Journal of Chromatography, 623 (1992) 289–295
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 463

Fast evaluation of the polarity of gas chromatographic columns using the difference in apparent carbon number of linear alkanes and alcohols with the same retention

Gianrico Castello* and Giuseppina D'Amato

Istituto di Chimica Industriale, Università, Corso Europa 30, 16132 Genova (Italy)

(First received February 18th, 1992; revised manuscript received June 30th, 1992)

ABSTRACT

A method for the measurement of the polarity order of gas chromatographic columns (liquid-packed, porous polymer beads, capillary) which does not require reference to standard phases and many probes, is suggested. The method is based on ΔC, *i.e.* the difference in apparent carbon number of linear alkanes and alcohols with the same retention time. The graphical measurement or mathematical calculation of the horizontal distance between the straight lines obtained by plotting the logarithm of the retention of linear alkanes and alcohols as a function of their number of carbon atoms allows the importance of hydrogen bonding with respect to the dispersion forces to be evaluated. All the retention data (adjusted retention times and volume, relative retention, adjusted, net and specific retention volumes) can be used for the calculations. The method is useful for the determination of the change in polarity of mixed or serially linked columns, for the evaluation of the performance of porous polymer beads with respect to liquid stationary phases and for the comparison of packed and bonded-phase capillary columns when polyglycol or polydimethylsiloxane phases are used.

INTRODUCTION

The classification of more than 200 liquid phases currently used in gas chromatography has been attempted using many methods which were found to be more or less adequate depending on the type of liquid phase. The methods cannot be applied with the same confidence to packed or capillary columns, to bonded liquid phases and to various adsorption phases such as carbon black and porous polymers.

An early empirical approach was derived from the classification of many organic compounds by Ewell *et al.* [1] on the basis of the probability of forming hydrogen bonds. The classification of stationary phases and solutes according to Ewell *et al.*'s method was carried out by McNair and Bonelli [2].

Kováts' retention index scheme for quantifying retention [3] has been used as the basis for the methods of Rohrschneider [4] and McReynolds [5] the latter being the most popular classification used by the producers of liquid phases to characterize their products and to establish when two or more phases show a similar behaviour, thus decreasing the stock of columns in the laboratory. The overall polarity of the phases can be obtained by the sum of some of the McReynolds' constants, the most common choice being those obtained with the probes benzene, *n*-butanol, 2-pentanone, 1-nitropropane and pyridine, indicated as $\sum_{MR}^{5}$. Unfortunately, some porous polymer beads react with nitro compounds, and therefore nitromethane and nitropropane cannot be used; with these columns the $\sum_{MR}^{4}$ sum is therefore reported [6]. A method based on the ratios of the retention index (I) values instead of the differ-

Correspondence to: Dr. G. Castello, Instituto di Chimica Industriale, Università, Corso Europa 300, 16132 Genova, Italy.

0021-9673/92/$05.00

ences has also been suggested [7] and is known as the "retention polarity" method.

The main problem with these procedures is the normalization with respect to squalane as the reference phase and to *n*-alkanes as the reference homologous series. Squalane (temperature limit 100–120°C) could be replaced with the synthetic phase $C_{87}H_{176}$ Apolane [8,9] for high-temperature analysis, whereas the use of linear alkanes has been criticized for polar phases and for porous polymers [10–12] because the difference in the I values is due to the change in retention of the reference value (smaller for polar phases and greater for porous polymers) rather than to the change in the retention of the probes. The use of different series of homologues or special probes [13–17] does no solve the problem, which is related to the fundamental concept of the methods which are essentially "relative" with respect to the reference stationary phase and the polarity probes. For the classification of the polarity of capillary columns, a method that in theory may be extended to packed columns was suggested by Chrompack International [18]. The "CP index" requires the determination of the ΔI values with squalane used as the lowest polarity limit and OV-275 cyanosilicone as the highest limit, with increasing complexity as it requires two reference columns.

In the classification of porous polymers negative values were obtained when squalane was used as the reference phase [9,19]. At the low temperatures used for gas analysis, classification methods based on the separation of C_2 hydrocarbons and CO_2 [20,21] and on McReynolds' probes with respect to the reference phase Chromosorb 106 [22], which was found to be the column with the lowest polarity, were suggested.

The selectivity triangle suggested for liquid chromatography by Snyder [23,24] was extended to gas–liquid chromatography by Klee *et al.* [25]. Only three probes (*n*-butanol, 1-nitropropane and 1,4-dioxane) were used, but this trio of solutes seems to be poor for gas chromatographic applications as they plot low-polar phases as SE-30 near to highly polar Carbowaxes. The choice of 1-nitropropane as one of the probes may exaggerate the contribution of the polarizability of the stationary phase, as it has a large dipole moment (3.7 Debye). Other solutes were used [26,27] but the calculation of McReynolds' relative ΔI values with respect of squalane are still necessary for the use of the selectivity triangle. Hepp and Klee [28] applied the same procedure to porous polymers by using as the reference phase graphitized carbon black, considered as representing the basic separation mechanism of the porous polymers and giving retention values due primarily to non-specific dispersive forces.

All the listed "relative" methods require reference phases and many reference probes. An "absolute" method, based only on the retention values of *n*-alkanes, was suggested by Fernandez-Sanchez *et al.* [29] which used Kováts' coefficient, K_c, used by Tarjan *et al.* [30], the ratio between the intercept and the slope of the straight line obtained by plotting the logarithm of the specific retention volume of the *n*-alkanes, V_g, as a function of the number of carbon atoms. Linear alkanes only are necessary as probes, and no reference column is used, but the calculation of V_g values is complex as it requires knowledge of the exact amount of liquid phase in the column and the application of the pressure correction factors of James and Martin [31], only the effect of dispersive forces is taken into account, whereas most of the "polarity" of a liquid phase is often due to hydrogen bonding. Swoboda [32] introduced the concept of the functional retention index, as similar substitution in similar compounds increases the retention index by the same amount for a given stationary phase [33]. Therefore comparison between the behaviour of linear alkanes, reference compounds of the Kováts index system, and of another homologous series may allow the measurement of different interaction parameters with respect to purely dispersive forces.

In a previous paper [34] a method based on the determination of the behaviour of linear-alkanes and alcohols was suggested for the evaluation of the change in polarity when different capillary columns were connected in series. This method can be easily applied to packed and capillary columns and to porous polymers.

EXPERIMENTAL

Analyses of samples of linear alkanes (C_4–C_{12}) and alcohols (C_2–C_8) were carried out at 100, 120, 140 and, when allowed by the temperature limit of the phase, at 160°C on different lengths and diame-

ters of columns filled with various liquid phases (20% concentration) on Chromosorb W, 80–100 mesh; a high concentration of liquid phase was used to allow comparison with McReynolds' data [35] ("m" in Table I), and to minimize interfacial and adsorption effects on the solid support. Phase loadings of 10% were also used for some liquid phases (polysiloxanes, polyglycols) and small effects on the results were observed.

Analyses were also carried out on columns filled with various porous polymer beads (Porapak N, P, Q, R, S, 80–100 mesh) and on wide-bore (60 m × 0.75 mm I.D.) glass capillary columns of different polarity, used alone or serially connected with the flow in the polar to non-polar and in the reversed direction. All the columns used are listed in Table I, and are indicated by "e". Some of the capillary results have been published previously and are given here to show how the proposed method allows a comparison of the behaviour of packed and capillary columns.

Fig. 1 (left) shows the linearity of the logarithm of the retention values of *n*-alkanes and *n*-alcohols on three stationary phases of low, intermediate and

TABLE I

ΔC AND $\sum_{MR}^{5}$ VALUES FOR VARIOUS COLUMNS (PACKED, POLYMER BEADS AND WIDE-BORE CAPILLARY) AND THEIR SELECTIVITY PARAMETERS WITH RESPECT TO BUTANOL, x_b, 1-NITROPROPANE, x_n AND DIOXANE, x_d

Temperature, 120°C.

Column		Notes[a]	ΔC	$\sum_{MR}^{5}$	$\sum \Delta I_i$	x_b	x_n	x_d
1	Squalane	e	1.48	0	0			
2	Porapak Q	e	1.82	−82		0.276[a]	0.366	0.358
3	Apiezon L	e, m	1.90	143	85	0.260	0.376	0.365
4	Porapak P	e	2.20	530		0.259[a]	0.371	0.371
5	Porapak R	e	2.25	177		0.290[a]	0.404	0.306
6	SE 30	e	2.43	217	161	0.329	0.400	0.273
7	SE 52	e	2.48	334	237	0.304	0.413	0.283
8	Porapak S	e	2.50	44		0.300[a]	0.374	0.326
9	OV 101	e	2.51	229	170	0.335	0.394	0.270
10	DC 200	e	2.52	227	169	0.337	0.390	0.272
11	Capillary SPB-1 (NP)	e, 1	2.55					
12	Porapak N	e	2.79	345		0.305[a]	0.375	0.320
13	DC 550	m	2.89	663	449	0.276	0.421	0.303
14	Dioctyl sebacate	m	3.42	651	454	0.370	0.397	0.233
15	Diisodecyl pthalate	m	3.43	767	521	0.332	0.418	0.249
16	Didecyl pthalate	e, m	3.43	1159	777	0.328	0.412	0.260
17	Dioctyl pthalate	m	3.49	831	562	0.331	0.420	0.249
18	QF 1	e	3.67	1500	976	0.239	0.474	0.287
19	Capillary NP + P	e, 2	4.40					
20	Hallcomid M18	m	4.46	945	596	0.450	0.372	0.178
21	Capillary P + NP	e, 3	5.00					
22	Tricresylphosphate	e, m	5.01	1420	949	0.338	0.394	0.268
23	Neopenthylglycol adipate	m	5.65	1870	1249	0.340	0.370	0.290
24	Neopenthylglicol succinate	e, m	6.14	2115	1425	0.328	0.378	0.294
25	Carbowax 20 M	e, m	6.93	2308	1542	0.348	0.371	0.281
26	Carbowax 6000	e, m	7.28	2320	1554	0.347	0.371	0.281
27	Ethylglycol adipate	m	7.35	2692	1784	0.324	0.367	0.308
28	Diethylglycol adipate	m	7.71	2764	1822	0.331	0.365	0.304
29	Capillary Supelcowax (P)	e, 4	7.75					
30	Carbowax 1000	e	7.85	2587	1726	0.352	0.363	0.286
31	Carbowax 400	e	8.20	2642	1731	0.352	0.363	0.287
32	Diethyl glycol succinate	m	9.89	3430	2271	0.323	0.367	0.310

[a] e = Experimental data; m = McReynolds' data [34]; 1 = non-polar wide-bore capillary (see text); 2,3 = series connection of capillary columns, polar + non-polar or reversed order; 4 = polar wide-bore capillary; a = calculated from Betts [27].

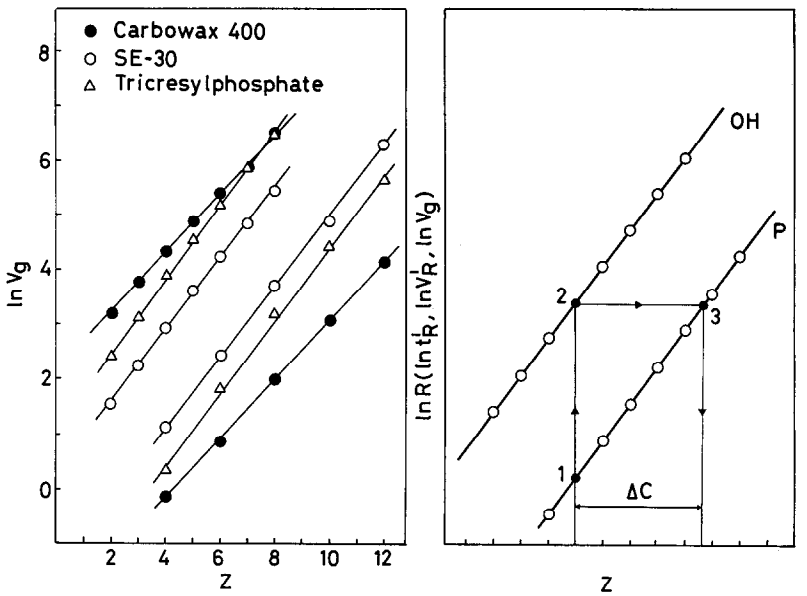

Fig. 1. Left: linear behaviour of the logarithm of the retention values of *n*-alkanes and *n*-alcohols on some columns at 120°C as a function of the number of carbon atoms in the molecule, Z. Right: schematic diagram showing the definition of ΔC values: (1) given linear akane; (2) linear alcohol with the same Z value as 1; (3) hypothetical alkane with the same retention as alcohol 2; ΔC = difference of Z value between alkanes 3 and 1.

high polarity as a function of the number of carbons atoms, Z:

$$\ln R_p = a_p + b_p Z \quad (1)$$

$$\ln R_{OH} = a_{OH} + b_{OH} Z \quad (2)$$

where R_p for paraffins and R_{OH} for alcohols may be adjusted retention times, t'_R, adjusted retention volumes, V'_R, and specific retention volumes, V_g. In fact, the following relationships hold:

$$V'_R = \phi_n t'_R \quad (3)$$

$$V_g = \phi j \frac{273}{TW} t'_R = K t'_R \quad (4)$$

where ϕ is the carrier gas flow-rate and K is a constant that contains the contribution of the compressibility factor of James and Martin, j, the absolute temperature, T, and the weight of stationary phase in the column, W. On a logarithmic scale the constant parts of eqns. 3 and 4 only shift the lines of Fig. 1 in vertical directions, without changing their horizontal distance.

$$\ln V'_R = \ln \phi + \ln t'_R = \text{const} + \ln t'_R \quad (5)$$

$$\ln V'_g = \ln \kappa + t'_R = \text{const} + \ln t'_R \quad (6)$$

The lines for different homologous series on the same column are parallel, as previously found by Hawkes [36], whereas a difference exists between different columns. For the three columns shown in Fig. 1, the values of b_p and b_{OH} are, respectively: Carbowax 400, 0.597 and 0.593; tricresylphosphate, 0.667 and 0.672; SE-30, 0.609 and 0.614. The horizontal distance between the two straight line (ΔC) is therefore a measure of the difference in behaviour of the non-polar and of the polar homologous series. This distance can be measured directly parallel to the abscissa: the experimental values of Fig. 1 (left) are 8.2 for Carbowax 400, 5.0 for tricresylphosphate and 2.4 for SE-30. They can be calculated:

$$a_{OH} - a_p = \Delta a \quad (7)$$

$$(b_{OH} + b_p)/2 = b^0 \quad (8)$$

$$\Delta C = \Delta a / b^0. \quad (9)$$

The averaged b^0 values are used to compensate the slight experimental fluctuations in the slopes due to measurement of the retention times of peaks that may have different shapes due to the different polarities of the samples.

RESULTS AND DISCUSSION

The ΔC value can be considered as the difference of apparent carbon number between linear alkanes and alcohols with the same retention or as the number of methylene groups that should be theoretically added to a linear alkane with Z carbon atoms to obtain an hypothetical alkane with the same retention of a linear alcohol with Z carbon atoms (see Fig. 1, right). The concept of apparent or equivalent carbon number or chain length was used as a means for the classification of the elution characteristics of various substances by James [37] and was replaced by the Kováts' retention index concept [3]. The ΔC values calculated with the above formulas from experimental or literature data are shown in the second columns of Table I. In the same table are also reported the values of the $\sum^5_{MR}$ (sum of the McReynolds constants for benzene, *n*-butanol, 2-pentanone, 1-nitropropane and pyridine), $\sum \Delta I_i$ (sum of the McReynolds' constants for *n*-butanol, 1-nitropropane and 1,4-dioxane, *i.e.* the divisor in Snyder's formula for the calculation of the selectivity parameter, which gives a measure of the importance of hydrogen bonds and dipole interactions with respect to the dispersive forces) and the selectivity parameters x_b, x_n and x_d calculated for the three probes used to obtain the position of each column on the selectivity triangle [23,24].

Fig. 2 compares the $\sum^5_{MR}$ and the ΔC values; the

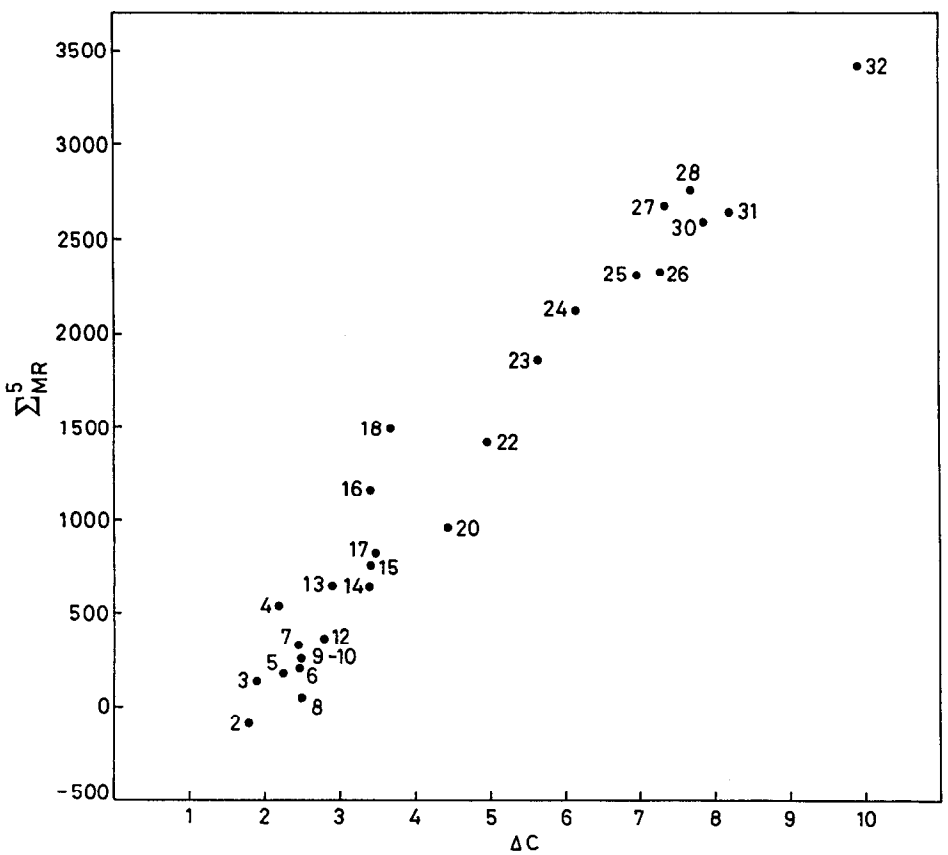

Fig. 2. Values of the sum of McReynold's constants, $\sum^5_{MR}$, for the five probes benzene, *n*-butanol, pentan-2-one, nitropropane and pyridine as a function of the ΔC values at 120°C.

general trend of the polarity measured with the two methods is similar. Some characteristics of the liquid phases are equally expressed by both methods, but some differences are better shown by the ΔC values.

For example, the different polarity of the Carbowaxes with different molecular weights [38] is shown by ΔC, whereas the $\sum_{MR}^{5}$ and the selectivity parameter are fairly similar. The polarity of the capillary column Supelcowax (polyglycol), which cannot be measured with the ΔI values, is easily obtained with the ΔC method and lies between CW6000 and CW1000. Phase 18 (QF 1) shows a very high polarity value with both the methods of McReynolds and Snyder due to the prevailing effect of the polarizability measured by 1-nitropropane. The analysis of pesticides and haloalkanes showed that a behaviour similar to that of esters is more probable. Again, phases 6, 7, 9 and 10 are chemically similar and the difference of $\sum_{MR}^{5}$ values is not justified. The ΔC value of the non-polar SPB-1 capillary column is very similar to that of methylsilicone-packed columns.

The ΔC value shows the changes in polarity that are obained when the flow direction in serially coupled columns is reversed, with the upstream column having a greater influence. This is clearly shown by the ΔC values for the NP + P and P + NP arrangements shown in Table I, compared with the ΔC values for the two separated columns.

A further advantage of the use of ΔC is that this parameter is obtained directly by injecting only two linear alkanes and two linear alcohols with a convenient difference of Z on the column to be classified, without any reference to the standard non-polar phase squalane, which cannot be used at high temperatures or with a bonded-phase capillary column. The use as the non-polar reference phase of methylsilicone-bonded phase columns (SE 30, BP-1) suggested as an alternative to squalane, gives fair results for high-polarity phases (*e.g.* polyglycols or cyanosilicones) but is misleading for other methyl and low phenyl polymers, as methylsilicones show a hydrogen bonding capacity due to the lone pairs of electrons on the oxygen atoms of the Si–O–Si bonds, and their McReynolds constants differ appreciably from zero. This was also confirmed by the greater polarity of silanized versions of Porapak P (Porapak PS) found by Hepp and Klee [28] with respect to the non-silanized version. It is evident that the presence of Si–O–Si bonds with lone electrons pairs on the oxygen atom will increase the polar interactions with respect to the behaviour of simple Porapak P, a pure polystyrene cross-linked polymer, whose possibility of hydrogen bonding with alcohols is only restricted to the limited availability of π electrons from the aromatic rings.

The application of the method to porous polymer columns also gives positive values for all phases, thus avoiding the negative polarity values obtained by applying McReynolds' method with respect to squalane [9,19].

All the retention values (t_R, V_R, V_g) can be used directly and previously tabulated retention data of alkanes and alcohols allow the ΔC values of any column to be obtained. Published values of I can also be used, as the knowledge of the retention times of two *n*-alkanes and the application of the reversed Kováts equation allow the t'_R or V'_R values to be easily calculated. The ΔC value depends on column temperature, but can be calculated by knowing the slope of the Arrhenius plot (logarithm of the retention as a function of the reciprocal of the absolute column temperature) for alkanes and alcohols on the various phases.

An objection to the generalized use of the ΔC values for the classification of all stationary phases is that only the effects of dispersive forces (measured by the behaviour of the alkanes) and of the hydrogen bonding (alcohols) are considered, and that columns whose action mainly depends on dipole interactions are not correctly classified. The trend in bonded phase capillary column technology is to try to obtain any possible intermediate polarity by the connection of various lengths of polydimethylsiloxane and polyglycol columns, by developing theoretical approaches [39] that allow the prediction of retention times in serially linked open-tubular columns and the optimization of column length. The validity of this approach was confirmed for narrow-bore and wide-bore columns [40]. In this mixed-phase system the hydrogen acceptor, donor and dispersive forces are the prevailing phenomena that control the separation, and therefore the use of the easily measured ΔC values allows the comparison of different column systems, rather than simple liquid phases, as it also considers the interaction with Si–O–Si bonds of the glass wall, of the support

and of the silanizing agents. It also allows an evaluation of the change in polarity due to column ageing and contamination or that obtained by connecting different lengths of polar and non-polar columns.

ACKNOWLEDGEMENT

This work was supported by the Italian Ministry of University and Scientific and Technological Research.

REFERENCES

1 R. N. Ewell, J. M. Harrison and L. Berg, *Ind. Eng. Chem.*, 36 (1944) 871.
2 H. M. McNair and E. J. Bonelli, *Basic Gas Chromatography*, Varian Aerograph, Walnut Creek, CA, 1965, p. 40.
3 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
4 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
5 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
6 G. Castello and G. D'Amato, *J. Chromatogr.*, 366 (1986) 51.
7 Z. Szentirmai, G. Tarjan and J. Takacs, *J. Chromatogr.*, 73 (1972) 11.
8 F. Riedo, D. Fritz, G. Tarjan and E. Kováts, *J. Chromatogr.*, 126 (1976) 63.
9 G. Castello and G. D'Amato, *J. Chromatogr.*, 269 (1983) 153.
10 C. F. Poole and S. K. Poole, *Chem. Rev.*, 89 (1989) 377.
11 C. F. Poole, S. K. Poole, R. M. Pomaville and B. R. Kersten, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 640.
12 J. Li, A. J. Dallas and P. W. Carr, *J. Chromatogr.*, 517 (1990) 103.
13 G. Castello, G. D'Amato and E. Biagini, *J. Chromatogr.*, 41 (1969) 313.
14 G. Castello and G. D'Amato, *J. Chromatogr.*, 54 (1971) 157.
15 G. Castello and G. D'Amato, *J. Chromatogr.*, 150 (1978) 319.
16 T. J. Betts, G. J. Finucane and H. A. Tweedie, *J. Chromatogr.*, 213 (1981) 317.
17 M. B. Evans and J. K. Haken, *J. Chromatogr.*, 472 (1989) 93.
18 *General Catalog*, Chrompack International, Middelburg, 1986, p. 7.
19 G. Castello and G. D'Amato, *J. Chromatogr.*, 366 (1986) 51.
20 G. Castello, G. D'Amato and G. Canciani, *Ann. Chim. (Rome)*, 68 (1978) 255.
21 G. Castello and G. D'Amato, *J. Chromatogr.*, 196 (1980) 245.
22 G. Castello and G. D'Amato, *J. Chromatogr.*, 254 (1983) 69.
23 L. R. Snyder, *J. Chromatogr.*, 92 (1974) 223.
24 L. R. Snyder, *J. Chromatogr. Sci.*, 16 (1978) 223.
25 M. S. Klee, M. A. Kaiser and K. B. Laughlin, *J. Chromatogr.*, 279 (1983) 681.
26 T. J. Betts, *J. Chromatogr.*, 354 (1986) 1.
27 T. J. Betts, *J. Chromatogr.*, 504 (1990) 186.
28 M. A. Hepp and M. S. Klee, *J. Chromatogr.*, 404 (1987) 145.
29 E. Fernandez-Sanchez, A. Fernandez-Torres, J. A. Garcia-Dominguez and J. M. Santiuste, *Chromatographia*, 31 (1991) 75.
30 G. Tarjan, S. Nyiredy, M. Györ, E. R. Lombosi, T. S. Lombosi, M. V. Budahegyi, S. T. Meszaros and J. M. Takacs, *J. Chromatogr.*, 472 (1982) 1.
31 A. T. Kames and A. J. P. Martin, *Biochem. J.*, 50 (1952) 679.
32 Swoboda, in M. van der Swaay (Editor), *Gas Chromatography 1960*, Butterworths, London 1962, p. 36.
33 E. sz. Kováts, *Adv. Chromatogr.*, 1 (1965) 239.
34 G. Castello, A. Timossi and T. C. Gerbino, *J. Chromatogr.*, 522 (1990) 329.
35 W. O. McReynolds, *Gas Chromatographic Retention Data*, Preston Technical Abstract, Evanston, IL, 1966.
36 St. J. Hawkes, *Chromatographia*, 25 (1988) 87.
37 A. T. James, in D. Glick (Editor), *Methods of Biomedical Analysis*, Interscience, New York, 1960.
39 J. R. Jones and J. H. Purnell, *Anal. Chem.*, 62 (1990) 2300.
40 T. C. Gerbino and G. Castello, in P. Sandra (Editor), *Proceedings of 13th International Symposium on Capillary GC, Riva del Garda, 1991*, Vol. I, Hüthig, Heidelberg, p. 889.