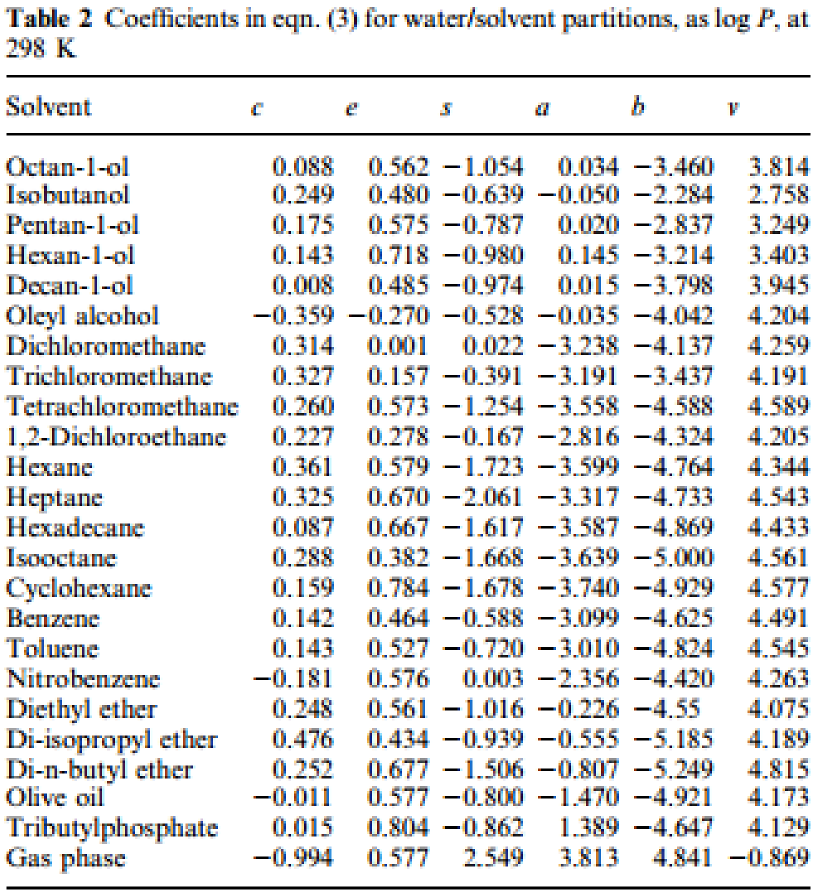

Table 2 Coefficients in eqn. (3) for water/solvent partitions, as log *P*, at 298 K

Solvent	*c*	*e*	*s*	*a*	*b*	*v*
Octan-1-ol	0.088	0.562	−1.054	0.034	−3.460	3.814
Isobutanol	0.249	0.480	−0.639	−0.050	−2.284	2.758
Pentan-1-ol	0.175	0.575	−0.787	0.020	−2.837	3.249
Hexan-1-ol	0.143	0.718	−0.980	0.145	−3.214	3.403
Decan-1-ol	0.008	0.485	−0.974	0.015	−3.798	3.945
Oleyl alcohol	−0.359	−0.270	−0.528	−0.035	−4.042	4.204
Dichloromethane	0.314	0.001	0.022	−3.238	−4.137	4.259
Trichloromethane	0.327	0.157	−0.391	−3.191	−3.437	4.191
Tetrachloromethane	0.260	0.573	−1.254	−3.558	−4.588	4.589
1,2-Dichloroethane	0.227	0.278	−0.167	−2.816	−4.324	4.205
Hexane	0.361	0.579	−1.723	−3.599	−4.764	4.344
Heptane	0.325	0.670	−2.061	−3.317	−4.733	4.543
Hexadecane	0.087	0.667	−1.617	−3.587	−4.869	4.433
Isooctane	0.288	0.382	−1.668	−3.639	−5.000	4.561
Cyclohexane	0.159	0.784	−1.678	−3.740	−4.929	4.577
Benzene	0.142	0.464	−0.588	−3.099	−4.625	4.491
Toluene	0.143	0.527	−0.720	−3.010	−4.824	4.545
Nitrobenzene	−0.181	0.576	0.003	−2.356	−4.420	4.263
Diethyl ether	0.248	0.561	−1.016	−0.226	−4.55	4.075
Di-isopropyl ether	0.476	0.434	−0.939	−0.555	−5.185	4.189
Di-n-butyl ether	0.252	0.677	−1.506	−0.807	−5.249	4.815
Olive oil	−0.011	0.577	−0.800	−1.470	−4.921	4.173
Tributylphosphate	0.015	0.804	−0.862	1.389	−4.647	4.129
Gas phase	−0.994	0.577	2.549	3.813	4.841	−0.869

- Last lecture

Retention Index (Rohrschnieder Constant)

Reports ΔI for different test solutes

$$\Delta I = I_{sp} - I_{\text{non-polar s.p.}}$$

From a table of ΔI values, one may choose the best stationary phase (s.p.) for a given class of solutes

Rules for Retention Index

1. R.I. increases 100 points for every CH_2 group in a molecule
2. ΔI for 2 isomers can be calculated from boiling points: $\Delta I \approx 5\ \Delta bp$
3. R.I. for non-polar compounds is constant for any stationary phase.
4. R.I. for ANY compound is constant for ALL non-polar stationary phases.
5. ΔI for a solute between a polar and a non-polar stationary phase is a characteristic of the solute and can be predicted.

Kovats Retention Indices of Selected Hydrocarbons through C_{10} on Bonded Phase Fused Silica Capillaries

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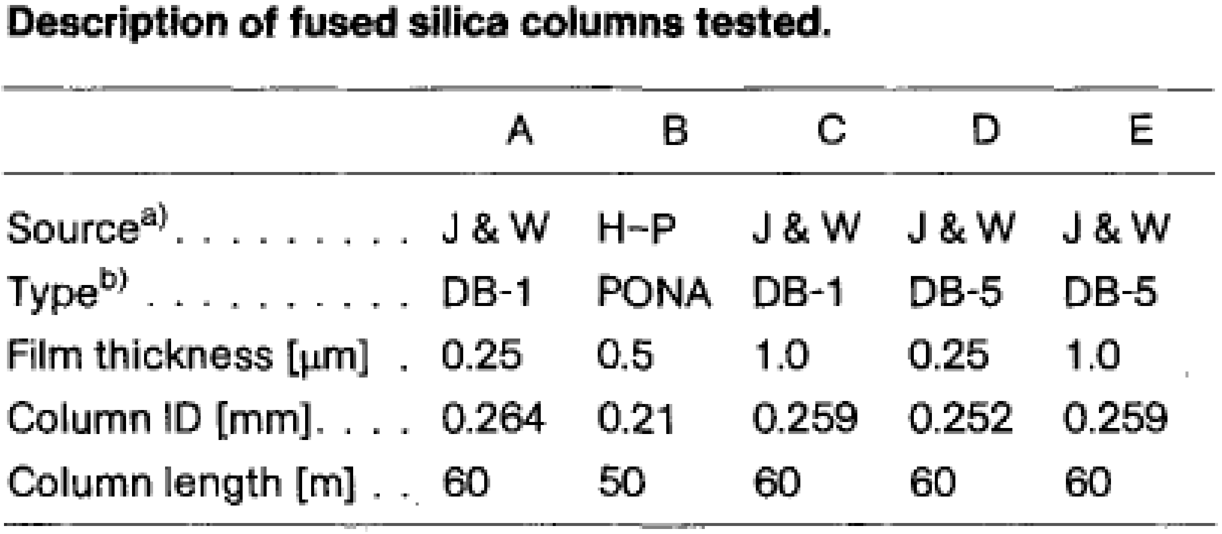

Description of fused silica columns tested.

	A	B	C	D	E
Source[a]	J & W	H–P	J & W	J & W	J & W
Type[b]	DB-1	PONA	DB-1	DB-5	DB-5
Film thickness [μm] .	0.25	0.5	1.0	0.25	1.0
Column ID [mm]. . . .	0.264	0.21	0.259	0.252	0.259
Column length [m] . .	60	50	60	60	60

DB-5 slightly more polar than DB-1

C thickness > A **E thickness > D**