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TRIANGULAR CHARACTERIZATION OF GAS CHROMATOGRAPHIC STATIONARY PHASES

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SUMMARY

Three solute probes used by McReynolds, butanol, pyridine and octyne, were selected to check retention index (I_R) values on various packed columns. Their ratios proved more consistent than their absolute values. A triangular plot of relative I_R suggested three groupings of stationary phases: polar, non-polar and intermediate. Three selected polysiloxanes should suffice to represent these groups for most work.

INTRODUCTION

Shah *et al.*[1] recently published a Snyder Triangle method for characterization of gas chromatographic (GC) stationary phases. Snyder[2] constructed his triangular plot for evaluating solvents, not stationary phases, using 1973 data recorded by Rohrschneider[3]. Snyder used, in effect, the expression

$$x_e + x_d + x_n = 1 \quad (1)$$

where x_e is the fraction of the polarity index of the solvent contributed by its interaction with the test solute ethanol; and similarly for dioxane (d) and nitromethane (n). These x values were plotted triangularly in an eccentric manner, and allowed Snyder to circle eight groups of solvents inside his triangle. A resulting problem was that water and chloroform were grouped together! It is notable that the above three test solutes had been used by Rohrschneider[4] or McReynolds[5] as probes in their evaluations of GC stationary phases.

Klee *et al.*[6] in 1983 applied such triangular plots in an attempt to formulate a systematic approach to the selection of GC stationary phases. They used ΔI for x in formula 1, where "corrected indices for the solutes on a deactivated squalane column were subtracted" from the retention indices of the probe solutes on the test stationary phase. In their triangular plots they shift the spatial positions of Snyder's solvent group circles, including the reversal of numbering for the first two. The Klee *et al.*[6] plots in fact do not correspond to Snyder's[2], for an inspection of the latter's work shows two axes are for 0.23–0.73, whilst the x_d axis is for 0.04–0.54. The Klee *et al.* triangle has two axes of 0.2–0.7, with an x_d axis of 0.1–0.6, which shifts its

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position significantly. Their triangle is cut from a complete triangular plot near to the ethanol axis, and hence it is unrealistic for them to remark on the need for "representative phases ... lying in the corners of the selectivity triangle"[6]. They could have produced them by cutting a different triangle!

Shah *et al.*[1] studied the use of two more McReynolds solute probes, but never three together! It seems sensible to make use of the extensive literature on such probe ΔI values. Shah *et al.* concluded, not surprisingly, that "the classification of GC phases is solute dependent ... the selection of the solute probe can greatly affect the location of the stationary phase in the selectivity triangle". Equally so by changing the axes of the triangle!

In some much earlier work (1963) on stationary phases by Brown[7] retention volumes were used for values of x. Two of his solute probes were later chosen by Rohrschneider[4] or McReynolds[5]. Brown noted that "the non-polar phases are close the the *n*-decane apex (of the triangle) while the (electron) donor-type phases are towards the trichloroethane apex", an example being polyethyleneglycol.

The present work was undertaken initially to use and check published McReynolds values for x, to see if they could characterize GC stationary phases in a triangular plot. Three groups of GC stationary phases were determined as a consequence.

EXPERIMENTAL

Instrumentation

A Pye-Unicam GCD gas chromatograph was used, fitted with a flame ionisation detector. The recorder was a Hewlett-Packard 3390A integrator. The column oven temperature was always 120°C, the injection port temperature 225°C and the detector temperature 300°C. The mobile phase was high purity nitrogen at 40 ml min^{-1} for 4-mm I.D. columns (20 ml min^{-1} for the 2 mm I.D. columns, see Table I). Hydrogen was supplied to the detector at about 30 ml min^{-1}.

Columns

Packed columns from our laboratory "library" were used, some purchased over ten years ago, some newly prepared for this work. The GC stationary phase loadings ranged from 1.5 to 15% (when prepared) on 80–100 mesh supports, some silanized. Further details in Table I.

Solutes for injection

Volumes of 0.1–0.2 μl of commercial grade solutes were injected together with items from a "McReynolds' Kit" (PolyScience Corp.) using a Hamilton microsyringe. Inspection of published McReynolds' values[5] and some trials suggested the selection of the following three solute probes: (i) 2-octyne as an aliphatic, non-polar hydrocarbon showing more discrimination than a fully saturated substance (McReynolds' k), (ii) *n*-butanol as an aliphatic, oxygen-containing, electrophilic compound (McReynolds' y'), and (iii) pyridine as an aromatic, nitrogen-containing nucleophilic substance (McReynolds' s'). These three have fairly short retention times on various GC stationary phases at 120°C, and their elution sequence alters according to the type of stationary phase.

TABLE I

OBSERVED AND CALCULATED I_R AND x VALUES FOR SOME PACKED GAS CHROMATOGRAPHIC COLUMNS

x = (I_R of solute)/Σ(I_R three solutes). Values in italics calculated from literature[5,8]. (ΔI for phase + I_R squalane) UV absorbance studies[11] suggest the phenyl content of OV-17 is just over 40%. SP-2330 contains 2% carboxamide groups[12].

Stationary phase	*Column details*	*n-Butanol*		*Pyridine*		*2-Octyne*	
		I_R	x	I_R	x	I_R	x
Squalane	10% in 1.0 m × 4 mm I.D. steel	610 *590*	0.282 *0.277*	705 *699*	0.325 *0.328*	852 *841*	0.393 *0.395*
OV-1 (methyl polysiloxane)	2% in 1.5 mm × 4 mm I.D. glass	663 *645*	0.294 *0.287*	737 *741*	0.326 *0.329*	859 *864*	0.380 *0.384*
SE-30 (methyl polysiloxane)	2% in 1.0 m × 4 mm I.D. steel	645 *643*	0.287 *0.286*	743 *740*	0.330 *0.330*	860 *863*	0.383 *0.384*
SP-2100 (methyl polysiloxane)	2% in 1.0 m × 4 mm I.D. glass	651 *647*	0.288 *0.287*	746 *742*	0.331 *0.329*	860 *866**	0.381 *0.384*
OV-17 (phenyl-methyl polysiloxane)	1.5% in 1.5 m × 4 mm I.D. glass	747 *748*	0.293 *0.288*	871 *901*	0.342 *0.347*	930 *946*	0.365 *0.365*
SP-2250 (phenyl-methyl polysiloxane	3% in 2.0 m × 4 mm I.D. steel	738 *748*	0.288 *0.288*	887 *901*	0.346 *0.347*	936 *946**	0.366 *0.365*
OV-210 (trifluoropropyl-methyl polysiloxane)	15% in 1.5 m × 2 mm I.D. glass New column	815 *828*	0.304 *0.303*	977 *1009*	0.364 *0.369*	891 *897*	0.332 *0.328*
OV-225 (cyanopropyl-phenyl-dimethyl polysiloxane)	3% in 1.0 m × 4 mm I.D. glass New column	939 *959*	0.317 *0.316*	1046 *1085*	0.353 *0.357*	980 *991*	0.330 *0.327*
SP-2330 (nonacyanopropyl-methyl polysiloxane)	10% in 1.0 m × 4 mm I.D. steel New column	1263 *1315*	0.336 *0.333*	1397 *1477*	0.372 *0.375*	1097 *1153**	0.292 *0.292*
PEG 1000 (polyethylene glycol mol.wt. ≈ 1000)	10% in 1.5 m × 2 mm I.D. glass	1159 *1197*	0.337 *0.336*	1228 *1288*	0.357 *0.361*	1052 *1081*	0.306 *0.303*
PEG 20M (polyethylene glycol mol.wt. ≈ 15000)	10% in 1.0 m × 4 mm I.D. steel	1104 *1126*	0.332 *0.331*	1180 *1209*	0.355 *0.356*	1041 *1062*	0.313 *0.313*
DEGS (diethylene glycol-succinate polymer)	15% in 1.0 m × 4 mm I.D. steel	1229 *1323*	0.331 *0.333*	1363 *1490*	0.368 *0.375*	1115 *1162*	0.301 *0.292*

* Estimated values, none being found in the literature.

RESULTS AND DISCUSSION

Whilst the use of retention index (I_R) values should be more reliable than retention volumes, there seems to be no point in subtracting from them a constant set of I_R values for reference squalane to obtain ΔI. Thus the probe I_R values were calculated from the literature[5,8] and also determined experimentally. Discrepancies were found, in some cases, which do not seem to be due to the differing ages and histories of the columns used. Newly prepared columns are indicated in Table I, where average results are recorded. x values from this table are plotted in Fig. 1, where the axes have been selected to best display the results. The experimentally obtained x values are in good agreement with those derived from the literature, even though I_R values are not always close. Results for SE-30, in an old steel column, are in closest agreement. As the solute probe I_R values increase with the study of more polar phases, so do the discrepancies. These are negative for the polar stationary

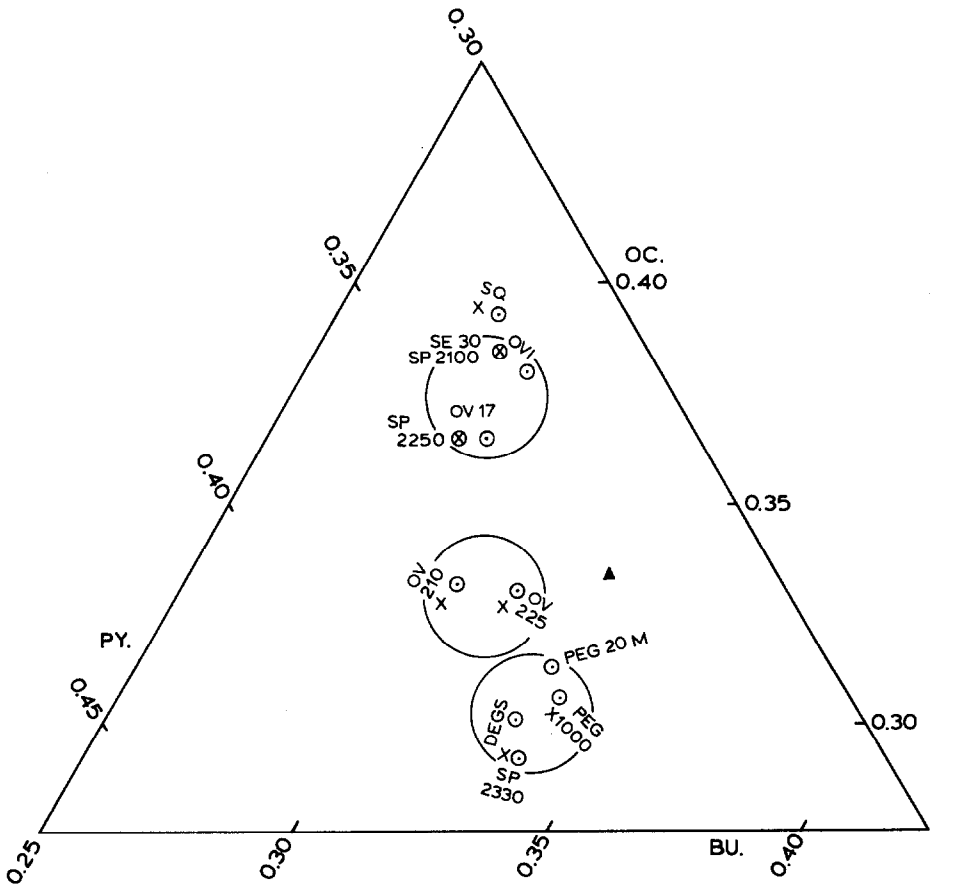

Fig. 1. Plot of relative I_R values of gas chromatographic stationary phases using solute probes of 2-octyne (OC.), *n*-butanol (BU.) and pyridine (PY.). (▲) Centre of full triangular plot; (⊙) experimental values; × values calculated from the literature, where different to experimental values. Given for squalane (SQ), OV-1, OV-17, OV-210, OV-225, PEG 1000, DEGS and SP-2330. See Table I for explanation of phases.

phases, but positive for the non-polar squalane. Shah *et al.*[1] reported great difficulty in obtaining I_R on squalane corresponding to "corrected" values of Klee *et al.*[6] and blamed this on free silanol support groups, and the need to deactivate the column wall. In theory, this should not matter, unless the probe solutes are retained differently to the reference alkanes used for I_R determinations. Also, theoretically, the column loading of stationary phase is irrelevant, for McReynolds[5] did not indicate what he used; nor if each column was freshly prepared for his studies, of the same dimensions, with the same mobile phase gas flow-rate. The only experimental detail in his paper is "all data were obtained at 120°C", and there is no indication of the reliability of his values, which have been quoted repeatedly in the literature without question. From the present work, it appears that ratios of I_R for several solutes may be more consistent than absolute I_R values. Second columns of SP-2100 and of PEG 20M gave very similar results to those quoted in Table I.

A GC stationary phase showing exactly equal affinity for each of the three solute probes will have the same x value for each, and will plot at 0.333 in the centre of the full triangle. As one x value increases, the other(s) must decrease, as the three total unity. The stationary phases coming nearest to 0.333 are polyethylene glycol 20M, and the cyanopropyl-, phenyl-, dimethylpolysiloxane OV-225, which are both favoured by the *British Pharmacopoeia*[9] in its monographs. Furthest removed from 0.333 are the fully methyl-polysiloxanes and, in a different direction within the triangle, the nonacyanopropyl-, methylpolysiloxane SP-2330. The lattermost forms a group of relatively polar GC stationary phases together with polyethylene glycols and the polyester phase which is enclosed on the triangular plot Fig. 1 with a circle of diameter 0.025 centred at about (0.365 pyridine, 0.333 butanol). The more stable polysiloxane phase could probably replace the others for general use as they all show the same sequence of solute probe retention times, octyne, butanol, pyridine (slowest), indicating their lack of affinity for the non-polar octyne.

The non-polar group of GC stationary phases is also enclosed by the same size circle in Fig. 1 centred at (0.375 octyne, 0.337 pyridine), consisting of the fully methyl and methyl-, phenylpolysiloxanes. Like squalane, their affinity for octyne is shown by the common solute sequence butanol, pyridine, octyne (slowest). This leaves an intermediate polarity group of phases characterised by the solute probe sequence butanol, octyne, pyridine. It includes the trifluoropropyl-, methylpolysiloxane OV-210, and OV-225 which are enclosed by a circle centred at (0.360 pyridine, 0.330 octyne). A conclusion that can be made is that GC laboratories, and *British Pharmacopoeia* monographs, could limit themselves to a "library" of columns of three types of polysiloxanes alone: the highly polar type with a high content of cyanopropyl side-chains; the low polarity type which are fully methyl; and an intermediate type with half the side chains trifluoropropyl groups. The only problem with the lattermost type of GC stationary phases is that a column loading of 15% or more is needed to avoid excessively brief retention times, and to show its "unique selectivity"[10].

Yancey[10] in a recent review of polysiloxane GC stationary phases notes the "selective retention of benzene" by cyanoalkyls, which is confirmed in this work by pyridine showing the highest I_R and x value of any phase examined. These stationary phases also show "a shorter retention for an acetylinic compound" confirmed by the SP-2330 x value for octyne.

The present author was dismayed to see that Klee *et al.*[6] concluded by antici-

pating a "computerised optimization" of mixed GC stationary phases. There are already far too many; let us not mix them! McReynolds in his paper, which consists mainly of a table of results, concluded that it would "show the similarity of many liquid phases now in use. It is hoped that this data will help to reduce the number of liquid phases being used"[5]. The publisher of the journal, Preston[13], supported this and suggested "selecting 10 or 20 of the most frequently used liquid phases and designating these as preferred". He listed those most used from recent (1969) publications, and they included the polysiloxanes SE-30 (fully methyl), QF-1 (partly trifluoropropyl), and XE-60 (partly cyanoethyl). These correspond to the three types recommended in this paper, fifteen years later!

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