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## SOLUTE CHARACTERIZATION IN GAS CHROMATOGRAPHY BY AN EXTENSION OF KOVÁTS RETENTION INDEX SYSTEM

### DISPERSION AND SELECTIVITY INDICES

M. B. EVANS\*

*Division of Chemical Sciences, The Hatfield Polytechnic, College Lane, Hatfield, Hertfordshire (U.K.)*

J. K. HAKEN

*Department of Polymer Science, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)*

and

T. TÓTH

*Department of Chemical Technology, Eötvös Lorand University, Budapest (Hungary)*

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#### SUMMARY

Kováts retention index system is extended by the introduction of new retention parameters, namely the dispersion and selectivity indices. The former is calculated from the molecular weight of an analyte and reflects the contribution to the overall retention of apolar forces, whilst the latter reveals the contribution of polar interactions, moderated by steric factors. Preliminary results are presented that indicate the potential value of the new parameters for the study of molecular structure-retention relationships, the prediction of retention data and the characterization of stationary phases.

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#### INTRODUCTION

The Purnell equation

$$R = 1/4 \left( \frac{\alpha - 1}{\alpha} \right) \left( \frac{k'}{1 + k'} \right) N^{1/2}$$

where  $R$  is the resolution;  $\alpha$  the separation factor;  $k'$  the capacity factor and  $N$  the plate number of the column, embodies the strategies available to the analyst for improving the separation of complex mixtures in gas-liquid chromatography. Both improvements in column efficiency and utilisation of selective stationary phases have been exploited with equal success. Because resolution is directly proportional to the square root of the plate number, the latter approach is frequently the more beneficial.

However, in order to employ column selectivity effectively it is necessary to define solute-solvent interactions in terms of retention units commonly used in qualitative analysis.

A number of systems have been developed based upon Kováts retention index<sup>1</sup>, the molecular retention index of Evans and Smith<sup>2</sup> and the Rohrschneider concept<sup>3</sup> of using selected solutes to reveal specific intermolecular forces of attraction involved in partition.

With the exception of that derived from the molecular retention index<sup>4</sup> these selectivity scales normally concentrate on defining the role of the stationary phase. For this reason, and the apparent unpopularity of the molecular retention index scale, we are of the opinion that there is scope for an alternative system that highlights analyte selectivity. The purpose of the present communication is to introduce a novel method of defining selectivity and to explore some of its applications.

## EXPERIMENTAL

Gas chromatograms were obtained using a Pye-Unicam 204 gas chromatograph equipped with glass columns and flame ionization detection. The columns (2 m × 4 mm I.D.) were packed with 5% (w/w) mixtures of stationary phase (for details see text) and non acid washed 100-120 mesh Chromosorb G. The packings were prepared by the normal slurry technique and purged continuously with oxygen-free nitrogen until required for use.

Relative retentions, in Kováts retention index units, were obtained from chromatograms of calibration mixtures containing *n*-alkanes as internal standards. Adjusted retention times were measured between the individual peak maxima and that of methane, used as void volume marker<sup>5</sup>, by a Spectra Physics SP4100 integrator. Values for *I* were computed by means of the expression

$$I = 100N + 100n \left( \frac{\log R_x - \log R_N}{\log R_{N+n} - \log R_N} \right)$$

where  $R_x$ ,  $R_N$  and  $R_{N+n}$  are the adjusted retentions of the solute and *n*-alkanes containing *N* and *N* + *n* carbon atoms, respectively.

Analytes and stationary phases used in this work were obtained from commercial sources with the exception of di-*n*-butyl sulphide, selenide and telluride which were kindly donated by Dr. M. R. Porter of the Malaysian Rubber Producers' Research Association.

## RESULTS AND DISCUSSION

For a particular solute the partition coefficient is determined by the magnitude of the intermolecular forces involved in its interaction with the stationary phase. With *n*-alkanes these forces are exclusively London dispersion forces, which are additive and increase with molecular weight. As heteroatoms and multiple bonds are introduced into a molecule, polar forces contribute increasingly to the overall retention. It is these forces, moderated by the influence of molecular shape, that account

for selectivity. Thus the retention behaviour of any solute is found to be dependent upon its size, shape and functionality.

On the assumption that the apolar forces involved in retention are directly proportional to molecular weight, retention index may be expressed in the form

$$I = I_M + I^*$$

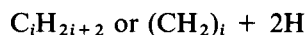
Where  $I_M$  is defined as the retention index of a hypothetical  $n$ -alkane having the same molecular weight as the analyte; its value being determined by means of the expression

$$I_M = \frac{M - 2.016}{0.14026}$$

An expression that arises from the definition of retention index in terms of the carbon number of a hypothetical  $n$ -alkane having the same retention as the analyte, *viz.*

$$I = 100i$$

where  $i$  is the carbon number of a hypothetical  $n$ -alkane



with a molecular weight of  $14.026 i + 2.016$ .

$I_M$  may be regarded to be equivalent to the contribution of London dispersion forces to the overall retention of a solute, assuming that orientation effects are the same as with  $n$ -alkanes.

By definition,  $I_M = I$  for  $n$ -alkanes. For all other solutes  $I$  need not necessarily be equal to  $I_M$ , the difference  $I^*$  reflecting the combined effects of molecular shape and functionality. For this reason we have coined the term selectivity index for  $I^*$  in contrast to dispersion index for  $I_M$ .  $I^*$  is the carbon number equivalent of  $\Delta M_e$ , which is given by the expression

$$\Delta M_e = M_e - M$$

where  $M_e$  is the molecular retention index, which arises from the logarithmic relationship between the retentions of  $n$ -alkanes and molecular weight, and  $M$  is the molecular weight of a particular solute.

Typical results shown in Table I indicate that in general solutes possessing polar functional groups tend towards positive  $I^*$  values whereas substituents with screened electrons yield negative values. Thus the bromoalkanes and iodoalkanes display strongly negative values whilst solutes possessing strong dipoles, such as the nitroalkanes and cyanoalkanes, yield large positive values for  $I^*$ . The parameter is also sensitive to structural features, in particular cyclic groups and chain branching, as illustrated by the data for  $\text{C}_6$  hydrocarbons and isomeric butanols in Table II. The reduction of  $I^*$  from  $n$ -butanol to *tert.*-butanol is consistent with the steric hindrance of the hydroxyl group. In the case of the isomeric hexanes the reduction of  $I^*$  with

TABLE I

DEPENDENCE OF SELECTIVITY INDEX UPON MOLECULAR SHAPE AND FUNCTIONALITY

Stationary phase: 5% dinonyl phthalate on Chromosorb G at 75°C.

<i>Solute</i>	<i>I</i>	<i>I<sub>M</sub></i>	<i>I*</i>
1-Iodo-2-methylpropane	851	1298	-447
1-Iodopropane	788	1198	-410
2-Bromopropane	646	863	-217
1-Bromopropane	693	863	-170
2,2,4-Trimethylpentane	691	800	-109
Diisopropyl ether	620	714	-94
Di- <i>n</i> -butyl ether	900	914	-14
Oct-2-yne	772	771	+1
1-Chloro-2-methylpropane	670	646	+24
<i>n</i> -Butyl acetate	871	814	+57
Pentan-2-one	775	600	+175
1-Nitropropane	882	621	+261
Butan-1-ol	795	514	+281
<i>n</i> -Propyl cyanide	805	478	+327

branching suggests that the dispersion forces involved in retention are reduced due to orientation effects. The strongly positive values for the cyclic hydrocarbons suggest enhanced dispersion interaction. With alkylbenzenes and alkenylbenzenes extension of the  $\pi$ -electron system increases selectivity on the apolar phase as indicated by the data in Table III. In the case of alkyl substitution  $I^*$  values appear to be dependent upon the nature and position of the substituent groups, as illustrated in Fig. 1, which was constructed using retention indices originally published by Macák *et al.*<sup>6</sup>. Particularly notable is the linear increase of selectivity index with contiguous methyl substitution. On the other hand, with 1,3-substitution the increase is less marked and with ethyl and iso-propyl groups  $I^*$  gradually falls with increased carbon number.

TABLE II

DEPENDENCE OF THE SELECTIVITY INDICES OF ISOMERIC BUTANOLS AND C<sub>6</sub>-HYDROCARBONS UPON MOLECULAR STRUCTURE

Stationary phases: 5% dinonyl phthalate on Chromosorb G at 75°C (butanols) and 5% squalane on Chromosorb G at 70°C (hydrocarbons).

<i>Solute</i>	<i>I</i>	<i>I<sub>M</sub></i>	<i>I*</i>
<i>n</i> -Butanol	795	514	+281
Butan-2-ol	720	514	+206
2-Methylpropan-1-ol	754	514	+240
2-Methylpropan-2-ol	638	514	+124
<i>n</i> -Hexane	600	600	0
2-Methylpentane	567	600	-33
2,2-Dimethylbutane	520	600	-80
Hex-1-ene	582	586	-4
Cyclohexane	667	586	+81
Benzene	642	542	+100

TABLE III

DEPENDENCE OF THE SELECTIVITY INDICES OF ALKYL BENZENES AND ALKENYL BENZENES UPON THE STRUCTURE AND POSITION OF SUBSTITUENTS

Stationary phase: squalane. Columns: wall-coated open tubular (WCOT) stainless-steel at 98°C (ref. 4).

<i>Solute</i>	<i>I</i>	<i>I<sub>M</sub></i>	<i>I*</i>
Benzene	650	542	+108
Toluene	757	642	+115
Ethylbenzene	848	742	+106
Styrene	874	728	+146
<i>n</i> -Propylbenzene	935	842	+93
Allylbenzene	920	828	+92
Isopropylbenzene	907	842	+65
$\alpha$ -Methylstyrene	960	828	+132
2-Methylethylbenzene	963	842	+121
2-Methylstyrene	974	828	+146
3-Methylethylbenzene	947	842	+105
3-Methylstyrene	979	828	+151
4-Methylethylbenzene	950	842	+108
4-Methylstyrene	980	828	+152

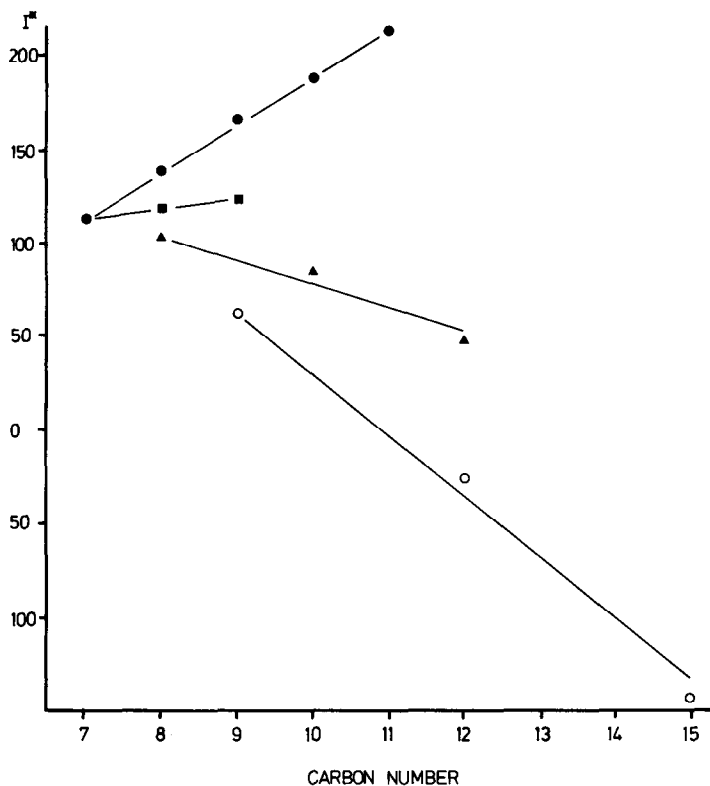


Fig. 1. Dependence of selectivity indices of alkylbenzenes upon substitution pattern. ● = 1,2-, 1,2,3-, 1,2,3,4-, 1,2,3,4,5-Methyl; ■ = 1,3-, 1,3,5-methyl; ▲ = 1,3-, 1,3,5-ethyl; ○ = 1,3-, 1,3,5-isopropyl.

TABLE IV

DEPENDENCE OF THE SELECTIVITY INDICES OF CHLORINATED PROPIONATE METHYL ESTERS UPON THE DEGREE OF SUBSTITUTION

Stationary phase: OV-101. Column: WCOT fused-silica capillary at 120°C (ref. 5).

Ester	<i>I</i>	<i>I<sub>M</sub></i>	<i>I*</i>
Propionate	629	614	+15
2-Chloro-	781	859	-78
3-Chloro-	833	859	-26
2,2-Dichloro-	859	1105	-246
3,3-Dichloro-	914	1105	-191
2,3-Dichloro-	927	1105	-178
3,3,3-Trichloro-	1015	1350	-335
2,3,3-Trichloro-	1031	1350	-319
2,2,3-Trichloro-	1031	1350	-319
2,3,3,3-Tetrachloro-	1137	1596	-459
2,2,3,3-Tetrachloro-	1156	1596	-440
Pentachloro-	1275	1841	-566

Halogen substitution of aliphatic and aromatic compounds invariably leads to increasingly negative values for  $I^*$  as illustrated by the retentions of chlorinated propionate esters shown in Table IV. Furthermore, it is found that there is normally a linear relationship between  $I^*$  and the number of substituents as illustrated in Fig. 2, which was constructed using data originally published by Haken and Korhonen<sup>7</sup>.

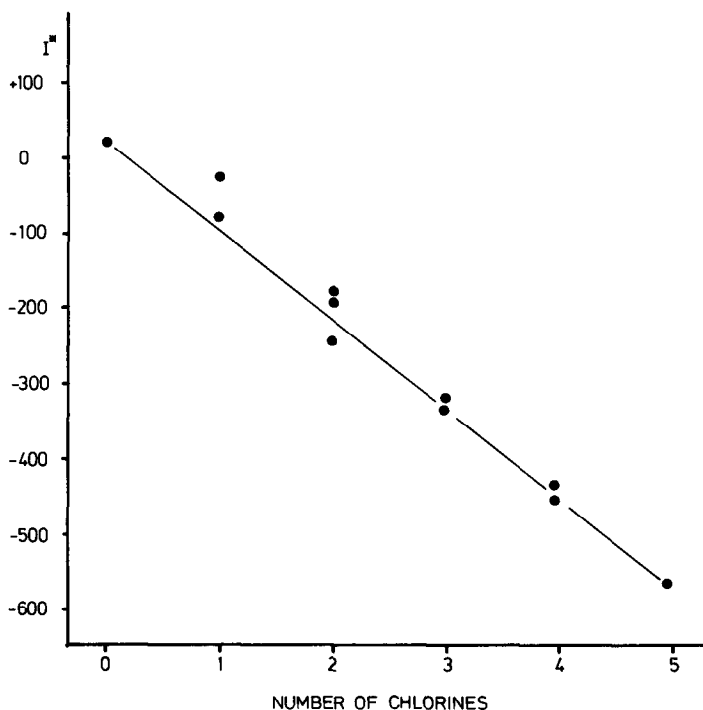


Fig. 2. Dependence of selectivity indices of chlorinated methyl propionates upon degree of substitution.

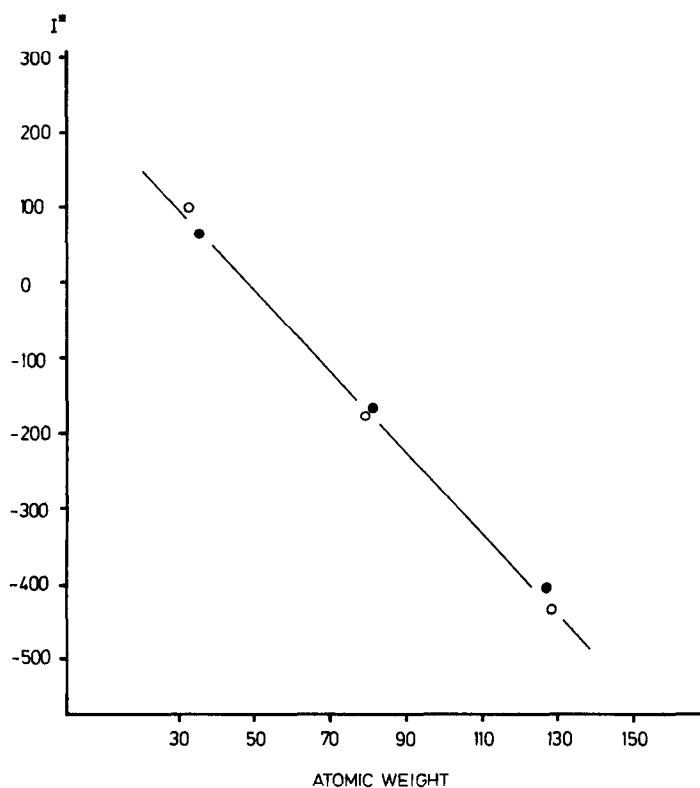


Fig. 3. Dependence of selectivity indices of alkyl compounds R-X and R-X-R upon the atomic weight of Group 6 and Group 7 heteroatoms. ● = 1-Chloro-, 1-bromo- and 1-iodohexane; ○ = di-*n*-butyl sulphide, selenide and telluride.

With these compounds the apparent negative selectivity suggests that a proportion of the electrons within the chlorine atoms are unable to participate in London dispersion interactions. Consistent with this view, values for  $I^*$  are found to become more negative in the series 1-chloro-, 1-bromo-, and 1-iodohexane. Here a linear relationship between  $I^*$  and atomic weight of the substituent, or its Periodic position,

TABLE V

COMPARISON OF THE RETENTION BEHAVIOUR OF DERIVATIZATION REAGENTS

Stationary phase: 5% OV-17 on Chromosorb G at 65°C. R = *n*-Butyl;  $\delta I^*$  = difference between the values for alcohol and derivative;  $M'$  = molecular weight of substituent group.

Solute	$I_M$	$I$	$I^*$	$\delta I^*$	$\delta I^*/M'$
R-OH	514	648	+134	—	—
R-OC <sub>2</sub> H <sub>5</sub>	714	671	-43	177	6.1
R-OSi(CH <sub>3</sub> ) <sub>3</sub>	1029	750	-279	413	5.6
R-OSi(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	1429	964	-465	599	5.2
R-OCOCH <sub>3</sub>	814	803	-11	145	3.4
R-OCOCF <sub>3</sub>	1199	646	-553	687	7.1

TABLE VI

## PREDICTION OF RETENTION DATA FOR THE TRIMETHYLSILYL DERIVATIVES OF ALKANE DIOLS

Stationary phase: 5% Carbowax 20M on Chromosorb G at 150°C. Primary TMS  $I^* = -250$ ; secondary TMS  $I^* = -323$ .

Solute	$I_M$	$I^*$	$I_{calc.}$	$I_{obs.}$
Propane-1,2-diol	1557	-573	984	992
Propane-1,3-diol	1557	-500	1057	1050
Butane-1,4-diol	1657	-500	1157	1164

is observed as illustrated in Fig. 3. Likewise the Group 6 elements show a similar trend in the form of di-*n*-butyl sulphide, selenide and telluride. In both cases, the proportion of unavailable or screened electrons would be expected to increase with atomic weight.

The examples cited thus far clearly demonstrate the systematic dependence of  $I^*$  values upon molecular structure. Furthermore, preliminary studies have revealed that selectivity index may be used to compare the efficiency of derivatization reagents and for the prediction of retention data.

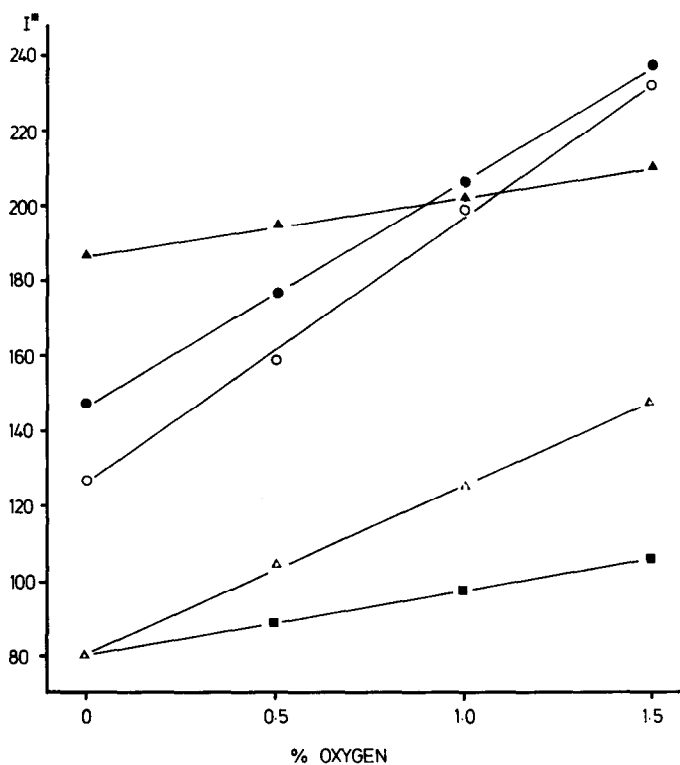


Fig. 4. Shifts of selectivity indices with oxygen content of squalene, farnesol mixed phases. ● = *n*-Butyl cyanide; ○ = butan-1-ol; ▲ = styrene; △ = *n*-octaldehyde; ■ = chlorobenzene.



The former application is illustrated by data obtained for butan-2-ol and a range of derivatives commonly used in analysis, see Table V. By taking the shift of  $I^*$  between the original solute and the derivative and dividing by the molecular weight of the substituent a derivatization efficiency rating may be obtained. In the present case, the trifluoroacetyl group would seem to be the most efficient in terms of speeding up the elution of analytes. In addition  $I^*$  values for substituents may be used to predict the retentions of derivatives, for example, the trimethylsilyl (TMS) derivatives of alkane diols, as shown in Table VI. Values for primary and secondary TMS groups were obtained using appropriate alkanols. These values were then used to predict the retention location on a chromatogram. In our experience this approach has saved much analysis time for systems involving multifunctional analytes where complete derivatization has proved difficult, for instance monoethanolamine and diethanolamine<sup>8</sup>.

As might be expected, selectivity indices are found to be sensitive to slight changes of stationary phase composition, as illustrated in Fig. 4. Here  $I^*$  values obtained using columns prepared from mixtures of squalene and small amounts of the C<sub>15</sub>-isoprenoid farnesol reveal a linear dependence upon the oxygen content of the mixed phase. As a corollary the new retention parameter would be expected to provide a means of characterizing stationary phases that is independent of a reference phase, such as squalane, as typified by the data in Table VII.

Previously Evans<sup>9</sup>, and Haken and Srisukh<sup>10</sup> independently have proposed the used of molecular retention index as a means of avoiding the dependence upon reference stationary phases in column characterization. Clearly the use of selectivity index in this context is not dissimilar to that of  $\Delta M_e$ . However, in contrast to Kováts retention index, the molecular retention index has attracted very little attention. According to a recent comprehensive review on retention index<sup>11</sup> over 1380 papers involving Kováts scale were published between 1958 and 1983, whereas in the same period only five featuring  $\Delta M_e$  were published. The latter unit, therefore, may be considered to be obsolete and we propose its replacement by selectivity index.

TABLE VII

## CHARACTERIZATION OF STATIONARY PHASES BY MEANS OF SELECTIVITY INDEX

$\sum_5^1 I^*$  is the sum of the selectivity indices for solutes 1 to 5.

Stationary phase	Values for selectivity index $I^*$					$\sum_5^1 I^*$
	Benzene	<i>n</i> -Butanol	Pentan-2-one	Nitropropane	Pyridine	
Squalane	110	76	27	31	149	393
Apiezon	141	98	42	61	189	531
Dinonyl sebacate	176	242	134	209	267	1028
Dinonyl phthalate	193	259	174	262	308	1196
Neopentylglycol sebacate	282	403	252	375	475	1787
Neopentylglycol succinate	382	545	393	570	623	2513
Carbowax 20M	432	612	395	603	659	2701
Carbowax 1540	481	715	480	697	790	3163

## CONCLUSIONS

A new retention parameter is introduced to measure the contribution of selective interactions to gas-liquid chromatographic retention in terms of Kováts retention index. Initial studies described in this paper indicate that the selectivity index could give a better understanding of the dependence of retention upon molecular structure. Furthermore, evidence is given to suggest that the new parameter may be useful in the prediction of retention data and the characterization of stationary phases in gas chromatography. Further work is now in progress designed to explore more fully the scope of selectivity index. The results of this work will be published elsewhere.

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