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CHARACTERISTICS OF LIQUID STATIONARY PHASES AND COLUMN EVALUATION FOR GAS CHROMATOGRAPHY

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Characteristics of liquid stationary phases and column evaluation for gas chromatography

Abstract - The choice of an appropriate stationary phase is one of the most important decisions to be made in developing a gas chromatographic method. Provided the support is reasonably inert and well covered its exact nature is not critical apart from its contribution to flow characteristics and hence to resolution. The following topics are discussed: (i) Basic characteristics of liquids for stationary phases; (ii) Definitions of column performance. Resolution equations. Trennzahl value. The Separation Factor; (iii) Selection of a liquid stationary phase for a particular separation, (a) empirical approach, (b) use of Rohrschneider and of McReynolds constants; (iv) Test mixtures; (v) Patterns of column selectivity behaviour; (vi) Sources for the chemical composition of liquid stationary phases; (vii) Conclusions.

BASIC CHARACTERISTICS OF LIQUIDS FOR STATIONARY PHASES

The choice of an appropriate stationary phase is one of the most important decisions to be made in developing a gas chromatographic method. Provided the support is reasonably inert and well covered, its exact nature is not critical apart from its contribution to column flow characteristics and hence to resolution. If the support is not inert it may contribute to retention as well as to physical and chemical changes in the liquid phase[1]. Liquids have several advantages as stationary phases for gas chromatography, summarised as follows[2]:

(1) Under normal operating conditions the partition isotherms are linear so that symmetrical peaks can be obtained.
(2) A great variety of liquid phases is available; thus for most separations adequate stationary phases can be found.
(3) The amount of liquid phase in a column can be easily varied; both preparative and analytical, and, in some cases, open tubular columns can be prepared with the same liquid phase.
(4) Liquid phases are available in great purity or in well defined quality and thus retention values are reproducible from column to column.

The greatest disadvantage of liquid phases lies in their volatility. However, many liquid phases are available which have sufficiently low vapour pressure even at quite high column temperatures. Bonding the stationary phase to a support or to the column wall imparts physical stability to the film and reduces loss by "bleeding" but may well show changes in polarity and selectivity compared to its use, non-bonded, on a support[3]. When selecting liquids as stationary phases the following characteristics have to be considered[2]:

(1) Low vapour pressure at the required operating temperature.
(2) Chemical stability over operating temperature range (high upper temperature limit).
(3) Sufficient selectivity for components of the sample required to be separated.
(4) High solubility for all components of the sample.
(5) Low viscosity at the desired temperature, also a low temperature for any solidification or phase change causing dramatic change in viscosity (low lower temperature limit).
(6) Reasonable solubility in a common volatile solvent.
(7) Ability to wet the support surface or column wall in an adequate manner.
(8) Liquid should be readily available, reproducible in content or performance if not a pure substance and preferably be inexpensive.

Chemical changes can occur to supported liquid phases. Condor and Young consider that this fact is not always appreciated by those engaged in physical chemical measurements by g.l.c.[4]. These chemical changes are usually temperature dependent and may occur either as a slow ageing process or more rapidly when the column is first heated up, especially at the higher than usual temperatures commonly adopted for "conditioning" the column. The presence of only very small concentrations of oxygen in the carrier gas can cause liquid phases to age by oxidation. Keller *et al.*[5] have classified the chemical changes as being due to:-

(1) impurities in the carrier gas, particularly oxygen;
(2) non-volatile impurities in the partitioning liquid, e.g. hydrogen ion;
(3) catalytic reaction with the support;
(4) catalytic reaction with the products of degradation of the liquid; or
(5) further condensation of a polymeric material.

In addition the ageing process was considered to include physical as well as chemical changes. Physical changes were identified as those which change the total amount of liquid and/or its distribution on the support. Such changes might arise from:-

(1) evaporation of the stationary liquid phase;
(2) loss of volatile impurities in the original liquid phase;
(3) effects from solvent introduced by deposition of the stationary phase from solution; or
(4) water sorbed from the atmosphere.

DEFINITIONS OF COLUMN PERFORMANCE

1. Theoretical plates

The performance of a column is usually stated in terms of the number of theoretical plates, n, calculated from the expression

$$n = 16 \times \left\{ \frac{\text{retention volume}}{\text{peak base width}} \right\}^2$$

The theoretical plate number may vary with the compound as well as the column therefore the compound used for its determination should be reported. The units used for retention and peak base width must be consistent so that their ratio is dimensionless. If the corrected retention volume is used, the observed peak width must be corrected for the pressure drop in the column.[6] The number of theoretical plates, n, for a packed column is shown by the van Deemter[7] equation to relate to flow rate, column packing and phase transfer rates hence the requirement for a low liquid phase viscosity.

2. Resolution

For a pair of compounds of interest the peak resolution, R_S, expressed as

$$\text{Resolution} = 2 \times \left\{ \frac{\text{difference between retention volumes}}{\text{sum of peak widths}} \right\}$$

is of interest[8] [9].

For two closely spaced peaks A and B the resolution, R_S, can be shown to be related to column parameters[10], separation factor, α , number of theoretical plates, n_A, and the mass distribution ratio D_{MA} where A is the slowest eluting band,

$$R_S = \frac{\alpha_{A/B} - 1}{\alpha_{A/B}} \cdot \frac{n_A^{\frac{1}{2}}}{4} \cdot \frac{D_{MA}}{1 + D_{MA}}$$

The mass distribution ratio $D_M = D_C/\beta$ where D_C is the concentration distribution ratio and β the phase (volume) ratio, i.e. volume of mobile phase to volume of stationary phase. The value of β is low (15-50) for a packed column and is high (100-1000) for open or capillary columns. Low values of β imply long retention times. D_C is a fundamental, temperature dependent, property and is determined by the solute and solvent.

Knox[11] has put forward a similar equation to that of Purnell for resolution based, however, on the average retention factors for the two peaks concerned,

$$R_S = \tfrac{1}{2} \cdot \frac{(\alpha_{A/B} - 1)}{(\alpha_{A/B} + 1)} \cdot \frac{\bar{k}}{1 + \bar{k}} \cdot n^{\frac{1}{2}}$$

where $\bar{k} = \frac{1}{2}(k_A + k_B)$.

Said[12] has given an even more mathematically exact equation for R_S,

$$R_S = \tfrac{1}{4} \cdot n^{\frac{1}{2}} \cdot \ln \frac{(1 + k_A)}{(1 + k_B)}$$

which however in practice gives almost identical results to the equation of Knox. The Purnell equation leads to slightly lower values for R_S.

3. Trennzahl values

Kaiser[13,14] suggested the use of TZ values (Trennzahl values) as a more meaningful visual alternative to plate numbers to express the separation efficiency of a column. TZ is defined as the resolution between two consecutive members of the n-paraffin homologous series C_x and C_{x+1}.

$$TZ = \frac{t_{R(x+1)} - t_{R(x)}}{W_{h(x+1)} + W_{h(x)}} - 1$$

where W_h is the peak width at half peak height.
In a practical sense TZ is the number of peaks which could be placed, if desired, between the C_x and C_{x+1} peaks separated with a resolution $R_S = 1.177$. The term "separation number", SN, is also used for TZ.

4. Retention factor (*k*)

The retention factor is a measure of the time the sample component spends in the stationary phase relative to the time it spends in the mobile phase: it expresses how a sample component is retarded by the stationary phase compared to the time that it would take to

travel through the column with the velocity of the mobile phase. Mathematically, it is the ratio of the adjusted retention volume (time) to the holdup volume (time):

$$k = V'_R/V_M = t'_R/t_M$$

The retention factor is also equal to the ratio of the amounts of a sample component in the stationary and mobile phases respectively, at equilibrium:

$$k = \frac{\text{amount of component in stationary phase}}{\text{amount of component in mobile phase}}$$

If the fraction of the sample component in the mobile phase is R then the fraction in the stationary phase is $(1-R)$; thus

$$k = (1 - R)/R$$

Note: In former nomenclatures and in the literature one may find the expressions Partition Ratio, Capacity Ratio, Capacity Factor or Mass Distribution Ratio to describe this term. It is felt that the present name best describes this term. The symbol k' is often used for these equivalent terms, particularly in liquid chromatography. The original reason for this was to clearly distinguish it from the partition coefficient (distribution constant) for which the symbol K had been utilized. Since, however, the distribution constants are all identified with a subscript there is no reason to add the prime sign to this symbol. It should be emphasized that all official nomenclatures (IUPAC, BSI, ASTMS) have always clearly identified the capacity factor with the symbol k and not k'.

5. Separation factor

For two peaks, A and B, the separation factor, $\alpha_{A/B}$ is given by

$$\alpha_{A/B} = \frac{D_{MA}}{D_{MB}} = \frac{\gamma_B \cdot p^\circ_B}{\gamma_A \cdot p^\circ_A}$$

where $\gamma_A \gamma_B$ and p°_A, p°_B are the activity coefficients and vapour pressures of A and B respectively. Separation is possible if $\alpha_{A/B}$ is not unity in value. The two extreme cases are $\gamma_A = \gamma_B$ when separation is only possible if $p^\circ_A \neq p^\circ_B$ (homologous series) and $p^\circ_A \sim p^\circ_B$ when separation is only possible if $\gamma_A \neq \gamma_B$ (the general case). The factors which cause $\gamma_A \neq \gamma_B$ are those of solute-solvent interactions. Apart from adduct formation and true chemical bond formation the forces of interaction are weak, which is the case for most systems. These weak forces involve dispersion or London forces, induction or Debye forces, orientation or Keesom forces and hydrogen bonding.

SELECTION OF A LIQUID PHASE FOR A PARTICULAR SEPARATION

a. Empirical approach

The earliest and simplest generalisation for the mutual solubility of two compounds is *similia similibus solvantur*, "like dissolves like"[15]. This idea has lead to various classifications of solvents and solutes based on the concept of polarity; the five class system (most polar, polar, intermediate, low polarity, non-polar) by Ewell *et al*[16] is useful. Using this system columns are selected to match solute polarity to maximise retention which usually results in better separation. This approach has been well described by McNair and Bonelli[17].

b. Use of Rohrschneider and of McReynolds constants

Several attempts have been made to put the concept of polarity on a less intuitive basis, that due to Rohrschneider[18] [19] being particularly important in that it lead to the now commonly used McReynolds[20] constants. Initially the polarity of a column was measured graphically by linear interpolation of the log of the relative retentions of a pair of solutes (butadiene and n-butane) on the column in question and on columns assigned zero polarity (squalane) and 100% polarity (β β-oxydipropionitrile)[21]. It was then found that the measured polarities depended on the test solutes used. Rohrschneider then recognised that the "polarity" of a column was dependent not only on the stationary phase but also upon the substance being chromatographed. The system developed requires the use of Kovats retention indices[22]. The change in retention index between two columns (phase b being more polar than phase a),

$$\Delta I = I^{b} - I^{a}$$

consists of two types of contribution, those which are sample component specific and those which relate to the stationary phase. The former were denoted by a, b, c, d and e and the latter by x, y, z, u and s. In the first publication[18] 3 test substances were used and in the second[19] 2 more test substances were added. Rohrschneider did not want to change the symbols for the existing constants, hence the irregular sequence .. z, u, s. The test solutes were chosen to represent typical organic groupings/interactions as shown in Table 1.

TABLE 1. Test Solutes proposed by Rohrschneider and the Organic Functional Groups Characterised by them.

Symbol	Test Solute	Organic Functional Group
x	benzene	aromatics, olefins
y	ethanol	alcohols, nitriles, acids; alkyl mono-, di- and trichlorides
z	methyl ethyl ketone	ketones, ethers, aldehydes esters, epoxides and di-methylamino derivatives
u	nitromethane	nitro and nitrile derivatives
s	pyridine	pyridine, dioxane

Thus for the five polarity factors for a single solute and a single stationary phase we have

$$\Delta I = ax + by + cz + du + es,$$

where x, y, z, u, s and a, b, c, d, e are the polarity factors characterising the stationary phase and the solute, respectively.

By chromatographing each of m solutes on each of n stationary phases, results are obtained that should allow the determination of 5m polarity factors of the components and 5n polarity factors of the stationary phases.
A system of mn equations with 5(m + n) unknowns is obtained. The system is difficult to handle.

$$
\begin{aligned}
\Delta I_1^1 &= a_1x_1 + b_1y_1 + c_1z_1 + d_1u_1 + e_1s_1,\\
\Delta I_2^1 &= a_1x_2 + b_1y_2 + c_1z_2 + d_1u_2 + e_1s_2,\\
&\vdots\\
\Delta I_n^1 &= a_1x_n + b_1y_n + c_1z_n + d_1u_n + e_1s_n,\\
\Delta I_1^2 &= a_2x_1 + b_2y_1 + c_2z_1 + d_2u_1 + e_2s_1,\\
&\vdots\\
\Delta I_n^m &= a_mx_n + b_my_n + c_mz_n + d_mu_n + e_ms_n.
\end{aligned}
$$

In order to solve this problem Rohrschneider chose as values for x, y, z, u and s for a particular phase,

$$x = \Delta I_{\text{benzene}}/100;\quad y = \Delta I_{\text{ethanol}}/100;\quad z = \Delta I_{\text{methylethylketone}}/100;$$
$$u = \Delta I_{\text{nitromethane}}/100;\quad s = \Delta I_{\text{pyridine}}/100.$$

where

$$\Delta I_{\text{benzene}} = I_{\text{benzene}}^{\text{phase in question}} - I_{\text{benzene}}^{\text{squalane}} \text{ etc.}$$

Hence for a stationary phase j and for a solute i,

$$\Delta I_i^j = a_i \frac{\Delta I^j_{C_6H_6}}{100} + b_i \frac{\Delta I^j_{C_2H_5OH}}{100} + c_i \frac{\Delta I^j_{C_4H_8O}}{100} + d_i \frac{\Delta I^j_{CH_3NO_2}}{100} + e_i \frac{\Delta I^j_{C_2H_5N}}{100}$$

The calculation of all the factors is laborious. But if the a, b, c, d and e factors of a solute chromatographed on five different stationary phases (on these phases the five reference solutes were chromatographed in order to obtain the polarity factors x,y,z,u, and s for each phase) are determined, then the behaviour of the solute can be predicted on any stationary phase for which the x, y, z, u and s factors have been determined.

The five polarities (a-e) of the substances were interpreted by Rohrschneider[9] as a measure of orientation forces (factor e) charge-transfer forces (donor and acceptor forces, a and d) and hydrogen bonding (H donor b, H acceptor c). Supina[23] has suggested the stationary phase factors (x....s) relate to intermolecular forces (x) electron attraction (y), electron repulsion (z) and that u and s are "complex"; in all cases it is necessary to know or estimate the dominant factors before attempting to select phases.

The scheme was extended to 10 test solutes by McReynolds[20]; the list of solutes and the organic functional groups (where available) characterised are given in Table 2.
The evolution and use of Rohrschneider's constants have been reviewed by Supina and Rose[24], Supina[23], Baiulescu and Illie[25], and by Ettre[26-28].

The evaluation of the constants was carried out as before except that the division of ΔI by 100 was omitted. Other differences between the two systems are the temperature - McReynolds used a slightly higher temperature of 120°C compared to 100°C used by Rohrschneider - and also higher molecular weight homologues for certain of the functional group test probes.

TABLE 2. Test Solutes proposed by McReynolds and the Organic Functional Groups they Characterise

Symbol	Test Substance	Substance/group
X'	benzene	aromatics, olefins
Y'	butanol-1	alcohols, nitriles, acids
Z'	methyl n-propyl ketone	ketones, ethers, aldehydes, esters, epoxides, dimethyl-amino derivatives
U'	nitropropane	nitro- and nitrile derivatives
S'	pyridine	pyridine
H'	2-methyl-pentanol-2	branched chain compounds particularly alcohols
J'	1-iodobutane	halogenated compounds
K'	2-octyne	
L'	1,4-dioxane	
M'	cis hydrindane	

The effect of temperature on Rohrschneider constants is not great although "polarity" and retention indices are temperature dependent [28]. Grob and Grob[29] consider that the variability of polarity with temperature is the major sources of inadequate reproducibility of fingerprint comparisons of traces obtained by gc/ms and by gc. Film thickness was also regarded as an essential column characterisation parameter because of its effect on capillary column operating temperatures and hence polarity.

The Rohrschneider approach can be extended to deal with polymeric sorbents such as those based on methacrylic acid esters by replacing squalane as the reference stationary phase by a non-polar absorbent[30].

Manufacturers of stationary phases now frequently quote McReynolds values; the first five are often used, as suggested by McReynolds, to estimate total "polarity" = (X'+Y'+Z'+U'+S').

Certain tables contain additional data such as the "b" and "r" constants[20][31]. The first constant, b, is the slope of the curve obtained when the logarithm of the net retention times of the n-alkanes is plotted as a function of the number of carbon atoms. The values were obtained from the retention times of decane and dodecane. The second constant is r, the ratio of the net retention times of adjacent n-alkanes. This was calculated from the square root of the ratio of the net retention times of dodecane and decane. The two constants are related since, b = log r.

There are several ways in which the Rohrschneider and the McReynolds systems are useful in gas chromatographic practice[23][24][31][32].

(1) Identification of duplicate stationary phases by checking for identical Rohrschneider or McReynolds constants.

(2) Identification of similar stationary phases by searching for those with similar Rohrschneider constants. From this it is possible to select the stationary phase with the best thermal stability, lowest viscosity or other desired properties.

3) Using and classifying stationary phases in an orderly manner covering the complete range of polarity based on five or ten different classes of interactions.

(4) Selection of columns based on interaction between components of the samples and the stationary phases by using a table of constants.

A selection of phases and their McReynolds constants is given in Table 3.

TABLE 3. Operating Range and McReynolds Constants for Some General Stationary Phases[24]

Phase	Temp. Limit °C Min./Max.	McReynolds Constants X'	Y'	Z'	U'	S'	H	J	K	L	M
QF-1	0/250	144	233	355	463	305	203	136	53	280	59
OV-210	0/275	146	238	358	468	310	206	139	56	283	60
Ethofat 60/25	50/125	191	382	244	380	333	277	168	131	279	73
OV-1	100/350	16	55	44	65	42	32	4	23	45	-1
OV-101	0/350	17	57	45	67	43	33	4	23	46	-2
SP-2100	0/350	17	57	45	67	43	-	-	-	-	-
DC-200	50/250	16	57	45	66	43	33	3	23	46	-3
SE-30	50/300	15	53	44	64	41	31	3	22	44	-2

The first three phases listed in Table 3 are almost identical in overall polarity as shown by the sum of the first five constants being 1500, 1520 and 1530 respectively. QF-1 and OV-210 will be almost identical in separation performance but Ethofat 60/25 is significantly different, the differences in Y' and Z' values produces a reversal of order of elution for an alcohol/ketone mixture on the two phases. The five phases OV-1 - SE-30 are all polydimethylsiloxanes and all have nearly identical separatory powers, but OV-101 and SP-2100 are useful over a wider temperature range making them the most useful of the five phases; DC-200 should be avoided because of its lack of thermal stability.

The "b" and "r" constants were included in McReynolds original paper[20]; they are omitted from many tabulations[24], but not from all[31]. These constants are useful in the selection of a stationary phase to give the best separation for an homologous series, for example - Apiezon L and SE-30 have almost identical McReynolds constants yet Apiezon L has higher "b" and "r" values. Therefore, Apiezon L should provide better separations of a homologous series of aliphatic compounds than SE-30. Yancey[31] would expect similar

improved separations for any series of homologous compounds using the phase with the higher "r" value.

The use of Rohrschneider or McReynolds constants will not answer every question concerning a gas chromatographic separation. They give no information concerning relative efficiencies and peak shape (tailing). Even though two phases have the same McReynolds' constants, the most efficient separation (sharpest peaks) will be given by the phase with lowest viscosity at the analysis temperature. McReynolds' constants are normally determined at 20% loadings to minimize the surface effects of the stationary phase. However, most g.c. work is done at much lower loadings and the active (non-silanised) surface of any support may well have some effect on the selectivity. Selectivity on capillary columns is reported to be somewhat different from that indicated by the McReynolds's constants[29]. No information is given about the tailing of the more polar compounds which can be caused by adsorption on the support. The estimated polarity of stationary phases may well be different at temperatures other than 120°C, the temperature at which McReynolds's constants are determined.

The McReynolds' constants provide the best information currently available for comparison of the selectivity of the g.c. stationary phases and aid in the selection of a new phase which might provide an improved g.c. separation for solving an analytical problem.

Rapid tests of "column polarity", examination of tailing, residual chemical reactivity and determination of ageing are usefully carried out using test mixtures designed for column evaluation.

TEST MIXTURES AND COLUMN EVALUATION

The relative retention of a sample containing components of similar boiling points but different polarities gives useful information on column polarity and also on performance. Averill[33] recommends the use of a so-called polarity mixture with the following composition:

TABLE 4. Averill Polarity Mixture

Component	Bp (°C)	Composition (volume ratios)
Ethanol	78.5	40
Methyl ethyl ketone	79.6	20
Cyclohexane	81.4	5
Benzene	80.1	10

Betts, Finucane and Tweedie suggest the use of (-) linalool, estragole and (+) carvone at 160° as a practical system for polarity testing of packed columns[34].

More complicated mixtures have been used to evaluate residual chemical reactivities and capillary column efficiency. For example Grob, Grob and Grob[35] use a 12 component mixture (Table 5) in a single temperature-programmed run to obtain quantitative information on the adsorption of hydroxygroups and of aldehyde groups, separation efficiency, acid-base behaviour and film thickness. Standardisation of conditions allowed the characteristics of columns with different stationary phases to be compared directly.

TABLE 5. Composition of Grobs' Test Mixture

Component	Concentration (mg/L)	Component	Concentration (mg/L)
C_{12}-acid methyl ester	41.3	Nonanal	40
C_{11}-acid methyl ester	41.9	2,3-Butanediol	53
C_{10}-acid methyl ester	42.3	2,6 Dimethylaniline	32
Decane	28.3	2,6 Dimethylphenol	32
Undecane	28.7	Dicyclohexylamine	31.3
1-Octanol	35.5	2-Ethylhexanoic acid	38

Of the various methods and quantities proposed to measure separation efficiency the Grob's prefer the use of TZ values. Should only the acid/base ratio of a column be required a simpler mixture consisting of 0.5mg/ml each of 2,6-dimethylaniline (DMA) and 2,6-dimethylphenol (DMP) in methylene chloride may be used[36]. Both "Grob" mixtures are available commercially prepared[37]. Poole and Schuette[38] state that the column test procedure designed by Grob is now universally used by both column producers and column users and it supplants the use of the various polarity test mixtures used previously. They also provide a useful summary chart for the stepwise procedure for performing the Grob test and point out three problems with the test. These are that it cannot be used to test columns coated with liquid phases of high melting point, that the elution order of the test mixture is not the same on all stationary phases and the occurrence of co-elution of peaks cannot be entirely eliminated. Temmerman and Sandra[39] have reported on the stability of the Grob polarity mixture; they found low responses for dimethylaniline and for nonanol, and that an extra compound eluted at high temperature. The structure of the extra compound was shown by m.s. to be the Schiff base formed between the two compounds and suggest the use of two mixtures one without the aldehyde and the other without the amine. Grob[40] accepts the findings and suggests it would be advantageous to design a new perfectly stable mixture. However the formation of the Schiff base(s) occurs only in the first few days after mixing. The corresponding loss of aldehyde and base can be empirically compensated.

It is thus interesting to note that Kimpenhaus, Richter and Rohrschneider's[41] test mixture (Table 6) does not contain an amine. They also favour TZ values and describe a computer programme for the column characterisation and testing.

TABLE 6. Components of Kimpenhaus *et al* test mixture

1	Methane = inert gas	5	n-Undecane	9	n-Tetradecane
2	n-Hexane	6	n-Dodecane	10	Methyl-n-undecanoate
3	n-Nonane	7	n-Tridecane	11	1-Dodecanol
4	n-Decane	8	Cyclododecane		

RECOGNITION OF PATTERNS OF COLUMN SELECTIVITY BEHAVIOUR

Simple graphical representation of data reaches its practical limit with the plotting of triangular diagrams thus correlating three variables in an easy visually acceptable format. Triangular diagrams are well established from their use in physical chemistry for the representation of ternary phase diagrams[42]. Since only three factors can be represented, it is necessary to select three columns or three solutes to test, or represent, the most significant retention mechanisms.

Brown[43] found that n-decane, 1,1,2 trichloroethane and dioxane or n-hexane, ethanol and 2-butanone were useful test solutes to classify stationary phases and that S.E.30, N.G.S. and Q.F.I. or squalane, P.E.G. and Fluorene picrate were useful stationary phases to classify solutes based on interactions with non-polar, electron acceptor and donor compounds or phases.

For solvent phase classification, Snyder[44] used test solutes ethanol, nitromethane and dioxane to test for hydrogen bonding interactions (proton donor, proton acceptor) and dipole interactions. Kovats indices[22] were calculated from adjusted retention times for each probe solute on each stationary phase. Corrected indices for the solutes on a deactivated squalane column were substracted to determine the ΔI values. Selectivities, x_i, were calculated and plotted on the face of the 'selectivity triangle' by using the equation:

$$x_i = \frac{\Delta I_i}{\Delta I_e + \Delta I_n + \Delta I_d}$$

Where ΔI_i, ΔI_e, ΔI_n and ΔI_d are differences in retention indices for probe solutes, ethanol, nitromethane and dioxane, respectively. The denominator of this ratio reflects excess retention due to polar interactions; the larger the $\Sigma\Delta I_i$, the more significant the polar contribution of the stationary phase to retention of a solute. Klee, Kaiser and Laughlin[45] use a five component mixture (Table 7) in which acetonitrile (strong dipole) 2-propanol (proton donor) and triethylamine (proton acceptor) are used in place of Synder test solutes to obtain the triangle for stationary phases. Phases with similar selectivity properties lie in the same region of the triangle.

TABLE 7. Composition and Physical Properties of Klee *et al.* test mixture

Solute	Boiling point (°C)	Molar Volume (ml/mole at 20°C)	Dipole moment (Debye)
Acetonitrile	81.6	52.5	3.44
2-Propanol	82.3	76.5	1.66
1,2-Dichloroethane	83.5	79.0	1.86
Triethylamine	89.3	139.1	0.66
Octane	125.7	162.6	0.0

Total "polarity" may be included in the graphical representation by plotting selectivity triangles against $\Sigma\Delta I$, analogous to the representation of four component phase diagrams,[46] [47] forming a triangular prism.

Some alternative concepts of polarity have been suggested based on well physicochemically defined quantities generally using two probe solutes[25]. For example Maier and Karpathy[48] use as polarity the retention ratio of a polar or polarizable solute RX to that of one which is non-polar RH, for a non-polar standard column, n, to which a zero polarity is attributed:

$$P_p = \log(V_p^{RX}/V_p^{RH}) - \log(V_n^{RX}/V_n^{RH}).$$

The retention ratio for another polar/non-polar pair of solutes in the liquid phase p is then expressed by:

$$\log(V_p^{RX'}/V_p^{RH}) = A^{RX'}P_p + \log(V_p^{RX'}/V_p^{RH})$$

where $A^{RX'}$ is a constant characteristic of the solute RX'. Chovin and Lebbe[49] expanded this polarity scale, which was based on a unit of the retention ratio of butadiene to n-butane and used the retention ratio of two consecutive paraffins; the more polar the phase the smaller the value of α :

$\alpha = V_{g(z+1)}/V_{g(z)}$. This was later given as "r" by McReynolds (16).

Littlewood[50] also used neighbouring paraffins and observed that the relative retention of two neighbouring paraffins is, as their vapour-pressure ratio, dependent upon the number of carbon atoms, at least for less than nine carbon atoms. Hence the relative retention of two n-alkanes is only characteristic for those phases in which the solutes are not very soluble, i.e. for polar and very polar stationary phases. On the other hand, for phases in which the solutes are more soluble, the variation of the relative retention with the phases was too small, and did not permit an accurate classification. Bonastre and Grenier[51] define polarity as

$$P = 10^3 \times \gamma^{\infty}_{z+1} \gamma^{\infty}_{z}$$

where γ^{∞}_{z+1} and γ^{∞}_{z} are the activity coefficients at infinite dilution of two neighbouring n-alkanes.

More recently Sevcik and Lowentap[52] have advocated a criterion "A" for the classification of stationary phase polarity. "A" is defined by the ratio of retention time differences for adjacent n-alkanes:

$$A = \frac{t'_{Rn+1} - t'_{Rn}}{t'_{Rn} - t'_{Rn-1}}$$

but determined using a series of results. The polarity criterion A represents dispersive interactions of the methylene group with the stationary phase. It depends on the structure and the number of functional groups in the stationary phase and its temperature:
$A = a \exp(bT^{-1})$. The constants a and b have an unequivocal physical meaning and allow the prediction of the polarity of a stationary phase at any temperature. The influence of pressure and carrier gas flow-rate on the polarity criterion "A" were found to be insignificant.

The disadvantage of the two-test-probe approaches to measurement of polarity is the possible underestimation of forces of interaction between a solute molecule and molecules of the stationary phase. The forces of interaction are complex and the use of a restricted range of test solutes might well ignore factors which may operate in a given separation, also a change in test solutes would almost certainly change the order of classification of a series of columns. Hence the Rohrschneider and McReynolds' constant systems are preferred even though it is more difficult to obtain the data.[53] Their application to given separations, based on recognition of key structural features of the molecules to be separated, is more likely to appeal to a broad spectrum of chemists as patterns of structurally related behaviour have to be deduced if they are not naturally based on the test solutes.

More comprehensive approaches involve clustering although other pattern recognition techniques have been used[54-57]. The basic principles and the application to the classification of stationary phases in g.l.c. have been reviewed by Massart *et al.*[58]. The clustering of common stationary phases has been evaluated using chlorophenoxy alkyl esters as test substances[59]. Huber and Reich[60] have compared four measures of polarity namely, the McReynolds polarity constant, the euclidian distance of the

selected phase relative to the most non-polar stationary phase (squalane), the mean of the retention indices of all key solutes, and the length obtained by transversal of the minimum spanning tree. Ten solutes were selected from 158 for the classification of phases by each system. Correlation coefficients of 1.0000 were found for the McReynolds and for the mean value systems.

CHEMICAL COMPOSITION OF LIQUID STATIONARY PHASES

The relative selectivity and overall polarity are functions of the chemical composition and physical state of the phases. The most comprehensive review of chemical composition of phases is that by Baiulesc and Ilie[25]. Many manufacturers now give much useful information[31]. A valuable set of reviews appeared in J. Chromat. Sci. starting in 1973 dealing with the common phases, polyethylene glycols[61], polyesters[62], methylsilicones[63], other silicones[64], E.G.S. and D.E.G.S.[65]. Haken has discussed the chemistry and use of polysiloxane phases[65][68] as has Yancey[69].

Laub and Purnell[70][71] have demonstrated the advantages of using mixed stationary phases. Using linear interpolation between the retention parameters in the pure phases and their volume fractions ϕ in mixtures one can calculate sets of retention data for mixed phases. Plotting ϕ for each pair of components against ϕ generates a window diagram, the best separation is the window with the highest α value.

CONCLUSIONS

(1) The McReynolds' constants currently provide the best information for the selection of gas chromatography stationary phases.

(2) If it is required to express the "polarity" of a stationary phase as a single number that the sum of the Rohrschneider-McReynolds X + Y' + Z' + U' + S' terms is the most suitable.

(3) For separation of a homolgous series on columns with a given polarity, the column with the highest value of b, the slope of the n-alkane, log (net retention time) against carbon number plot, should be used.

(4) For a given set of McReynolds values (or polarity) and value of b the phase with the lowest viscosity gives the best resolution.

(5) When stationary phases are equivalent in polarity etc. that with the widest useful temperature range should be obtained.

(6) For column evaluation the Grob mixture and test procedure is now widely used and for most purposes supplants the various polarity mixtures used earlier.

REFERENCES

(1) G Hesse, Z. Anal. Chem., 211, 5, (1965).
(2) C Horváth, "Columns in Gas Chromatography" in L S Ettre and A. Zlatkis (editors), "The Practice of Gas Chromatography" Interscience, New York, (1967).
(3) T Juutilainen and J Enquist, J. Chromat., 279, 91, (1983).
(4) J R Conder and C L Young, "Physical chemical Measurement by Gas Chromatography", Wiley, Chichester, (1979).

(5) R A Keller, R Bate, B Costa and P Forman, J. Chromat., 8, 157, (1962).

(6) "Recommendations on Nomenclature for Chromatography", Pure and Applied Chemistry, 37, 445, (1974).

(7) J J van Deemter, F J Zuiderweg and A Klinkenberg, Chem. Eng. Sci., 5, 271, (1956).

(8) H M N H Irving, H Freiser and T S West (eds), "Compendium on Analytical Nomenclature", Pergamon, (1978).

(9) "Annual Book of ASTM Standards Part 42. Analytical Methods - Spectroscopy; Chromatography in Computerised Systems." ASTM, Philadelphia, (1980).

(10) J H Purnell, J. Chem. Soc., 1268, (1960).

(11) J H Knox (ed), "High-Performance Liquid Chromatography", Edinburgh University Press, Edinburgh, (1978), p.7.

(12) A S Said, "The Theory and Mathematics of Chromatography", A. Huthig Verlag, Heidelberg, (1981).

(13) R E Kaiser, Chromatographia, 9, 337 and 463, (1976).

(14) R E Kaiser and R Rieder, Chromatographia, 10, 455, (1977).

(15) J H Hildebrand and R.L. Scott, "The Solubility of Nonelectrolytes", 3rd. ed., Reinhold, New York, (1950).

(16) N Ewell, J M Harrison and L Berg, Ind. Eng. Chem., 36, 871, (1944).

(17) H M McNair and E J Bonelli, "Basic Gas Chromatography", 5th ed, Varian Aerograph, Walnut Creek, (USA), (1969).

(18) L Rohrschneider, J. Chromat., 17, 1, (1965).

(19) L Rohrschneider, J. Chromat., 22, 6, (1966).

(20) W O McReynolds, J. Chromat. Sci., 8, 685, (1970).

(21) L Rohrschneider, Z. Anal. Chem., 170, 256, (1959).

(22) E Kováts, Helv. Chim. Acta, 41, 1915, (1958).

(23) W R Supina, "The Packed Column in Gas Chromatography", Supelco, Bellifonte, (USA), (1974).

(24) W R Supina and L P Rose, J. Chromat. Sci., 8, 214, (1970).

(25) G E Baiulescu and V A Ilie, "Stationary Phases in Gas Chromatography", Pergamon, Oxford, (1975).

(26) L S Ettre, Chromatographia, 6, 489, (1973).

(27) L S Ettre, Chromatographia, 7, 39, (1974).

(28) L S Ettre, Chromatographia, 7, 261, (1974).

(29) K Grob and G Grob, Chromatographia, 17, 481, (1983).

(30) J Lukáš, J. Chromat., 190, 13, (1980).

(31) J A Yancey (ed), "Guide to Stationary Phases for Gas Chromatography", 11 edn, Analabs, North Haven, (USA), (1977).

(32) S M McCowan and K L Tuttle and C G Manos, Int. Lab. 80 (Nov/Dec), 1979.

(33) W Averill in N Brenner, J E Callen and M D Weiss (eds), "Gas Chromatography", Academic Press, New York, (1962) pp. 1-6.

(34) J T Betts, G J Finucane and H A Tweedie, J. Chromat., 213, 317, (1981).

(35) K Grob, G Grob and K Grob, J. Chromat., 156, 1, (1978).

(36) K Grob and G Grob, Chromatographia, 4, 422, (1971).

(37) For example see Supelco Chromatography Catalogue 21, (1983).

(38) C F Poole and S A Schuette, "Contemporary practice of chromatography", Elsevier, Amsterdam, (1984).

(39) I Temmerman and P Sandra, J. High Res. Chromat. and Chromat. Comm., 7, 332, (1984).

(40) K Grob, J. High Res. Chromat. and Chromat. Comm., 7, 333, (1984).
(41) W Kimpenhaus, F Richter and L Rohrschneider, Chromatographia, 15, 577, (1982).
(42) G Masing (B A Rogers trans), "Ternary Systems", Dover, New York, (1960).
(43) I Brown, J. Chromat., 10, 284, (1963).
(44) L R Snyder, J. Chromat., 92, 223, (1974).
(45) M S Klee, M A Kaiser and K B Laughlin, J. Chromat., 279, 681, (1983).
(46) D A Clibbens, "The Principles of Phase Theory", MacMillan, London, (1920).
(47) F Tamás and L Pál (L S Ward trans ed.), "Phase Equilibria Spatial Diagrams", Akadémiai Kiadó, Budapest, (1970).
(48) H J Maier and O C Kárpáthy, J. Chromat., 8, 308, (1962).
(49) P Chovin and J Lebbe, Separation Immediate et Chromatographie 1961, GAMS, Paris, 1961, p.61.
(50) A B Littlewood, J. Gas Chromat., 1, 16, (1963).
(51) J Bonastre and P Grenier, Bull Soc chim Fr., 1395, (1967); 118, (1968).
(52) J Ševčík and M S H Löwentap, J. Chromat., 217, 139, (1981).
(53) P Souter, J. Chromat., 92, 231, (1974).
(54) S Wold and K Andersson, J. Chromat. 80, 43, (1973).
(55) D H McCloskey and S J Hawkes, J. Chromat. Sci., 13, 1, (1975).
(56) J J Leary, J B Justice, S Tsuge, S R Lowry and T L Isenhour, J. Chromat. Sci., 11, 201, (1973).
(57) M Chastrette, J. Chromat. Sci., 14, 357, (1976).
(58) D L Massart, M Lauwerys and P Lenders, J. Chromat. Sci., 12, 677, (1974).
(59) J O De Beer and A M Heyndrickx, J. Chromat., 235, 337, (1982).
(60) J F K Huber and G Reich, J. Chromat., 294, 15, (1984).
(61) H E Persinger and J T Shank, J. Chromat. Sci., 11, 190, (1973).
(62) D G Anderson and R E Ansel, J. Chromat. Sci., 11, 192, (1973).
(63) C R Trash, J. Chromat. Sci., 11, 196, (1973).
(64) A E Coleman, J. Chromat. Sci., 11, 198, (1973).
(65) R F Kruppa and R S Henly, J. Chromat. Sci., 12, 127, (1974).
(66) J K Haken, J. Chromat., 73, 419, (1972).
(67) J K Haken, J. Chromat., 141, 247, (1977).
(68) J K Haken, J. Chromat., 300, 1, 1984.
(69) J A Yancey, J. Chromat. Sci., 23, 161, (1985).
(70) R J Laub and J H Purnell, J. Chromat., 112, 71, (1975).
(71) J H Purnell, Phil Trans R. Soc. Lond., A305, 657, (1982).