A GENERALIZATION OF THE RETENTION INDEX SYSTEM INCLUDING LINEAR TEMPERATURE PROGRAMMED GAS–LIQUID PARTITION CHROMATOGRAPHY

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The determination of retention data serves different purposes and the choice of the type of retention parameter depends on the purpose.

If the investigation is concerned with the study of the physical phenomena underlying the behaviour of compounds in gas chromatographic systems, the specific retention volume will be the parameter of choice. Defined as:

$$V_{g(x)} = RT/M_L\gamma_x P^\circ_x \qquad (1)$$

it describes peak positions in terms with a physical meaning.

However, the majority of the users of the gas–liquid partition chromatography (GLPC) technique are not directly interested in the study of these physical phenomena but in the identification of the components of mixtures. The difficulties encountered in the accurate determination of the specific retention volume (the more as many instrument manufacturers tend to forget the installation of proper gauges for measurement of column inlet pressures) and the reproduction of these determinations, together with the elaborate calculations involved, make this parameter impractical for routine identification work. The necessity of simple and reproducibly determinable retention parameters for this type of work was very clearly expressed by PRIMAVESI[1].

To achieve this goal, it is obvious that the accurate determination of as many operational variables as possible must be eliminated.

The first attempt in this direction was the *relative retention*, defined as:

$$r_{x,s} = V_{g(x)}/V_{g(s)} = t'_x/t'_s \qquad (2)$$

This relative retention eliminated, it is true, many operational variables; it has, however, the drawback that the choice of the reference material is completely at the discretion of the investigator. And apart from the often used *n*-pentane, one may encounter in the literature reference materials such as carbon tetrachloride[2], hexadecanal[3] and coumarone[4].

To obtain a fixed reference point SMITH[5] introduced the *theoretical nonane system*. This system is based on the fact that under identical, isothermal conditions, the higher members of a homologous series show the relationship:

$$\log V_{g(x)} = A + Bn_x \qquad (3)$$

between the retention volume and the number of C-atoms. Using the normal paraffins as the reference series, the constants A and B are calculated and the value $n_x = 9$ is substituted in the equation to find the reference point. The theoretical nonane index is now defined as:

$$r_{x,9} = \frac{V_{g(x)}}{V_{g(9)}} = \frac{t'_x}{t'_9} \tag{4}$$

The principal disadvantage of this system is the determination of the reference point by extrapolation and not by direct observation.

The *retention index system*, introduced by KOVÁTS[6] was also based on the *n*-paraffinic series as the reference materials. However, by using the *n*-paraffins eluting directly before and after the compound under investigation as the reference points the extrapolation was eliminated. Fixed reference points are obtained in this way by attaching to each *n*-paraffin the retention index:

$$I = 100\, n \tag{5}$$

The position of the peak of a compound is now found from:

$$I = 100\, i \frac{\log V_{g(x)} - \log V_{g(n)}}{\log V_{g(n+i)} - \log V_{g(n)}} + 100\, n \tag{6}$$

It should be noted here that KOVÁTS uses the logarithms of the retention volumes and further that he showed that I is linearly dependent on temperature with in most cases a very small temperature coefficient.

It is an advantage of isothermal GLPC that when comparing retention data obtained in one chromatogram it is permissible to replace V_g by t'. In temperature

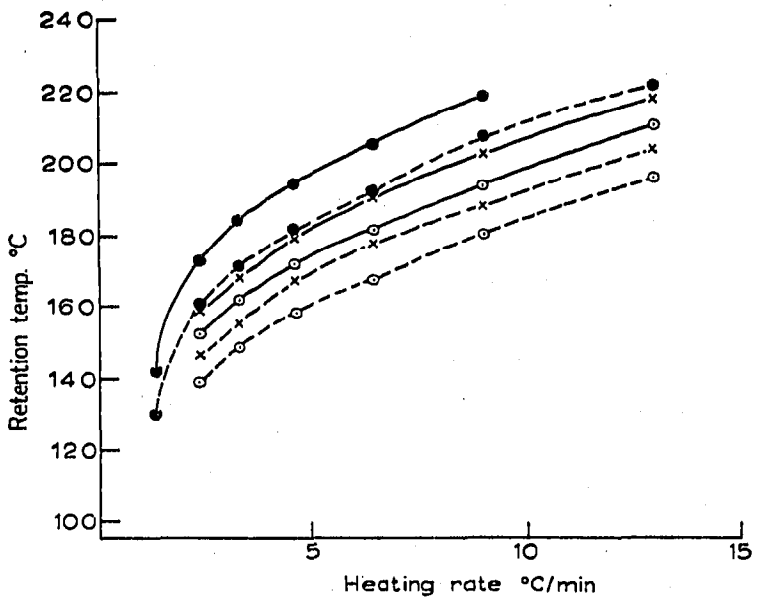

Fig. 1. Retention temperatures. Program start: 80°, program end: 225°. — — — benzyl acetate; ——— benzyl butyrate; ●——● flow rate 25.2 ml/min; ×——× flow rate 51.3 ml/min; ⊙——⊙ flow rate 75.0 ml/min.

programmed GLPC, however, this replacement is not allowed, which makes direct application of the retention parameter systems described impossible.

The retention parameter most frequently encountered in linear temperature programmed GLPC is the *retention temperature*. Unless applied under strictly identical conditions, this parameter will vary depending on heating rate and carrier gas flow-rate. In Fig. 1 this is shown for two benzyl esters. However, as might be seen from Fig. 2, the difference in retention temperatures between two compounds is remarkably constant.

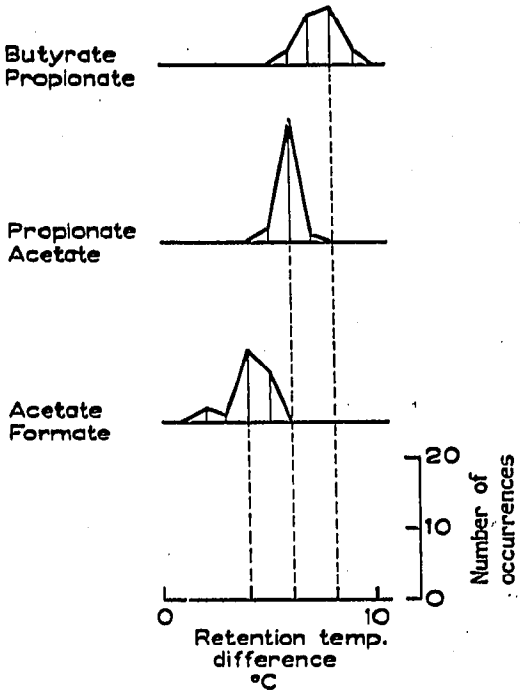

Fig. 2. Benzyl esters. Program start: 80°. Program end: 225°. Heating rates: 1.3; 2.3; 3.3; 4.6; 6.4; 9.0; 13°/min. Flow rates: 25.2; 51.3; 75.0 ml/min.

Remembering that in many cases in linear temperature programmed GLPC for the members of a homologous series the equation:

$$t'_x = C + Dn_x \tag{7}$$

will hold, we found that the retention index may be generalized to include also linear temperature programmed GLPC by rewriting eqn. (6) as:

$$I = 100\, i \frac{X - M_{(n)}}{M_{(n+i)} - M_{(n)}} + 100\, n \tag{8}$$

In isothermal GLPC, the retention index is found now by substituting for X, $M_{(n)}$ and $M_{(n+i)}$ the logarithms of the adjusted retention volumes (adjusted retention times) of respectively the compound and both markers. In linear temperature programmed GLPC for X, $M_{(n)}$ and $M_{(n+i)}$ either the retention temperatures or the adjusted retention times are substituted. Here an advantage of this way of operation over isothermal operation demonstrates itself, as gas holdup-time does not need to be

measured, which is specifically of importance in detectors which are relatively insensitive to air.

Using the same column packing, we expected that in all cases in which the temperature coefficient of the retention index is small the retention index for a compound would be practically the same in isothermal and in linear programmed GLPC, thus extending the usefulness of the retention index. The expectation proved to be true (Table I).

TABLE I

RETENTION INDICES UNDER VARIOUS CONDITIONS OF OPERATION

Instrument: F & M 500; katharometer. Stationary phase: Carbowax 20M, 20 % on Celite

Compound	*Isothermal at 125°*		*Programmed 75–228° at 4.6°/min*
	Flow rate (ml/min)		*Flow rate (ml/min)*
	55.6	*80.0*	*80.0*
Ethyl formate	820	822	822
Ethyl butyrate	1032	1032	1032
Ethyl valerate	1130	1136	1130–1128
Ethyl hexanoate	1226	1228	1228–1227

Although the retention index system is based on the *n*-paraffinic series, it is sometimes useful to have at hand a secondary reference set. If the retention indices of the members of the secondary set are known, values obtained in the secondary system may be converted into standard retention indices, using the equation:

$$I = \frac{[S_{(x)} - S_{M(n)}]\,[I_{M(n+i)} - I_{M(n)}]}{100\,i} + I_{M(n)} \qquad (9)$$

In our work we found the ethyl esters of the *n*-fatty acids to be a useful secondary reference set, in which case we attach to each ethyl ester the index $S = 100\,(n-2)$. The standard retention indices of these esters are given in Table II, together with the retention indices of many other compounds. From this table also an impression may

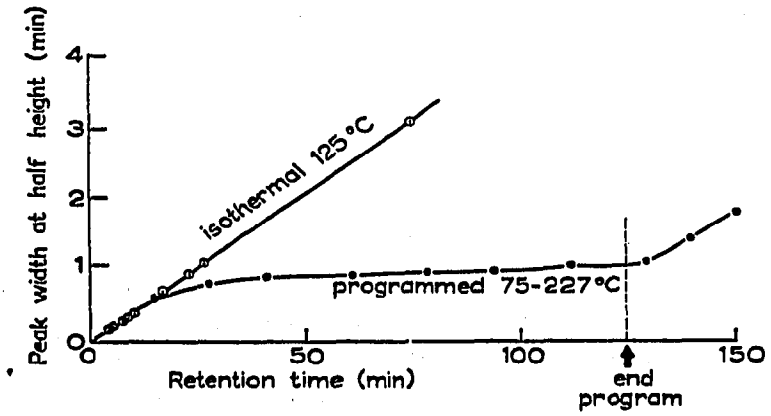

Fig. 3. Peak width.

TABLE II

RETENTION INDICES OF ESTERS AND OTHER COMPOUNDS

Compound	Column	
	SE 30*	Carbowax 20 M**
Methyl ester of		
Propionic acid		885–885
Butyric acid		970–972–971
Isobutyric acid		903
Valeric acid	808	1081–1081–1085
Isovaleric acid		1013
Hexanoic acid	907	1183–1182–1183
Isohexanoic acid		1094
Heptanoic acid	1008	1282–1281
Octanoic acid	1109	1378–1380
Nonanoic acid	1211	1484–1487
Decanoic acid	1310	1584–1588
Undecanoic acid	1410	1694–1696
Dodecanoic acid	1513	1800–1801
Myristic acid	1714	2002–1998
Hexadecanoic acid	1911	2190
Octadecanoic acid	2098	
Benzoic acid	1080	1631
Phenylacetic acid	1156–1154	1759–1761–1762
Salicylic acid	1181–1181	1794
p-Hydroxybenzoic acid	1435	
o-Hydroxyphenylacetic acid	1260–1269	
p-Hydroxyphenylacetic acid	1460	
Cinnamic acid	1363	2065
o-Hydroxycinnamic acid	1430	
m-Hydroxycinnamic acid	1690	
p-Hydroxycinnamic acid	1498	
Anthranilic acid	1325	2259
β-Hydroxybutyric acid	1320	1464–1457
2-Hydroxyisobutyric acid	1118	
2-Methylbutyric acid	758	980
2-Keto-octanoic acid	1200	
Crotonic acid		1102
Furoic acid	950	
Dimethyl ester of		
Oxalic acid	837	1381–1383
Malonic acid	895	1489–1489–1490
Succinic acid	1000–1004	1576
Glutaric acid	1105	1686–1687–1689
Adipic acid	1213	1804
Pimelic acid	1313	1908–1909
Suberic acid	1416	2010
Azelaic acid	1519	2102–2100
Sebacic acid		2213–2210
Ethyl ester of		
Formic acid		822
Acetic acid		866
Propionic acid	700	940
Butyric acid	787	1032
Isobutyric acid		950
Valeric acid	884	1130–1128

(continued on p. 468)

TABLE II (*continued*)

Compound	Column	
	*SE 30**	*Carbowax 20 M***
Isovaleric acid		1064
Hexanoic acid	979–983	1228–1227
Heptanoic acid	1080–1081	1324–1327
Octanoic acid	1181	1422–1427
Decanoic acid	1379–1379	1631
Lauric acid	1579	1840
Myristic acid	1780	2038
Palmitic acid	1979	2238
Stearic acid	2175	
Salicylic acid	1261	1828
Cinnamic acid	1447	2108
Lactic acid	801	
Diethyl ester of		
Oxalic acid	948	
Malonic acid	1035	
Succinic acid	1139	
Propyl ester of		
Acetic acid	704	
Isopropyl ester of		
Acetic acid		866–866
Butyl ester of		
Acetic acid	802	1065
Benzoic acid	1360	1871
Isobutyl ester of		
Acetic acid		1002–1002
Isobutyric acid	901	1090
Cinnamic acid	1598	
Benzoic acid	1318	1799
Amyl ester of		
Acetic acid	896–900	1169
Benzoic acid	1462	
Salicylic acid	1535	
Isoamyl ester of		
Acetic acid	853	1116–1116
Benzoic acid	1425	1921
Hexyl ester of		
Formic acid	913	1216
Acetic acid	993–993	1264
Butyric acid	1177	1406
Isobutyric acid		1337
Benzoic acid	1565	2068–2070
Salicylic acid	1684	2208
Hexanoic acid	1371	1606
Isohexyl ester of		
Acetic acid		1208

(*continued on p. 469*)

TABLE II (*continued*)

Compound	*Column*	
	*SE 30**	*Carbowax 20 M***
Heptyl ester of		
Acetic acid	1096	
Octyl ester of		
Salicylic acid	1895	
Nonyl ester of		
Acetic acid	1296	1569
Decyl ester of		
Acetic acid	1395	1674
Dodecyl ester of		
Acetic acid	1595	
Benzyl ester of		
Formic acid	1057	1687
Acetic acid	1141	1728
Propionic acid	1237	1791
Butyric acid	1325	1870
Cinnamic acid	1682	
Phenylethyl ester of		
Cinnamic acid	2143	
Anthranilic acid	2088	
Cinnamyl ester of		
Formic acid	1332	
Acetic acid	1422	2125
Propionic acid	1519	2194
Isobutyric acid	1562	2179
Isovaleric acid	1663	2289
Cinnamic acid	2052	
Allyl ester of		
Hexanoic acid	1062–1060	1360
Heptanoic acid	1163	1463
Octanoic acid	1262	1566
Alcohols		
Methanol		866–866
Ethanol		895–899
Isopropanol		866–866
Butanol		1121–1130
Isobutanol		1067
Amyl alcohol		1228–1228
Isoamyl alcohol	723	1184
Hexanol	854	1325–1323
Heptanol	957	1422–1422–1427
Octanol	1057–1058–1059	1533
Benzyl alcohol	1020	1858–1860
Phenylethyl alcohol	1197	1893–1895
Cinnamyl alcohol	1295	2238–2238

(*continued on p. 470*)

TABLE II (*continued*)

Compound	Column	
	*SE 30**	*Carbowax 20M***
Aldehydes		
Butanal		866
Hexanal		1080–1080
Heptanal	895	1184–1183
Nonanal	1091	1387–1385
Decanal	1193	1498–1498
Undecanal	1296	1603–1608
Dodecanal	1397	1711–1708
Tridecanal	1501	1815–1817
Hydratropic aldehyde	1080	1631
o-Methoxycinnamaldehyde	1512	
Vanillin	1379	
Ethylvanillin	1446–1442	
Ketones		
Acetone		822
Methyl ethyl ketone		882–882
Methyl isobutyl ketone	719	
Methyl amyl ketone	873	1184–1178
Methyl hexyl ketone	973	1280–1276
Methyl heptyl ketone		1383–1380
Methyl nonyl ketone	1280	1597–1596
Methyl decyl ketone	1384	
Methyl undecyl ketone	1485	1807–1809
Diacetyl		956
Miscellaneous		
Dihydrocoumarin	1361	
Anisole	902	1341

* 25% Silicone rubber SE 30 on Celite; operated under linear temperature programmed conditions.

** 25% Carbowax 20M on Celite; operated under linear temperature programmed conditions.

be obtained of the reproducibility. The difference between two determinations ranged from 0 to 9 with an average difference of 2.

In practice, we run chromatograms of the mixture under investigation without and with a set of reference materials from which we determine the retention indices. By marking the temperature on the chart at 5° intervals and using the chart as a graph we not only easily obtain at the same time retention temperatures and the accurate end point of our program, but also have a control on the regularity of the rise in temperature.

It should be further remarked here that in quantitative work in linear temperature programmed gas–liquid partition chromatography the method for calculation of peak areas by using retention time × peak height is not applicable (see Fig. 3). Hence also the method of SMITH AND LEVI[7] for the estimation of peak width-at-half-height from a graph of known peak widths-at-half-height *versus* retention time is not applicable.

SYMBOLS USED

V_g	specific retention volume
R	gas constant
T	absolute temperature (°K)
M_L	molecular weight of the stationary phase
γ	activity coefficient
$P°$	saturated vapor pressure
$r_{x,s}$	relative retention of compound X with regard to the reference material S
t'	adjusted retention time
n	number of carbon atoms in the compound
I	retention index
i	difference in numbers of carbon atoms of the reference materials
$M_{(n)}$; $M_{(n+i)}$	reference material with (n); $(n + i)$ carbon atoms
S	retention index in the secondary reference system
A; B; C; D	constants
subscripts	refer to the compounds

SUMMARY

The different ways of describing peak positions on gas chromatograms are reviewed. The retention index is preferred to the theoretical nonane system and the relative retention.

The equation given by KOVÁTS for the calculation of the retention index in case of isothermal operation is transformed to a more general form to include also the case of linear temperature programmed operation. This generalized equation gives the same retention index for both ways of operation.

REFERENCES

1 G. R. PRIMAVESI, *Informal Symposium of the Gas Chromatography Discussion Group of the Hydrocarbon Research Group of the Institute of Petroleum*, Liverpool, 1960.
2 P. W. WEST, B. SEN, B. R. SANT, K. L. MALLIK AND J. G. SEN GUPTA, *J. Chromatog.*, 6 (1961) 220.
3 G. M. GRAY, *J. Chromatog.*, 6 (1961) 236.
4 J. W. SWEETING AND J. F. K. WILSHIRE, *J. Chromatog.*, 6 (1961) 385, 391.
5 J. F. SMITH, *Chem. Ind. (London)*, (1960) 1024.
6 E. KOVÁTS, *Helv. Chim. Acta*, 41 (1958) 1915.
7 D. M. SMITH AND L. LEVI, *J. Agr. Food Chem.*, 9 (1961) 230.