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Note

Practical system for polarity rating of packed gas–liquid chromatography columns

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The polarity of the stationary phase is accepted as being a significant factor in obtaining any separation of solutes by gas–liquid chromatography since the initial studies of Rohrschneider[1] in 1959. As absolute values of polarity cannot be obtained. relative values are utilised. Rohrschneider was the first to select squalane as the standard non-polar liquid phase, and he compared another test phase with it utilising two solute probes —an alkane and an alk(di)ene. A logarithmic ratio of retention volumes was involved, but following Kováts' introduction of retention indices[2] these were utilised by Rohrschneider[3] with firstly two solute probes, then five[4] and then seven[5], involving ratios again. In 1970 McReynolds[6] extended the number to ten probes, and worked at 120°C instead of the 100°C used by Rohrschneider. Over 200 stationary phases were compared with squalane, and this study has been much quoted and utilised, at times with only five probes, *e.g.* to obtain an average polarity expression[7]. However, although the probes used differ in polarity, all McReynolds values (ΔI_R, inappropriately termed "constants") are based on the ultimate non-polar series of *n*-alkanes used to determine retention indices (I_R). For any particular probe at 120°C:

$$\Delta I_R = I_{R_{\text{test phase}}} - I_{R_{\text{squalane}}} \text{ (against } n\text{-alkanes)} \quad (1)$$

Manufacturers of stationary phases quote them[8], perhaps for only five probes, most of them being positive numbers, sometimes as large as over 1000. They can be used to forecast whether two different stationary phases will behave in very similar or in quite different fashion, and thus facilitate the choice of substitute columns already possessed for a published procedure, or for the selection of radically different columns in an attempt to improve the separation of a previously poorly resolved mixture. McReynolds values indicate, for example, that various methyl polysiloxanes[8] (*e.g.* SE-30, OV-1, OV-101 and SP-2100) should function virtually identically.

Novák and Růžičková in 1974[9] introduced a "generalization" of the retention index system, pointing out that originally it indicated by a hundredfold the apparent carbon number (usually quoted with an excess of precision to one decimal place) of a solute *if* it were an *n*-alkane, and suggesting that it equally could be based on other homologous series such as 2-ketones, *n*-alcohols, or acetate esters of these. Kováts discussed this as long ago as 1965[10]. Others, too, have recommended polar *n*-al-

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cohols[11,12], and recently *n*-aldehydes[13] have been suggested as the ideal base series, being of intermediate polarity.

Many gas–liquid chromatographic procedures are best performed at temperatures higher than 120°C, and attempts have been made to determine a relationship between I_R and column temperature[14]. It has been claimed that I_R varies less than one unit per degree temperature rise[15], but for ΔI_R determination there is the limitation that the squalane standard phase is too volatile to be used above 140°C. The methyl polysiloxane SE-30 has been used as an alternative standard phase[16] and this withstands high temperatures, whilst hydrogenated Apiezon MH has been used at 160 to 190°C with five aromatic probe solutes[17]. A "g-pack" of six probes, including the monoterpene limonene, the terpene alcohol linalool with its acetate ester, and cinnamyl alcohol which is typical of volatile oil aromatics, has recently been adopted[18] to check —together with *n*-alkanes— that polyethyleneglycol columns are in suitable condition for volatile oil "fingerprinting" at up to 225°C.

The McReynolds system, or variations on it, is designed to characterise the liquid stationary phase, but not a packed column —unless it has been freshly prepared for this experimental purpose. After a period of use, when it may have "mellowed" satisfactorily, there is no easy way to determine the loading of stationary phase remaining in the column. It has been found[19] that nearly 9% of the medium-molecular-weight polyethylene glycol 6000 may evaporate from a support after only 2 h at 100°C.

McReynolds values also imply using identical concentrations of test and standard stationary phases in identical columns. In practice, gas–liquid chromatography is not like this. Polysiloxanes are commonly prepared with a 2 to 5% loading, whilst polyglycols and polyesters are often present initially at 3 to 15% of the weight of column packing. Thus a *practical* system of values is needed to express the relative polarities of the "library" of columns kept by each laboratory. This automatically takes account of the varied history and possible misuse of individual columns.

Eqn. 1 can be adapted for this purpose by selecting a higher temperature with appropriate probes, utilising other standard series besides *n*-alkanes, selecting a higher temperature reference stationary phase (*i.e.* replace squalane), and examining test phases as they have been loaded (and used) in columns. The work reported here involves a study of five of our packed columns (three containing polysiloxanes), with three standard series, and three probes.

EXPERIMENTAL

Apparatus and materials

A Pye 104 gas chromatograph was used, fitted with a flame ionisation detector used at 175°C together with a Linear Instruments recorder.

Columns packed with stationary phase on support were those in the laboratory "library", and are described in Table I.

Solutes were laboratory grade, from various commercial sources.

Procedure

A temperature of 160°C was chosen as being of more general value than 120°C; and three C_{10} volatile oil substances which had short retention times (<9 min) with

nitrogen flow-rate at 40 ml/min, and which represented a range of chemical structures, were selected as probes. They were, in constantly observed retention time (t_R) sequence:

(−)-linalool (alcohol, acyclic, unsaturated (2Δ))	shortest t_R
estragole (aromatic ether, *p*-methoxy-allylbenzene)	medium t_R
(+)-carvone (ketone, cyclic, unsaturated (2Δ))	longest t_R

Each of the five columns, prepared at different times in the past, and used for various purposes, was allowed to stabilise under the standard operational conditions and then received successive and repeated injections of: (i) mixture of the three probes in alcohol, (ii) mixtures of appropriate *n*-alkanes (PolyScience Corp., Niles, IL, U.S.A.), (iii) mixture of *n*-aldehydes in alcohol (C_8 and C_{10} used), (iv) mixture of *n*-alcohols in alcohol (C_8, C_{10} and C_{12} used).

The various retention indices of the three probes were obtained from graphic plots on semi-log paper of t_R (log scale) against carbon number of the three standard series (*n*-alkanes, *n*-alcohols and *n*-aldehydes). Probe I_R against each series is a hundred times the apparent carbon number, by definition. In theory these plots are accepted as straight lines; however a curve was apparent in some cases, especially for the lower alkanes. The graphical determination clearly indicates the limitations of accuracy not apparent in the formula method of Kováts[2] and should be less subject to error[20].

RESULTS AND DISCUSSION

The retention indices observed from repeated observations on the five selected columns are detailed in Table I. Very consistent results were obtained against alkanes on all the polysiloxanes, against alcohols on SP-2250 and PEG 20M, and against aldehydes on OV-1, SP-2250 and DEGS.

In other cases, results showed a surprising variation for what should be a standard procedure. The consistent results obtained with the SP-2250 column led to its selection as the polarity reference base column for *this* laboratory, despite it being not the least (nor most!) polar of the columns studied. Table II gives ΔI_R values against this polarity base column obtained with the other four columns for each probe, referred to each of three standard series (alkanes, alcohols and aldehydes). The average ΔI_R for the set of three probes against each series is also given, together with combined averages against alkanes and alcohols, which seem to provide satisfactory column polarity ratings. Values both negative and positive resulted.

It is notable that the two fully methyl polysiloxane columns, OV-1 and SP-2100, which should behave identically, show different ΔI_R values. This is least apparent when they are rated against the aldehydes series, for which their average values are similar. However, when compared using alkanes and alcohols, they are dissimilar, one being almost twice as non-polar as the other, possibly reflecting their differing history of use, or that the SP-2100 is on a silanized support, which minimises support interaction[21]. The DEGS column is clearly the most polar, but the apparent polarity of the PEG column changes with the reference series used. Against alcohols (which have great affinity for it) it is less polar than the base SP-2250, although it is clearly more polar than the base against alkanes or aldehydes. Using only the classic retention index standard of paraffins, Schomburg observed[22] that a silicone oil stationary

TABLE I

AVERAGE GRAPHICALLY DETERMINED I_R AND t_R OBSERVED AT 160°C WITH NITROGEN FLOW-RATE 40 ml/min

Average results are shown in italics, with the range observed where variation was found.

	Stationary phase				
	OV-1 polysiloxane (fully methyl)	*SP-2100 polysiloxane (fully methyl)*	*SP-2250 polysiloxane (phenyl–methyl, 50:50)*	*PEG 20M polyethylene glycol (20,000 mol. wt.)*	*DEGS polyester (diethyleneglycol succinate)*
	Column details				
	2% on Diatomite CQ 120–150 mesh in glass, 1.5 m × 4 mm I.D. (old)	*2% on Chromosorb W AW DCMS 80–100 mesh in glass, 1.5 m × 4 mm I.D. (recent)*	*3% on Supelcoport, 100–120 mesh in stainless steel, 3.0 m × 5 mm I.D. (recent)*	*10% on Diatomite C AW 100–120 mesh in stainless steel, 1.5 m × 5 mm I.D. (old)*	*15% on Chromosorb W AW 80–100 mesh in stainless steel, 1.5 m × 5 mm I.D. (old)*
I_R vs. n-alkanes					
Linalool	1061—*1068*—1076	1152—*1156*—1160	*1173*	1489—*1500*—1510	1780 approx.
Estragole	*1167*	*1227*	*1342*	1655—*1660*—1665	*
Carvone	1225—*1228*—1231	1258—*1265*—1272	1403—*1405*—1407	1724—*1731*—1738	*
I_R vs. n-alcohols					
Linalool	765— *773*— 781	820— *828*— 837	814— *822*— 830	795— *797*— 800	814— *820*— 832
Estragole	860— *865*— 870	928— *930*— 933	*993*	943— *948*— 955	1035—*1042*—1052
Carvone	943— *945*— 947	987— *991*— 996	1052—*1056*—1060	1017—*1025*—1028	1155—*1161*—1170
I_R vs. n-aldehydes					
Linalool	*875*	836— *861*— 891	879— *882*— 885	988—*1000*—1013	1040—*1045*—1051
Estragole	*962*	950— *975*—1002	*1073*	1182—*1190*—1199	1290—*1293*—1296
Carvone	*1052*	1022—*1045*—1072	1158—*1161*—1165	1278—*1282*—1287	*1427*
Approx. t_R (min)					
Linalool	0.50	1.05	1.50	2.30	3.20
Estragole	0.60	1.20	4.80	3.85	6.05
Carvone	0.70	1.40	6.05	4.95	8.40

* Relevant *n*-alkanes not resolved; determination impossible.

TABLE II

ΔI_R CALCULATED FROM TABLE I*

	Column			
	OV-1	*SP-2100*	*PEG 20M*	*DEGS*
Vs. n-alkanes				
Linalool	−105	−17	+326	+605 approx.
Estragole	−175	−115	+318	**
Carvone	−177	−140	+326	**
Average (P)	−152	−91	+324	+605 approx.
Vs. n-alcohols				
Linalool	−49	+6	−25	−2
Estragole	−128	−63	−45	+49
Carvone	−111	−65	−31	+105
Average (A)	−96	−41	−34	+51
Average of above (P and A)	−124	−66	+145	+330 approx.
Vs. n-aldehydes				
Linalool	−7	−21	+118	+163
Estragole	−111	−98	+117	+220
Carvone	−109	−116	+121	+226
Average	−76	−78	+119	+203
Column polarity rating	← less polar than base* —| — more polar than base* →			

* Base column 3% SP-2250.
** Relevant *n*-alkanes not resolved.

phase was "less polar" than an Apiezon grease with a benzene probe, but that the reverse held for an ester probe solute, confirming that changes in apparent polarity occur.

These results suggest that *n*-alkanes alone, as used by Kováts and McReynolds for I_R and ΔI_R, are not the best choice of standard series as they may exaggerate the relative polarity of the more polar stationary phases, and because paraffin mixtures are not resolved on some highly polar columns (*e.g.* DEGS). According to Martin[23], this lattermost would be due to an adsorption, as well as partition, effect by the polar stationary phase. Others consider this may be a minor influence[24]. Urone and Parcher's work[21] would implicate a column support effect that whilst obviously more relevant at low stationary phase loadings, can still exert an influence at above 10% loads. The DEGS column used here had a nominal 15% loading. Whatever the cause of the results obtained, they indicate that another series of polar compounds such as alcohols should also be used together with alkanes. If one series only is to be chosen as reference, the *n*-aldehydes suggested by Heldt and Köser[13] might be the one of choice, being themselves intermediate in polarity between paraffins and alcohols, although discrepancies may result (see below).

Although the reference base column for our laboratory is an SP-2250 column, any column giving consistent results with good efficiency and reasonably short retention times could have been selected. The method used here is still applicable for

practical comparisons. Other laboratories may make another choice. However, the intermediate polarity of a phenyl–methyl (50:50) polysiloxane should be considered, so that test columns are rated against it on a more or less polar scale. For example, using the procedure here, our 10% polyester SP-1000 column rated identically to PEG using only standard series *n*-alcohols, but at +104 (41 units less polar than PEG) using an average of alkanes and alcohols. Our 5% trifluoropropyl polysiloxane QF-1 column was similar on average to the SP-2250 base using only alcohols, but was +28 more polar using the alkane and alcohol average. Using only *n*-aldehydes, the ratings were +132 for SP-1000 but −104 for QF-1. It seems ridiculous to rate QF-1 as less polar than a fully methyl polysiloxane, so the use of the aldehyde reference series alone is questionable with polysiloxanes, and the double reference of alkanes and alcohols is to be preferred. "A method is needed that will enable an individual chromatographer to characterise his own set of columns"[25]. The method given here may serve this purpose.

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