



ELSEVIER

Journal of Chromatography A, 837 (1999) 153–170

JOURNAL OF
CHROMATOGRAPHY A

Influence of temperature on the polarity of porous polymer beads stationary phases for gas chromatography

G. Castello*, S. Vezzani, L. Gardella

Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, 16146 Genova, Italy

Received 24 July 1998; received in revised form 18 December 1998; accepted 8 January 1999

Abstract

The change in polarity as a function of temperature of gas chromatographic columns packed with Porapak and Chromosorb 'Century series' porous polymer beads was investigated by using as a polarity indicator the difference in apparent carbon number of linear alkanes and alcohols with the same retention time, ΔC . The results were compared with those obtained by using the retention indices of the McReynolds' probes and the retention of light hydrocarbons. Some capillary columns with porous polymeric layer were compared with the corresponding type of polymer beads in packed columns. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, GC; Temperature effects; Polarity; Polymer phases; Retention indices; Alkanes; Alcohols; Hydrocarbons

1. Introduction

From the year 1966 porous polymer beads (PPBs) have been used as stationary phases in gas chromatography [1,2]. The first types available were styrene-divinylbenzene or ethylvinylbenzene-divinylbenzene polymers, known under the trade names of Porapak P and Q (Waters, Framingham, MA, USA) and were widely applied to the analysis of gases, replacing the silica gel or alumina columns previously used [3] as their hydrophobicity avoided the adsorption of water which influenced the retention times and the baseline on hygroscopic stationary phases. The low retention of water and the sharpness of its peak also promoted the use of PPBs for the analysis of water-containing samples, and the determination of very small amounts of humidity in

hydrocarbons by electron capture detection [4]. The negligible bleeding of PPBs columns also permitted their use with the very sensitive helium detector [5–7]. At low temperature the PPBs show a gas–solid separation mechanism, and long columns filled with Porapak Q were used at -70°C for the determination of traces of oxygen in argon. Separation of saturated and unsaturated light hydrocarbons and of reactive inorganic gases was also carried out at room temperature. At high temperature the PPBs behave as gas–liquid stationary phases, owing to the increasing importance of solution phenomena with respect of surface adsorption and pore interaction.

Table 1 shows the names, composition and some characteristics of PPBs of different polarity produced under the trade names of Porapak (Waters) and Chromosorb Century Series (Johns-Manville, Denver, CO, USA) [2,8,9]. Other (HayeSep, Tenax, Polysorb, Cekachrom, Synachrom) are available

*Corresponding author.

Table 1

Chemical composition, surface area and maximum temperature of the used PPBs (from Refs. [2,8,9] and from manufacturers' catalogs). Sty=Styrene; DVB=divinylbenzene; EVB=ethylvinylbenzene; EGDMA=ethylene glycol dimethacrylate; ACN=acrylonitrile

PPB	Composition	Surface area (m ² /g)	Max. temperature (°C)
Porapak N	Vinylpyrrolidone	225–350	220
Porapak P	Sty-DVB	100–200	250
Porapak Q	EVB-DVB	500–600	250
Porapak R	Vinylpyrrolidone	450–600	250
Porapak S	Vinylpyridine	300–450	250
Porapak T	EGDMA	250–350	190
Chromosorb 101	Sty-DVB	<50	275–235
Chromosorb 102	Sty-DVB	300–400	250–300
Chromosorb 103	Polystyrene ^a	15–25	275–300
Chromosorb 104	ACN-DVB	100–200	250
Chromosorb 105	Acrylic ester	600–700	250–275
Chromosorb 106	Polystyrene	700–800	250–275
Chromosorb 107	Acrylic ester	400–500	250–275
Chromosorb 108	Cross linked acrylic	100–200	250–275
PoraPLOT Q	Sty-DVB		250 ^b
PoraPLOT U	DVB-EGDMA		190

^a The surface is basic.

^b A high temperature version (PoraPLOT Q-HT) with $T_{\max} = 290^{\circ}\text{C}$ is available.

[10]. The comparison among many PPBs was carried out by Dave [8], Supina and Rose [11] and others [12–16]. The separation capability of the different types was investigated at low temperature by using as probes methane, ethane, ethylene and acetylene [17–20] and at high temperature with the McReynolds' constants [21–23]. It was found that Porapak and Chromosorb PPBs made with the same polymer do not behave in an identical way, probably owing to the different polymerisation process, molecular weight, pore dimension, active area etc. The tuning of the selectivity for a given separation can be improved by using composite columns made with PPBs of different polarity [24].

The first PPBs capillary columns, made by direct polymerisation of the monomer into the small diameter tubing have shown severe tailing of the polar compounds, in contrast with the packed PPB columns [25]. Highly efficient micro-packed columns were prepared by filling a silica capillary with small particles of Chromosorb 102 (90–100 μm) [26], but the column length had a limitation due to the high pressure required to obtain a suitable carrier gas flow rate. True open bore capillary columns having the properties of standard PPBs were made by coating the inner wall of fused-silica tubing with very small particles of polymer (1–2 μm): the main disadvan-

tage of the micro packed columns, i.e. their high pressure drop, was eliminated and very long columns could be prepared. The first column commercially available, PoraPLOT Q (Chrompack, Middelburg, The Netherlands) was prepared with styrene-divinylbenzene polymer having properties similar to the standard Porapak Q [27–29]. Columns of different polarity were prepared by adding methacrylate groups to the polymer [30] and wide-bore-metal capillary columns are also available [31,32]. Further improvement was achieved by direct polymerisation of the styrene-divinylbenzene monomer on the column walls (PoraBOND columns, Chrompack). The inconveniences previously observed [25] on columns prepared with a similar technique were avoided [33,34].

Porous polymer-filled PLOT (porous-layer open tubular) columns are now available from different producers (e.g. HP-PLOT Q from Hewlett-Packard, Palo Alto, CA, USA; GS-Q from J&W Scientific, Folsom, CA, USA; Rt-Q PLOT from Restek, Bellefonte, PA, USA) and many applications were described [32–37]. Both the packed and the capillary PPBs columns can be used in a wide temperature range from -100°C to $200\text{--}325^{\circ}\text{C}$ (Table 1). The styrene-type polymers permit a higher temperature to be used for long times; vinylpyrrolidone or meth-

acrylate polymers are less temperature-resistant and their properties are modified after continuous heating [38,39]. If the polarity of a column changes with changing the temperature of analysis, the identification of compounds carried out in isothermal conditions cannot be used in different isothermal or programmed temperature runs, due to the possible inversion of the elution order or to coincidence of some peaks. It is therefore necessary to know if the polarity of the used stationary phase depends on temperature. The temperature dependence of the behaviour of some liquid-phase packed or bonded-phase capillary columns was investigated previously [40] by using a polarity indicator based on the difference in apparent carbon number of linear alkanes and alkanols with the same retention time, ΔC , which evaluates the relative contribute to the retention of the dispersion forces and of the hydrogen bonds and dipole moment [41–43]. Other methods, as the McReynolds' phase constants [18,19], the Snyder's selectivity parameters [44–46], the Kováts' coefficient K_c [47,48] the RP values [49] and the solvation parameters model of Abraham et al. [50–54] were also used to investigate the sorption properties of porous polymers [55].

In this paper the dependence on temperature of the performance of packed columns filled with several PPBs is investigated at high temperature by using the ΔC method and at low temperature with the behaviour of saturated and unsaturated light hydrocarbons. Some comparison has been carried out with two types of capillary PPBs columns.

2. Experimental

The packed columns, stainless steel, 3 m×1/8 in. O.D. (1 in.=2.54 cm), were filled with 80–100 mesh PPBs of the various kinds listed in Table 1 and installed in a gas chromatograph equipped with a thermal conductivity detection (TCD) system (Varian Associates, Palo Alto, CA, USA). For some types of PPBs, different column length and mesh sizes were also tested, in order to check if these parameters could modify the ΔC value. Helium was used as the carrier gas, at a flow rate of 30 cm³ min⁻¹. The analyses were performed at temperature ranging from 140 to 220°C. Samples of various mixtures of

n-alkanes (C₁–C₉) and *n*-alkanols (C₁–C₆) were analysed. The smallest amount of sample detectable at the highest sensitivity was injected, in order to obtain peaks as symmetrical as possible. The PorapLOT columns were installed in a gas chromatograph Model 3800 (Varian) with flame ionisation detector. A volume of 0.1 μl of a solution of 1 g/l of the polarity probes in dichloromethane was injected with a split ratio of 1/20. The polarity was calculated from experimental t'_R values with the ΔC method by measuring the horizontal distance between the two straight lines having the equation $\ln t'_R = a + b z$, obtained by plotting $\ln t'_R$ as a function of the number of carbon atoms, z , for *n*-alkanes and *n*-alkanols respectively. The advantage of using this technique instead of measuring the vertical distance between the two lines or mathematically calculating the average distance was discussed previously [40]. The first five McReynolds' probes (benzene (BE), *n*-butanol (BUA), 2-pentanone (MPK), pyridine (PY) and 1-nitropropane (INP)) were also injected along with reference *n*-alkanes in order to measure their Kováts' retention indices, I , and the McReynolds phase constants ΔI . Light hydrocarbons (methane, ethane, ethylene and acetylene) were injected with gas-tight syringes.

3. Results and discussion

Styrene-divinylbenzene polymers (see Table 1) are considered to be non-polar adsorbents, but weak interactions may also occur with the π -electrons of phenyl and phenylene groups. They can be classified as type III adsorbents according to Kiselev's classification [56,57], bearing centres of higher electron density on the surface, even if non-specific dispersion forces predominate. Polar polymers with cyano, aminic, nitro, carboxylate or hydroxyl groups may interact specifically with molecules having an electron density localised on some bonds or atoms (type B adsorbates) or containing functional groups as OH, NH, etc., and can be graded as type III and partially as type II adsorbents. Table 2 shows the ΔC values at various temperatures obtained with the above described method. The values obtained with gas-liquid packed columns filled with 10% of Squalane and Carbowax 20M on Chromosorb W 80–100 mesh

Table 2

ΔC values of different PPB packed and capillary columns as a function of temperature. The values of squalane and Carbowax 20M gas-liquid phases (10% on Chromosorb W 80–100 mesh) are shown for comparison

PPB	Temperature (°C)				
	140	160	180	200	220
Porapak N			3.41	3.40	3.39
Porapak P	2.66	2.74	2.86	2.94	
Porapak Q			2.14	2.18	2.27
Porapak R	2.88	2.82	2.75	2.72	
Porapak S		2.75	2.71	2.69	2.67
Porapak T	4.76	4.54	4.48		
Porapak Q+S ^a			2.30	2.36	2.39
Chromosorb 101			2.78	2.84	2.98
Chromosorb 102			2.67	2.71	2.80
Chromosorb 103		3.43	3.48	3.52	3.60
Chromosorb 104		4.96	4.98	5.06	
Chromosorb 105		2.86	2.90	2.96	3.00
Chromosorb 106			1.97	2.02	2.00
Chromosorb 107			3.26	3.24	3.30
Chromosorb 108			4.28	4.37	4.50
PoraPLOT Q		2.19	2.18	2.21	2.22
PoraPLOT U	2.94	2.98	3.00	3.02	
Squalane	1.97	1.97	1.97	1.98	
Carbowax 20M	7.00	7.02	7.04	7.06	7.08

^a Values of a mixed Porapak Q plus Porapak S column (30:70, w/w, ratio).

are shown for comparison purposes with the standard non-polar column and with a widely used polar column (polyglycol). Figs. 1 and 2 show the behaviour of the ΔC as a function of temperature; different scales of the y axis are used in the two figures in order to display all the plots without interference. Porapak N is shown in both figures as a reference between high-polarity and low polarity PPBs. All the PPBs tested have ΔC ranging from values similar to that of Squalane (for Chromosorb 106) or slightly greater (for Porapak Q and PoraPLOT Q) up to values similar to those of some polyesters as neopentyl glycol adipate (ΔC of about 6). The most polar PPBs do not reach the ΔC values of polar liquid phases as the Carbowaxes (about 7) or diethyl glycol adipate (7.7) or diethyl glycol succinate (about 9.9) [40]. The majority of the PPBs have ΔC values similar to that of polydimethylsiloxanes as SE-30 or SE-52; mixed phase columns show a behaviour averaged between those of the two polymer used for their preparation: the column filled with 30% of Porapak Q (average ΔC 2.2) and 70% of

Porapak S (ΔC 2.7) mixed together has an average ΔC of 2.35.

Porapak T, Chromosorb 104 and 108 show the greatest polarity and an appreciable dependence on temperature. Porapak T was tested at temperatures lower than 200°C because, as observed previously [39] and discussed below, this polymer changes appreciably its properties at high temperature and after thermal ageing. Also the Porapak N, R and S show a decrease of the ΔC with increasing temperature, whereas the values for all other PPBs increases slightly. The negative dependence of the ΔC on temperature seems to be correlated with the composition of the monomer used for the preparation of the PPB (vinylpyridine, vinylpyrrolidone, EGDMA, acrylic esters, see Table 1). The presence of oxygen and nitrogen atoms in the chains or in the crosslinked network is responsible of the polarity of these polymers, that can be classified as belonging to the third polarity class of Ewell (electron-donor atoms) [58]. The behaviour of these polar PPBs is therefore correlated with the simultaneous effect of the dispersion forces and of the hydrogen bonding, whereas polystyrene-type polymers act mainly through dispersion forces and weak interactions with the π -electrons of phenyl and phenylene groups [55,59]. The change of ΔC values with changing temperature means that the distance between the plots for *n*-alkanes and *n*-alkanols is modified due to a different temperature dependence of either or both plots. Both dispersive and polar interaction would be expected to decrease as the column temperature increases, but the rate of decrease will vary from one stationary phase to another. As an example, Fig. 3 shows that on Porapak T the logarithm of the t'_R of alcohols decreases more rapidly than that of *n*-alkanes with increasing temperature and that the ΔC values decrease, as shown by their graphical representation with the segments A and B in the figure. For non-polar stationary phases, it has been shown [60,40] that the cavity-dispersion interaction becomes less favourable for solute transfer at higher temperatures and that interfacial adsorption plays a dominant role in the retention of hydrocarbons [59–61]. For those compounds which are retained by a mixed solution/adsorption mechanism the relative contribution from adsorption decrease with increasing temperature. It was found that for OV-17 liquid phase (50% phenyl

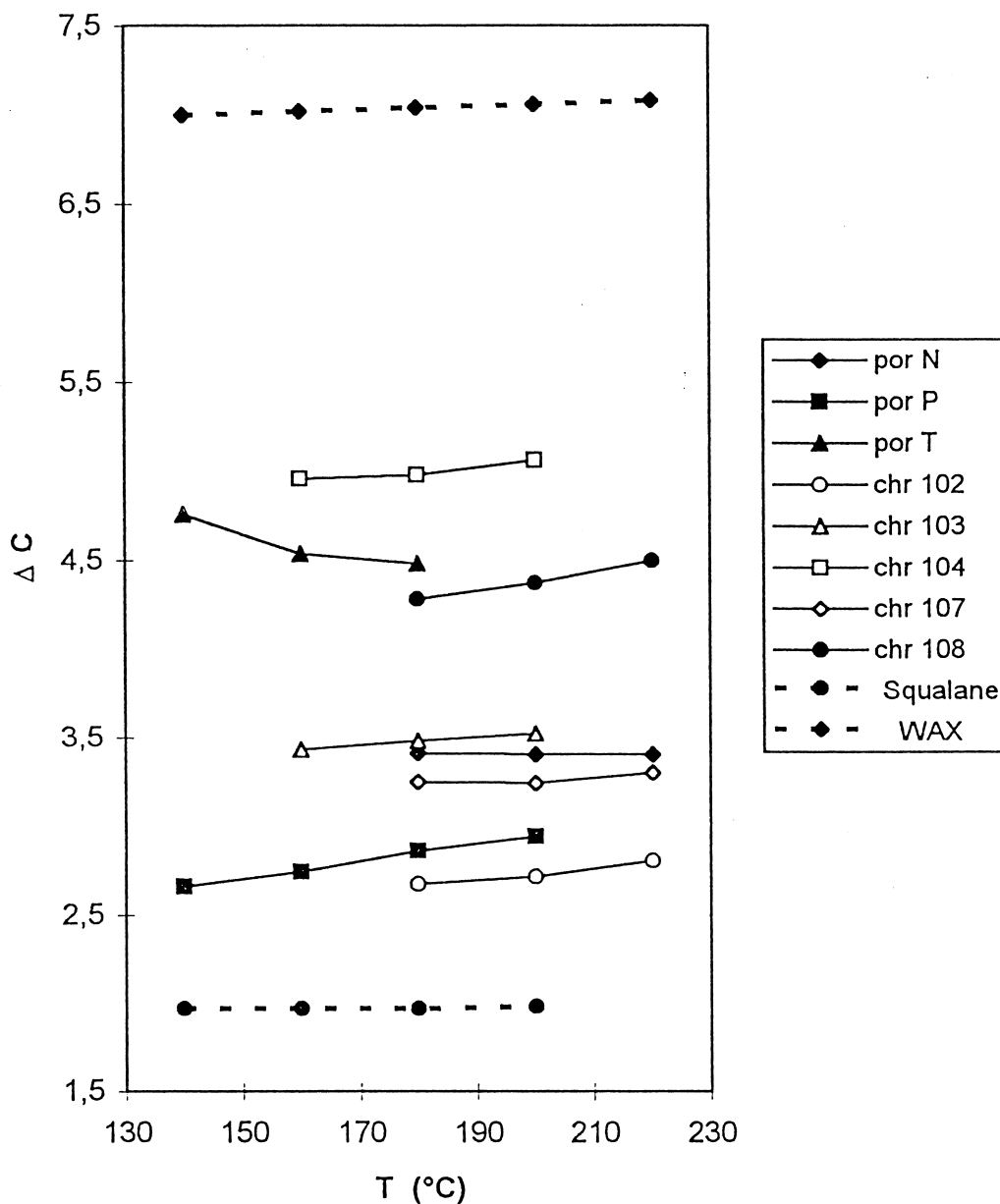


Fig. 1. ΔC values of packed columns filled with some Porapak and Chromosorb "Century Series" porous polymer beads at different temperatures. The behaviour of gas-liquid stationary phases squalane and Carbowax 20M (WAX) is shown for comparison purposes.

silicone and therefore with interaction mechanism similar to styrene-divinylbenzene polymers due to the effect of π -electrons of the aromatic rings) the adsorption contribute for tridecane and heptan-1-ol is the same (2.3% at 81.2°C and 0.6% at 121.2°C) whereas for other low-polarity phases the effect of

temperature on alkanes is greater [60]. This means that for non-polar PPBs the distance between the *n*-alkanols and *n*-alkanes plots does not increase or changes only slightly with increasing temperature, leading to constant or slowly increasing ΔC values.

The effect of the length and of the mesh size was

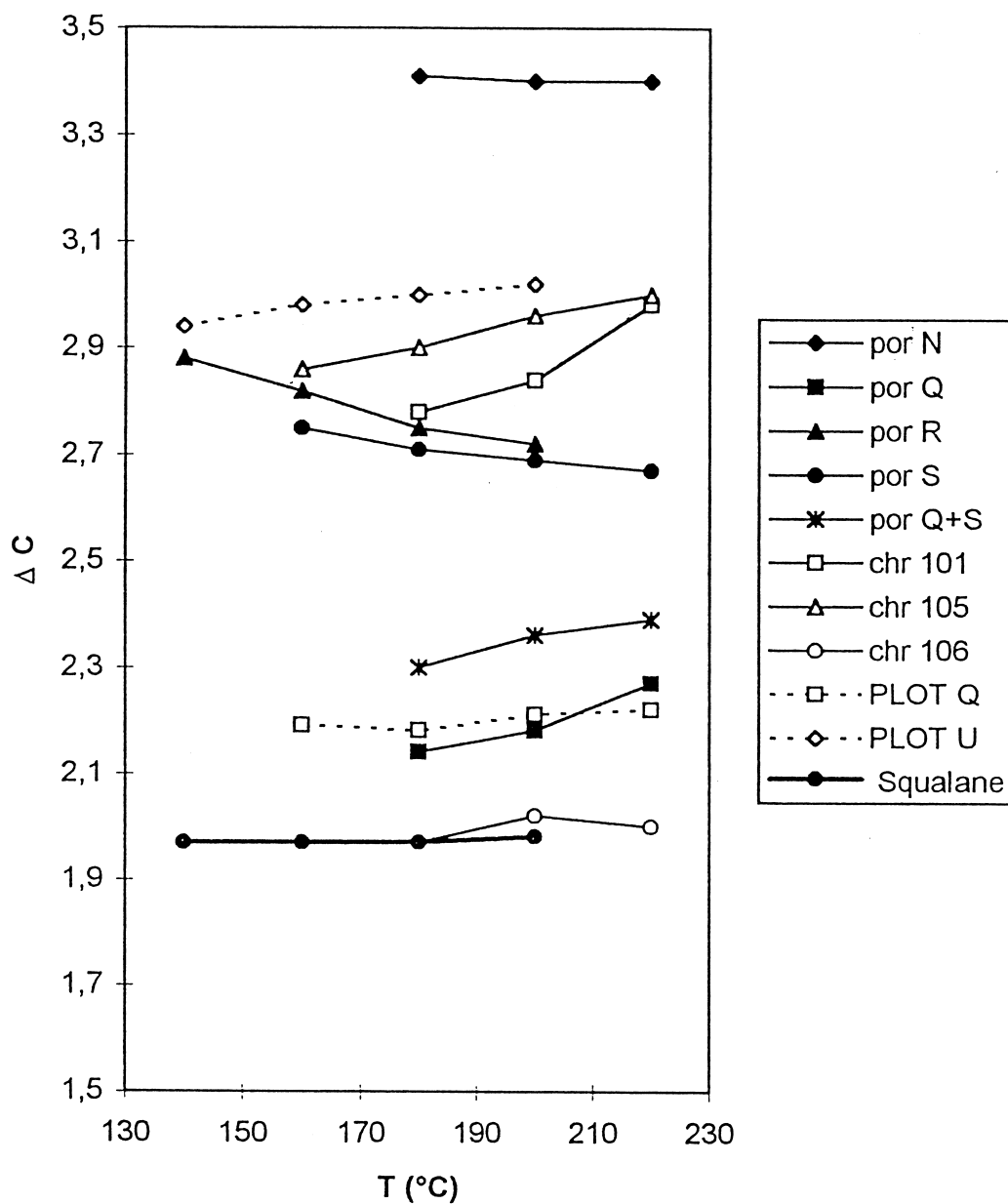


Fig. 2. ΔC values of some packed Porapak and Chromosorb "Century Series" columns and of two capillary PoraPLOT columns at different temperatures, plotted with enlarged vertical scale with respect of Fig. 1. The behaviour of the Porapak N and of the non-polar gas-liquid stationary phase squalane is shown for comparison with the data of Fig. 1.

also investigated for some packed columns. The first variable should not have any effect on the polarity, as the solute-solvent interactions are characteristic of the chemical composition of the polymer and should

not be influenced by the amount or by the macrostructure of the stationary phase. No effect of the length of columns packed with the same batches of polymer on the ΔC values was observed within the

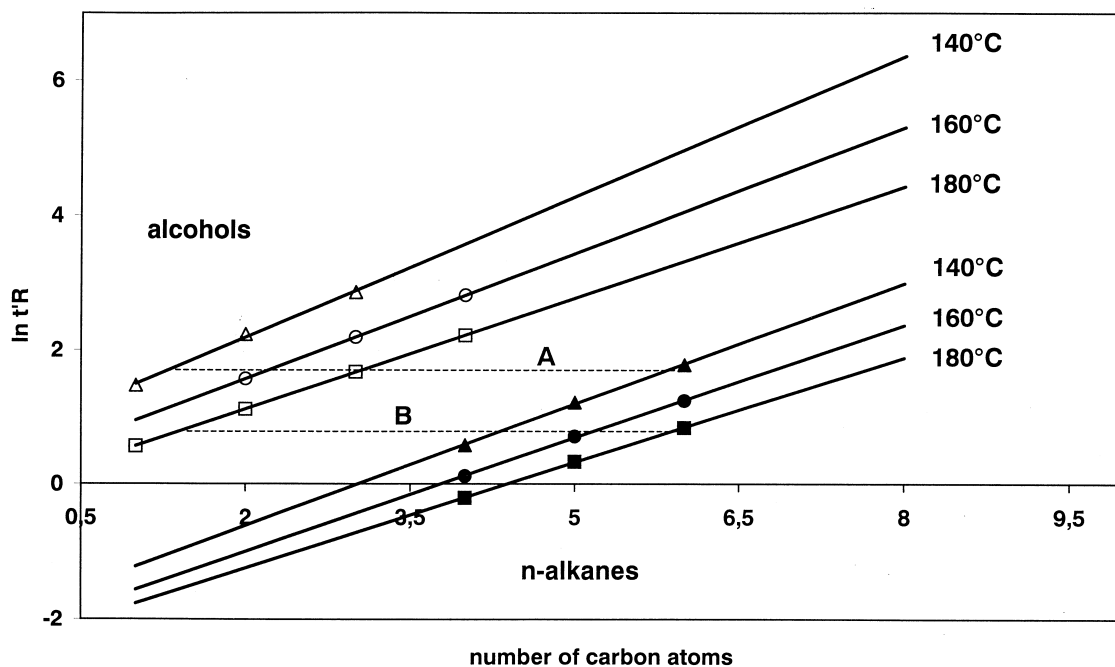


Fig. 3. Values of the $\ln t'_R$ on Porapak T column of linear alcohols and alkanes as a function of the number of carbon atoms. The ΔC values, indicated by the length of the dashed lines A and B, decrease with increasing temperature.

tested range (from 150 to 400 cm). However, some effect may be correlated with the mesh size as it can modify the surface area/bulk volume ratio of the stationary phase and influence the adsorption of the probes at the gas–polymer interface, being this phenomenon predominant for hydrocarbons on polar phases [59]. An effect on the ΔC values should be therefore possible on polyvinylpyrrolidone or vinylpyridine polymers, which have a high selectivity for hydrogen-bond acids [55]. Some difference was in fact observed among polar columns (Porapak N, R and S) filled with different mesh sizes; the greatest difference was found on Porapak R column, for which the values obtained with 120–150 mesh are about 4% greater than those observed with 80–100 mesh size. These fluctuations, which are slightly greater than the change of retention observed by using columns prepared with different batches of the same nominal mesh size, may also depend on the change in composition from batch to batch of the polymer used [20].

The values of ΔC at 200°C were compared with the McReynolds' constants, ΔI , measured with re-

spect of the retention on squalane extrapolated to 200°C from the maximum temperature of this liquid phase (125°C). As this extrapolation could cause an error, the ΔI values were also measured with respect of the synthetic hydrocarbon $C_{87}H_{176}$ apolane (22,24-diethyl-19,29-dioctadecylheptatetracontane) suggested by Riedo et al. as the reference non polar phase in the range 30–300°C [62]. Table 3 shows the values of the retention indices measured on apolane, squalane, various packed column filled with PPBs and capillary PoraPLOT Q and U. The values for 1-nitropropane cannot be measured on Porapak S and Chromosorb 103 columns because this probe reacts with the polymer forming very broad or multiple peaks. The I values on apolane are slightly greater than those measured on squalane, according to the greater interaction of this liquid phase previously observed when comparing linear and branched alkane phases as non polar reference materials [63,64]. The I values of benzene and pyridine on some PPBs are smaller than those on the reference squalane or apolane, as shown by the negative values in Fig. 4 where the ΔI measured with respect of squalane

Table 3

Retention index values of the firsts five McReynolds' probes at 200°C on various packed columns of PPBs, on packed apolane and squalane and on PoraPLOT Q and U capillary columns

Probe	BE	BUA	MPK	PY	INP
Apolane	702	610	636	757	678
Squalane	675	600	631	740	667
Porapak N	666	708	730	770	784
Porapak P	746	698	732	847	809
Porapak Q	623	609	651	687	661
Porapak R	647	677	693	741	732
Porapak S	633	652	680	713	–
Porapak T	729	782	800	860	951
Chromosorb 101	723	675	714	810	780
Chromosorb 102	648	625	669	722	697
Chromosorb 103	763	765	770	880	–
Chromosorb 104	861	929	961	1077	1125
Chromosorb 105	647	661	693	746	730
Chromosorb 106	616	599.4	647	672	658
Chromosorb 107	670	738	753	812	839
Chromosorb 108	748	814	809	903	924
PoraPLOT Q	622	617	662	699	677
PoraPLOT U	666	702	726	765	779

Notes: McReynolds' probes: BE: benzene; BUA: butanol; MPK: 2-pentanone; PY: pyridine; INP: 1-nitropropane. Porapak S and Chromosorb 103 react with 1-nitropropane yielding multiple or asymmetric peaks.

column are plotted. The average polarity expressed as the sum of the ΔI of the first McReynolds' probes, $\sum_{5 MR}$, is plotted in Fig. 5 as a function of the ΔC . The values for Porapak S and Chromosorb 103 are not reported on the vertical axis because 1-nitropropane reacts with the polymer and the $\sum_{5 MR}$ cannot be calculated. The ΔC values of these two phases can be determined and are plotted on the abscissa for comparing them with those of the other columns. The points for the less polar columns Porapak Q, Chromosorb 106 and PoraPLOT Q lie below the zero level conventionally represented by the squalane. This confirms the ambiguities in the use of McReynolds' phase constants as polarity indicators [61,65,66], due to the choice of *n*-alkanes as the reference standards and ascribed, for columns filled with conventional liquid phases on inert support, to the high contribution of interfacial adsorption at the gas–liquid and phase-support interfaces. In this instance, because on styrene-divinylbenzene or polystyrene polymers the main contribution to the retention is dispersion, while dipole-type interactions

are not significant and very weak hydrogen-bond (acid or basic) interactions were identified [55], the partitioning of the retention index markers *n*-alkanes is greater than that of some McReynolds polarity probes. As a consequence, when the retention of the *n*-alkanes increases, the *I* values of these probes decrease, the sum of ΔI values is smaller than that of squalane and an apparent negative polarity is found. Furthermore, the McReynolds' method cannot be applied to polymers which react with nitroalkanes. This inconveniences are not observed when the ΔC method is used for the classification of the stationary phases. Table 2 and Figs. 1 and 2 show that no PPB exhibits an apparent polarity below that of squalane. The polymer considered as the less polar, Chromosorb 106, where the contribution from solvent cavity formation and dispersion interaction was found to be prevailing [55] as in squalane [59], shows ΔC values very close or coincident with those of squalane. However, Fig. 5 shows that the polarity order measured with the ΔC values is similar to that given by the McReynolds' constants and confirms that, independent on the method used for the determination, the Chromosorb 106 is the less polar and Chromosorb 104 the most polar of all the porous polymers tested.

The retention index values on capillary PPBs columns slightly differ from those obtained on packed columns filled with the same type of polymer [27], probably owing to the different polymerisation procedure and to the influence of additional reagents necessary to bond the porous polymer into the capillary. The residual hydrogen bonding effect of unshielded silanolic groups of the inner surface of the silica tubing the may also play an appreciable role. The behaviour of the capillary PoraPLOT Q and U is similar to that of packed Porapak Q and N, respectively. This could be expected for the Q type packed and capillary columns, both composed by crosslinked polystyrene, whereas the EGDMA composition of PoraPLOT U would suggest a behaviour more similar to that of Porapak T, made with this polymer. However, as the PoraPLOT U contains a divinylbenzene-EGDMA copolymer (see Table 1), its behaviour could be similar to that of mixed packed columns discussed above, being the average of the ΔC values proportional to the relative amount of the two monomers.

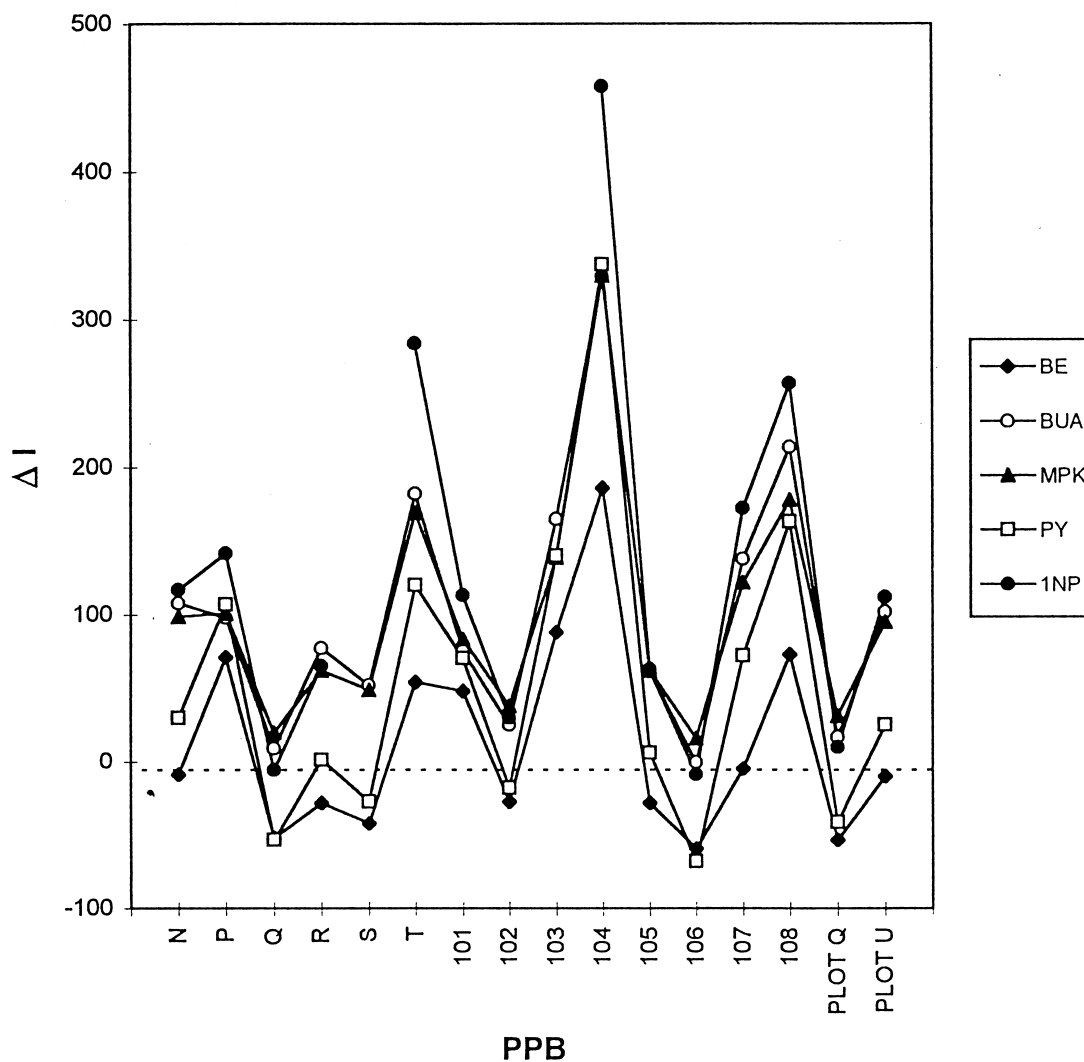


Fig. 4. ΔI values with respect of the reference liquid phase squalane of the first five McReynolds' probes measured at 200°C on Porapak, Chromosorb "Century Series" and PoraPLOT Q and U columns. BE: benzene; BUA: butanol; MPK: 2-pentanone; PY: pyridine; 1NP: 1-nitropropane. Porapak S and Chromosorb 103 react with 1-nitropropane yielding multiple or asymmetric peaks and the corresponding values of ΔI are not shown.

4. Polymer classification at low temperature

Neither the McReynolds' method nor the ΔC can be used for the classification of the PPBs columns at temperature below 100°C, as the retention times of the compounds used for the determination of ΔI or ΔC are very great, and for this reason various kinds of PPBs are used as sorbents for the preconcentration of organic compound in both air and water samples

[67]. In Table 4 are shown the t'_R values of pentane and ethanol measured at 180°C and those extrapolated at 30°C by using the linear correlation between the $\ln t'_R$ and the reciprocal of the absolute temperature of the column. Similar values are shown by the McReynolds' probes. Reasonably low retention values are found by using the first members of the *n*-alkanes series, but it is practically impossible to obtain suitable values for the other reference series

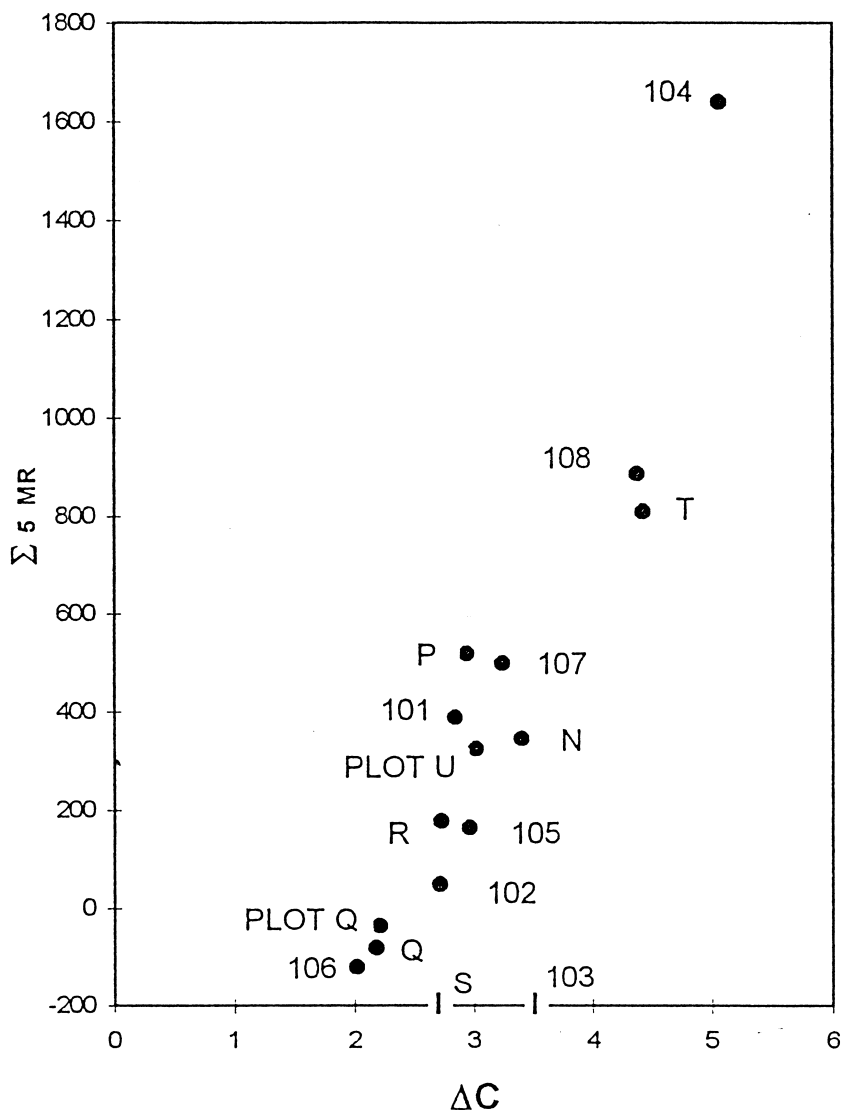


Fig. 5. Sum of the ΔI values of the first five McReynolds' probes, $\Sigma_{5 MR}$, measured at 200°C on Porapak, Chromosorb "Century Series" and PoraPLOT Q an U columns, plotted as a function of the ΔC at the same temperature. As Porapak S and Chromosorb 103 react with 1-nitropropane yielding multiple or asymmetric peaks and the corresponding values of ΔI cannot be calculated, their ΔC values are only indicated with marks on the x-axis.

or probes. Therefore, different methods were suggested for the characterisation of the PPBs columns at low temperature, based on the observation that the different polymers show a different behaviour in the separation of saturated and unsaturated light hydrocarbons. In this method [18,19,24,38], some Porapak and Chromosorb polymers were classified by using the retention relative to ethene of methane, ethane,

ethyne and carbon dioxide. Ethene was used as the reference because its retention is ever the smallest of those of the C_2 hydrocarbons and does not show interference with other peaks. It was observed that the ratio of the retention of ethyne and ethene is very close to unity for non-polar PPBs as the Porapak Q and the Chromosorb 106, and increases with the polarity of the column, showing the greatest values

Table 4

Adjusted retention times t'_R (min) of pentane and ethanol on various packed columns of PPBs at 180°C, carrier flow rate 30 ml/min, and values extrapolated at 30°C

PPB	t'_R at 180°C		t'_R at 30°C	
	Pentane	Ethanol	Pentane	Ethanol
Porapak N	3.23	4.03	802	1417
Porapak P	0.67	0.68	76	42
Porapak Q	7.21	3.58	740	171
Porapak R	3.48	2.71	205	297
Porapak S	3.27	2.41	2270	1682
Porapak T	0.81 ^a	1.75 ^a	42	183
Chromosorb 101	1.04	0.83	99	32
Chromosorb 102	3.08	2.24	470	174
Chromosorb 103	0.61 ^a	0.78 ^a	37	55
Chromosorb 104	0.94	2.27	86	426
Chromosorb 105	3.03 ^a	2.77 ^a	468	323
Chromosorb 106	10.41	4.40	2330	486
Chromosorb 107	3.46	4.00	763	1176
Chromosorb 108	0.96	1.83	85	520

^a Values measured on a new column: the retention change with ageing of the phase at high temperature.

for Chromosorb 104 and Porapak T. This may be due to the increased influence of the π -electrons of the acetylenic bond. The $\alpha_{C_2H_2/C_2H_4}$ values have previously shown a fair correspondence with the polarity order measured with the McReynolds' constants [68]; therefore these values are compared with the ΔC measured in this work.

The adjusted retention times were measured using as the dead time marker on packed columns the retention of hydrogen, corresponding to that of helium within the accuracy limit of the data system used (± 0.01 min). The dead time on capillary PLOT columns could not be measured neither with hydrogen, air or inert gas, nor with methane as this compound is retained at low temperature by the porous polymers. Theoretical calculation of the dead time was therefore carried out [69]. Table 5 shows the values of $\alpha_{C_2H_2/C_2H_4}$ measured at 30 and 55°C on various PPBs columns and the ΔC measured at 200°C and extrapolated at 30°C by using the values shown in Table 2. In Fig. 6 the values of $\alpha_{C_2H_2/C_2H_4}$ at 30°C are compared with the ΔC at 200°C and a suitable correlation is observed, thus confirming that the polarity order or the similarities of the various PPBs can be expressed both by the ΔC values (at high temperature) and by the $\alpha_{C_2H_2/C_2H_4}$ when the columns are used for gas analysis. As seen previous-

Table 5

Experimental ΔC values measured at 200°C, ΔC at 30°C calculated by linear extrapolation from the values of Table 2, $\alpha_{C_2H_2/C_2H_4}$ measured at 30 and 55°C

PPB	ΔC 200°C	ΔC 30°C	α 30°C	α 55°C
Porapak N	3.40	3.44	2.40	1.94
Porapak P	2.94	2.13	1.17	1.10
Porapak Q	2.18	1.64	1.03	0.98
Porapak R	2.72	3.18	1.31	1.22
Porapak S	2.69	2.91	1.37	1.26
Porapak T	4.31	5.50	3.05	2.45
Chromosorb 101	2.84	2.02	1.26	1.17
Chromosorb 102	2.71	2.17	1.08	1.07
Chromosorb 103	3.52	3.18	1.33	1.27
Chromosorb 104	5.06	4.33	3.02	2.48
Chromosorb 105	2.96	2.54	1.48	1.33
Chromosorb 106	2.02	1.87	1.01	1.00
Chromosorb 107	3.24	3.05	2.68	2.4
Chromosorb 108	4.37	3.99	2.93	2.66
PoraPLOT Q	2.21	2.27	1.09	1.02
PoraPLOT U	3.02	2.80	2.42	2.07

ly for some PPBs in the range 30–70°C [18,19], the $\alpha_{C_2H_2/C_2H_4}$ values decreases slightly with increasing temperature, owing to the different dependence on temperature of the retention times of the two hydrocarbons. Fig. 6 shows that also by using the $\alpha_{C_2H_2/C_2H_4}$ the behaviour of the PoraPLOT Q and U is close to that of the packed columns Porapak Q and N, respectively. This is confirmed by the Figs. 7 and 8 where the α of methane, ethane and ethyne with respect of ethene are plotted as a function of $1/T$ in the range 30–120°C for PoraPLOT Q and Porapak Q and 30–100°C for the PoraPLOT U and Porapak N.

5. Effect of high temperature ageing on ΔC values

It was found previously [39] that the retention times of both the *n*-alkanes and the McReynolds' probes on some polar PPBs changes after thermal ageing, modifying the values of the stationary phases constants and as a consequence that of $\Sigma_5 MR$. Also the ΔC values are influenced by this behaviour. Table 6 shows the t'_R values of the first five McReynolds' probes, of ethanol and of two *n*-alkanes measured on Porapak T, Chromosorb 103, 107 and 108 after the first conditioning of the new column and after 3 weeks of continuous heating at

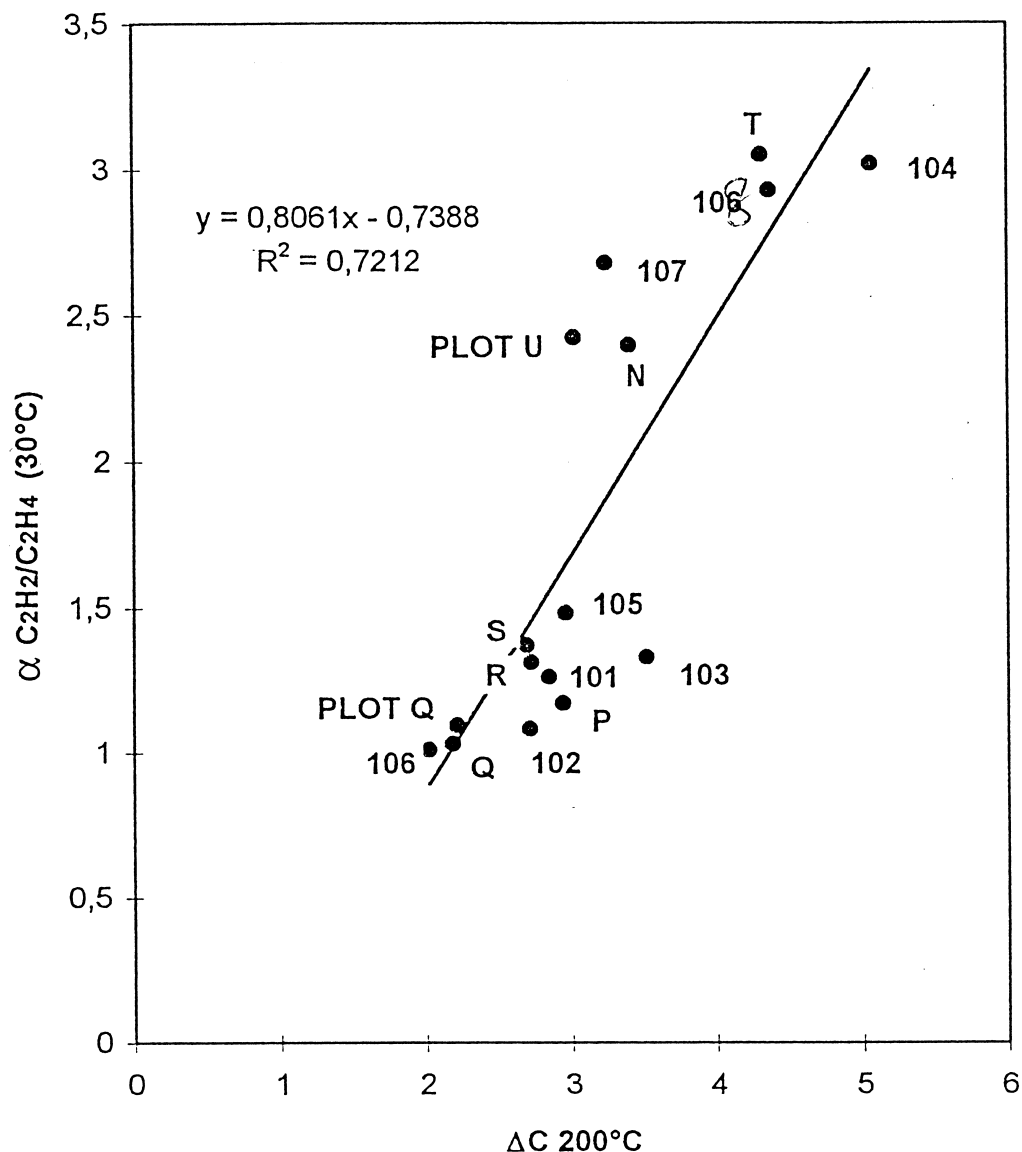


Fig. 6. Values of the ratio of the adjusted retention times of ethyne and ethene, $\alpha_{C_2H_2/C_2H_4}$, measured at $30^\circ C$ on Porapak, Chromosorb "Century Series" and PorapLOT Q an U columns, plotted as a function of the ΔC at $200^\circ C$ on the same columns

$200^\circ C$ with a helium flow-rate of $20 \text{ cm}^3/\text{min}$. By using as the references the two alcohols and the two alkanes, the ΔC values were calculated and are shown in the last row. The logarithm of t'_R values of the compounds decrease with the ageing time in a linear way for Porapak T, and show an asymptotic decreasing behaviour on Chromosorb 107 and 108. As the slope of the decreasing lines is not the same

for the probes and the *n*-alkanes, and the values for the reference compounds decrease more rapidly, the *I* values of the probes show an increase with ageing time, straight for Porapak T and with a curvature for Chromosorb 107 and 108. Crossing lines are also observed with inversion of the elution sequence of some compounds (see Figs. 9 and 10). Therefore, both the McReynolds constants and the ΔC values

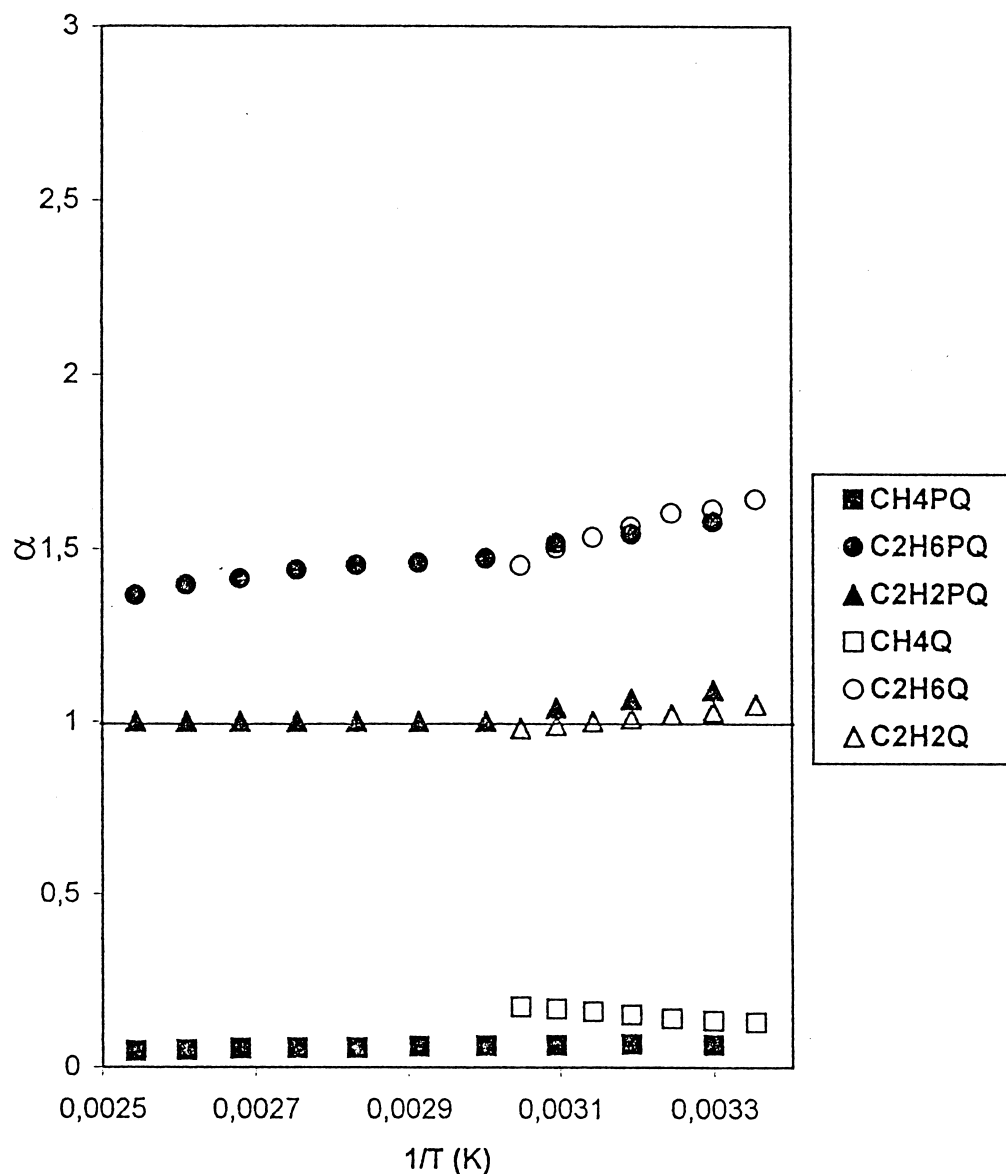


Fig. 7. Ratio of the adjusted retention times, α , of methane, ethane and ethyne with respect of ethene, plotted as a function of $1/T$ in the range 30–120°C for PorapLOT Q (PQ, black symbols) and Porapak Q (Q, white symbols).

change during the high temperature ageing of these stationary phases, due to a sharper decrease of *n*-alkanes' retention with respect of that of the probes, which may depend on the decrease of interfacial adsorption of the alkanes, to increase of the hydrogen bonding of the polar probes with the oxygen atoms of the ethylene glycol dimethacrylate in Porapak T and acrylic esters in Chromosorb 107 and

108, or to a combination of both effects. Thermal ageing could increase the crosslinking and reduce the microporosity within the polymer, thus decreasing the possibility of interfacial adsorption with no or less influence on the electrons-donor properties of the oxygen atoms in the chain. This increases the relative importance of polar with respect of interfacial effects. Chromosorb 103 (polystyrene) shows an

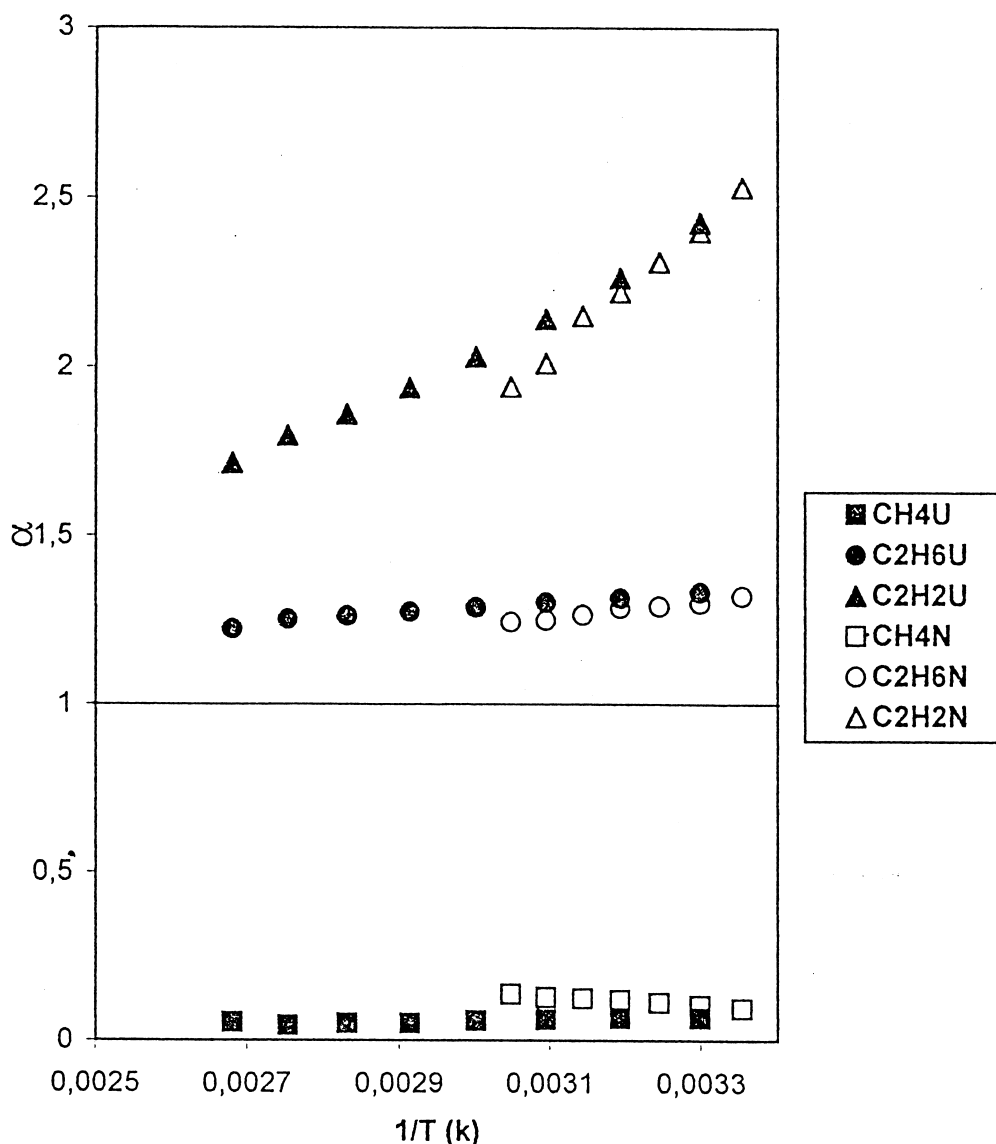


Fig. 8. Ratio of the adjusted retention times, α , of methane, ethane and ethyne with respect of ethene, plotted as a function of $1/T$ in the range 30–100°C for the PorapLOT U (U, black symbols) and Porapak N (N, white symbols).

appreciable increase of the retention of all the compounds in the first week of ageing, a lower and steady increment in the following period but, as the behaviour is similar for all the compounds because no strong polar effect and only dispersion and weak π -electrons interactions are possible, the I values are nearly constants with the exception of a crossing between the lines for benzene and *n*-butanol. No

appreciable change of retention times and of I values was observed for Chromosorb 106 which has the same nominal composition of Chromosorb 103 (see Table 1) but different surface area and average pore diameter (0.35 μm for 103 and 0.005 μm for 106, as given by the producer); one can suppose that cross-linking due to thermal ageing reduces the pore diameter of Chromosorb 103 thus increasing the

Table 6

t'_R values (min) of the first five McReynolds' probes, of ethanol and of two *n*-alkanes measured on Porapak T, Chromosorb 103, 107 and 108 after the first conditioning of the new column and after 20 days of continuous heating at 200°C with a helium flow-rate of 20 cm³/min. ΔC values are shown in the last row

Probe	Porapak T		Chromosorb 103		Chromosorb 107		Chromosorb 108	
	t'_R initial	after 20 days	t'_R initial	after 20 days	t'_R initial	after 20 days	t'_R initial	after 20 days
Benzene	7.63	3.27	2.47	2.70	10.4	8.72	5.30	3.52
Butanol	10.49	4.46	2.32	2.83	15.9 ^b	12.5	7.00 ^b	4.80
2-Butanone	12.25	4.21	2.52	2.89	17.6	14.1	7.30	4.76
Nitropropane	14.23	8.32	^a	^a	27.3	23.2	12.5	8.75
Pyridine	15.69	7.30	4.60	5.07	21.3 ^b	19.7	11.1 ^b	7.82
Ethanol	2.90	1.51	0.78	0.92	3.65 ^b	3.08	2.25 ^b	1.48
<i>n</i> -Pentane	2.04	0.85	0.60	0.67	3.34	2.52	1.53	0.88
<i>n</i> -Octane	11.18	3.80	2.90	3.40	23.9	15.2	7.36	4.08
ΔC	3.72	4.19	3.51	3.62	3.25	3.48	3.79	4.11

^a The probe reacts with the stationary phase.

^b Tailing peaks.

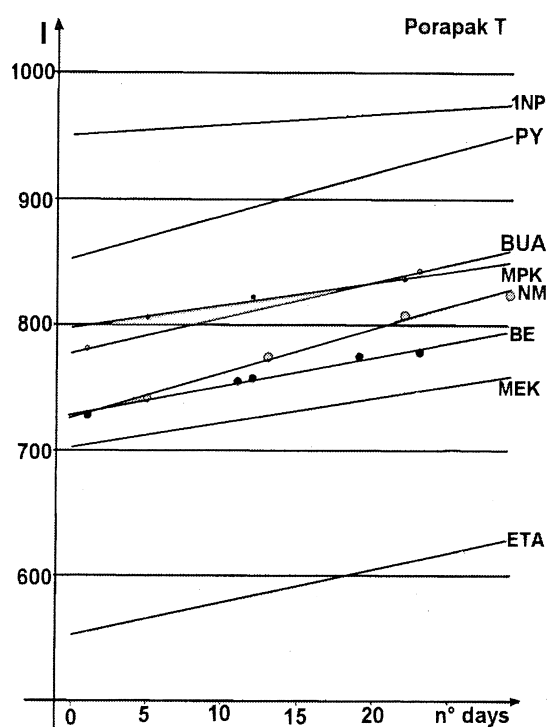
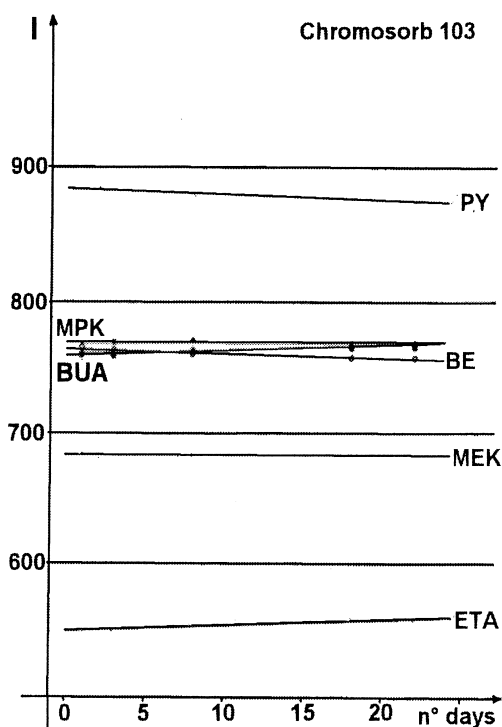


Fig. 9. Change of the retention index values of some McReynolds's and Rohrschneider's probes on Chromosorb 103 and Porapak T columns as a function of the ageing time at 200°C with a helium flow rate of 20 cm³/min.

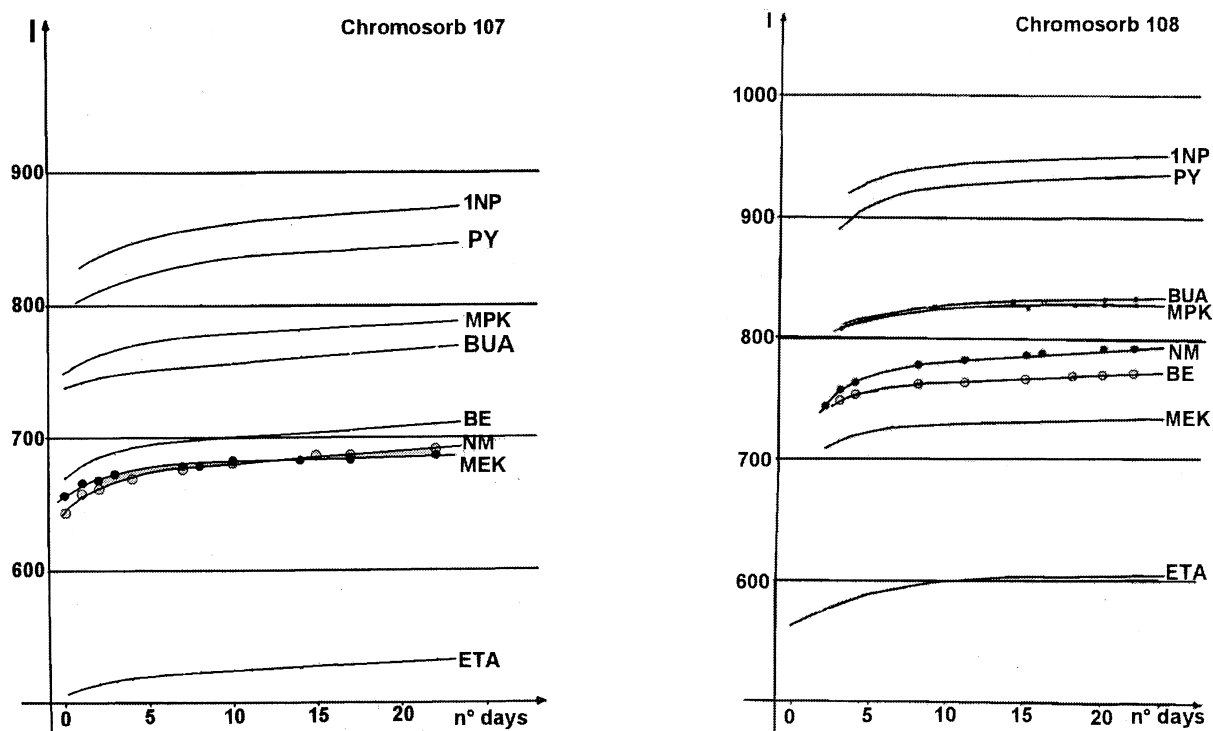


Fig. 10. Change of the retention index values of some McReynolds's and Rohrschneider's probes on Chromosorb 107 and 108 columns as a function of the ageing time at 200°C with a helium flow rate of 20 cm³/min.

retention, that cannot in any case reach the high values of Chromosorb 106. For example, the t'_R of *n*-pentane at 200°C on Chromosorb 103 changes from 0.61 to 0.67 min after 20 days of ageing, whereas it is much greater and fairly constant (10.68 ± 0.19 min) on a Chromosorb 106 column of the same diameter, length and mesh size subjected to the same ageing procedure. All other PPBs did not show appreciable change of t'_R after ageing and as a consequence both the retention indices, the McReynolds' constants and the ΔC values remain nearly unchanged.

6. Conclusions

The majority of the porous polymers do not change appreciably the polarity with changing temperature; this means that the identifications carried out in an isothermal analysis can be extended both to

other temperatures and to programmed temperature runs. Some exceptions are shown by the PPBs with the greatest polarity that, on the other hand, change their properties after high-temperature ageing of the column and cannot therefore be used for long time at elevated oven temperature. The capillary columns tested, PoraPLOT Q and U, exhibit a behaviour similar to that of the packed columns filled with Porapak Q and Porapak N respectively. Both the sum of the McReynolds' phase constants, the ΔC and the $\alpha_{C_2H_2/C_2H_4}$ parameter can be used as a mean for comparing the behaviour of packed and capillary columns filled with different types of PPBs. The sum of the ΔI of the first five McReynolds' probes, $\Sigma_5 MR$, can only be used at high temperature, with some exception for the less polar polymers which, by using this parameter, seem to be less polar than the standard reference squalane. Instead, the extrapolated ΔC and the $\alpha_{C_2H_4}$ give suitable results at the low temperature used for gas analysis.

Acknowledgements

This work was supported by the Italian Ministry of University and Scientific Research (MURST). The PoraPLOT columns used were kindly supplied by Chrompack International B.V., Middelburg, Netherlands. The authors wish to thank Dr. Maria Bevilacqua, which supplied some data measured on the PoraPLOT columns.

References

- [1] O.L. Hollis, *Anal. Chem.* 38 (1996) 309.
- [2] O.L. Hollis, W.V. Hayes, *J. Gas Chromatogr.* 4 (1966) 235.
- [3] P.G. Jeffery, P.J. Kipping, *Gas Analysis by Gas Chromatography*, Pergamon Press, London, 1964.
- [4] G. Castello, S. Munari, *J. Chromatogr.* 31 (1997) 202.
- [5] C.H. Hartmann, K.P. Dimick, presented at the Pittsburgh Conference on Analytic Chemistry and Applied Spectroscopy, Pittsburgh, March 1965.
- [6] G. Castello, S. Munari, *Chim. Ind.* 51 (1969) 469.
- [7] G. Castello, *J. Chromatogr.* 58 (1971) 117.
- [8] S.B. Dave, *J. Chromatogr. Sci.* 7 (1969) 389.
- [9] S.B. Dave, *I&EC Prod. Res. Develop.* 14 (1975) 85.
- [10] H. Rotzche, *Stationary Phases in Gas Chromatography* (*Journal of Chromatography Library*, Vol. 48), Elsevier, Amsterdam, 1991, p. 125.
- [11] W.R. Supina, P. Rose, *J. Chromatogr. Sci.* 7 (1969) 192.
- [12] T.N. Gvosdovich, Ja.I. Jashin, *J. Chromatogr.* 49 (1970) 36.
- [13] T.A. Gough, C.F. Simpson, *J. Chromatogr.* 51 (1970) 129.
- [14] K. Sakodinsky, L. Panina, *Chromatographia* 4 (1971) 113.
- [15] R.G. Hackman, *J. Chromatogr. Sci.* 10 (1972) 509.
- [16] H.L. Gearhart, M.F. Burkem, *J. Chromatogr. Sci.* 15 (1977) 1.
- [17] G. Castello, G. D'Amato, *J. Chromatogr.* 196 (1980) 245.
- [18] G. Castello, G. D'Amato, *J. Chromatogr.* 212 (1981) 261.
- [19] G. Castello, G. D'Amato, *J. Chromatogr.* 243 (1982) 25.
- [20] G. Castello, G. D'Amato, *J. Chromatogr.* 349 (1985) 189.
- [21] W.O. McReynolds, *J. Chromatogr. Sci.* 8 (1970) 685.
- [22] W.O. McReynolds, *Gas Chromatographic Retention Data*, Preston, Evanston, IL, 1966.
- [23] G. Castello, G. D'Amato, *J. Chromatogr.* 366 (1986) 51.
- [24] G. Castello, G. D'Amato, *Ann. Chim. (Rome)* 69 (1979) 541.
- [25] O.L. Hollis, *J. Chromatogr. Sci.* 11 (1973) 335.
- [26] W.K. Al-Thamir, *J. High Resolut. Chromatogr. Chromatogr. Commun.* 8 (1985) 143.
- [27] J. de Zeeuw, R.C.M. de Nijs, J.C. Buyten, J.A. Peene, in: P. Sandra (Ed.), *Proc. 8th Int. Symp. Capillary Chromatography*, Riva del Garda, 19–21 May 1987, Vol. 1, Hüthig, Heidelberg, 1987, p. 171.
- [28] J. de Zeeuw, R.C.M. de Nijs, J.C. Buyten, J.A. Peene, M. Mohnke, *J. High Resolut. Chromatogr. Chromatogr. Commun.* 11 (1988) 162.
- [29] J. de Zeeuw, in: P. Sandra (Ed.), *Proc. 9th Int. Symp. Capillary Chromatography*, Monterey, CA, 16–19 May 1988, Hüthig, Heidelberg, 1998, p. 482.
- [30] H. Heijmans, J. de Zeeuw, J. Buyten, J. Peene, M. Mohnke, *Int. Chromatogr. Lab.*, 22, 2.
- [31] J. de Zeeuw, J. Buyten, J. Peene, M. Mohnke, in: P. Sandra, G. Devas (Eds.), *Proc. 16th Int. Symp. Capillary Chromatography*, Riva del Garda, 27–30 Sept. 1994, Vol. 1, Hüthig, Heidelberg, 1994, p. 219.
- [32] T.C. Shen, Mei-Ling Wang, *Proc. 17th Int. Symp. Capillary Chromatography and Electrophoresis*, Wintergreen, VA, 7–11 May 1995, p. 222.
- [33] C. Duvekot, J. de Zeeuw, P. Heynsdijk, J. Buyten, N. Vonk, M. Mohnke, J. Peene, *Proc. 20th. Int. Symp. Capillary Chromatography*, Riva del Garda, 26–29 May 1998, B.03.
- [34] G.A. Sturrock, P.G. Simmonds, G. Nickless, D. Zwiep, *J. Chromatogr.* 648 (1993) 423.
- [35] J. de Zeeuw, D. Zwiep, J.W. Marinissen, *Int. Lab.* 26 (1996) 12J.
- [36] R. Allegro, G. Castello, in: P. Sandra, G. Devos (Eds.), *Proc. 18th Int. Symp. Capillary Chromatography*, Riva del Garda, 20–24 May 1996, Vol. 2, Hüthig, Heidelberg, 1996, p. 1365.
- [37] R. Allegro, G. Castello, *Proc. 20th Int. Symp. Capillary Chromatography*, Riva del Garda, 26–29 May 1998, N.17.
- [38] G. Castello, G. D'Amato, G. Canciani, *Ann. Chim. (Rome)* 68 (1978) 255.
- [39] G. Castello, G. D'Amato, *J. Chromatogr.* 248 (1982) 391.
- [40] G. Castello, S. Vezzani, G. D'Amato, *J. Chromatogr. A* 779 (1997) 275.
- [41] G. Castello, A. Timossi, T.C. Gerbino, *J. Chromatogr.* 582 (1990) 329.
- [42] G. Castello, G. D'Amato, *J. Chromatogr.* 623 (1992) 289.
- [43] G. Castello, G. D'Amato, S. Vezzani, *J. Chromatogr.* 646 (1993) 361.
- [44] L.R. Snyder, *J. Chromatogr.* 92 (1974) 223.
- [45] L.R. Snyder, *J. Chromatogr. Sci.* 16 (1979) 223.
- [46] M.S. Klee, M.A. Kaiser, K.B. Laughlin, *J. Chromatogr.* 279 (1983) 681.
- [47] G. Tarjan, S. Nyiredi, M. Györ et al., *J. Chromatogr.* 472 (1982) 1.
- [48] E. Fernandez-Sanchez, A. Fernandez-Torres, J.A. Garcia-Dominguez, J.M. Santiuste, *Chromatographia* 31 (1991) 75.
- [49] Z. Szentirmai, G. Tarjan, J. Takacs, *J. Chromatogr.* 73 (1972) 11.
- [50] M.H. Abraham, G.S. Withering, R.M. Doherty, W.J. Shuely, *J. Chromatogr.* 518 (1990) 329.
- [51] M.H. Abraham, G.S. Withering, R.M. Doherty, W.J. Shuely, *J. Chromatogr.* 587 (1991) 213.
- [52] M.H. Abraham, G.S. Withering, R.M. Doherty, W.J. Shuely, *J. Chromatogr.* 587 (1991) 229.
- [53] M.H. Abraham, G.S. Withering, *J. Chromatogr.* 594 (1992) 229.
- [54] M.H. Abraham, *Chem. Soc. Res.* 22 (1993) 73.
- [55] S.W. Poole, C.F. Poole, *Analt. Commun.* 33 (1996) 353.
- [56] A.V. Kiselev, Ya.I. Yashin, *Gazo-Adsorbtsionnaya Khromatografiya*, Nauka, Moscow, 1967; *Gas Adsorption Chromatography*, Plenum Press, New York, 1969.

- [57] A.V. Kiselev, Ya.I. Yashin, Gas- und Flüssigkeits-Adsorptions-Chromatographie, VEB Deutscher Verlag der Wissenschaften, Berlin, 1985.
- [58] R.N. Ewell, J.M. Harrison, L. Berg, *Ind. Eng. Chem.* 30 (1944) 871.
- [59] C.F. Poole, T.O. Kollie, S.K. Poole, *Chromatographia* 34 (1992) 281.
- [60] S.K. Poole, T.O. Kollie, C.F. Poole, *J. Chromatogr. A* 664 (1994) 229.
- [61] K.G. Furton, R. Morales, *J. High. Resolut. Chromatogr.* 14 (1991) 62.
- [62] R.F. Riedo, D. Fritz, G. Tarján, E.sz. Kováts, *J. Chromatogr.* 126 (1976) 63.
- [63] G. Castello, G. D'Amato, *J. Chromatogr.* 171 (1979) 27.
- [64] G. Castello, G. D'Amato, *J. Chromatogr.* 269 (1983) 153.
- [65] C.F. Poole, S.K. Poole, R.M. Pomaville, B.R. Kersten, *J. High. Resolut. Chromatogr. Chromatogr. Comm.* 10 (1987) 670.
- [66] B.K. Kersten, C.F. Poole, K.G. Furton, *J. Chromatogr.* 411 (1987) 43.
- [67] J.F. Pankow, W. Luo, L.M. Isabelle, K.M. Hart, D.F. Hagen, *J. Chromatogr. A* 732 (1996) 317.
- [68] G. Castello, G. D'Amato, *J. Chromatogr.* 254 (1983) 69.
- [69] G. Castello, S. Vezzani, P. Moretti, *J. Chromatogr. A* 677 (1994) 95.