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# Effect of temperature on the polarity of some stationary phases for gas chromatography

G. Castello\*, S. Vezzani, G. D'Amato

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

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## Abstract

The behaviour of the polarity of some stationary phases as a function of temperature was investigated by using gas–liquid packed columns, open-tubular bonded-phase and carbon and graphite layer capillary columns modified with different percentages of polar liquid phases. The change in polarity of gas chromatographic columns packed with twenty different liquid phases and of nine capillary columns as a function of temperature was measured by using as a polarity indicator the difference in apparent carbon number of linear alkanes and alcohols with the same retention time,  $\Delta C$ . Some phases were found to have a constant  $\Delta C$  value over a wide temperature range, whereas other phases change their behaviour and can therefore cause an inversion of the elution order of polar and non-polar compounds at different temperature or during temperature programmed analysis. © 1997 Elsevier Science B.V.

*Keywords:* Stationary phases, GC; Polarity parameters

## 1. Introduction

When the elution times of compounds of different polarity separated by a gas chromatographic column change with changing the temperature of analysis, their identification carried out on the basis of the retention values at one temperature 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. This effect may be useful to separate closely eluting compounds of different polarity, whose retentions change in a different way with temperature, but requires a new calibration when the analytical parameters are changed. The methods used for the prediction of the retention values in temperature programmed analyses

[1] yield the best results when applied to columns having a constant polarity. They can also be used when the polarity of the columns changes, but in this case the determination of the isothermal retention data used as the starting values for the calculations must be made in a wide temperature range with great accuracy. It is therefore necessary to know if the behaviour of the used stationary phase depends on temperature.

A method for the classification of gas chromatographic columns, based on the difference in apparent carbon number of linear alkanes and alcohols with the same retention,  $\Delta C$ , was introduced in papers published previously [2–4] and compared with other polarity indicators, such as McReynolds' constants [5,6], Snyder's selectivity parameters [7–9], the Kováts' coefficient  $K_c$  [10,11] and RP values [12]. The  $\Delta C$  method can be considered as a measure of

\*Corresponding author.

the number of methylene groups that should be theoretically added to a linear alkane with  $Z$  carbon atoms to obtain a hypothetical alkane with the same retention time of a linear alcohol with  $Z$  carbon atoms. The concept of apparent or equivalent carbon number or chain length was initially used for the classification of elution characteristics by James [13].

Evaluation of the polarity of liquid phases for gas chromatography (GC) was carried out in detail by Haken and Abraham [14], Abraham et al. [15] and Poole and Kollie [16–19], who examined many aspects of the interactions described by the general solvation equation and investigated the influence of temperature on the solvation properties of stationary phases and on the retention mechanism. The method used, applied to many liquid phases in packed columns yields very interesting results but seems to be a little exoteric to be easily applied in routine works when the researcher only needs to know if two columns have similar properties and if the different polarity effects change with temperature resulting in different elution order of the analytes. For this reason, a simple polarity parameter should be useful for routine application.

As shown previously [2,3] the correspondence between  $\Delta C$  values and the above listed polarity indicators (McReynold's constants, Snyder's selectivity, Kováts' coefficient, RP values) is fairly linear and therefore the  $\Delta C$  method offers a fast procedure for the evaluation of the behaviour of GC columns. An advantage of the use of  $\Delta C$  with respect to other polarity indicators is that it is obtained directly by injecting only linear alkanes and 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 methyl-silicone-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 McReynold's constants differ appreciably from zero. All the retention values ( $t_R$ ,  $V_R$ ,  $V_g$ ) can be used directly and retention data of alkanes

and alcohols taken from literature allow the  $\Delta C$  values of any column to be obtained. Published values of the retention index,  $I$ , 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.

An objection to the generalized use of the  $\Delta C$  values for the classification of all stationary phases may be 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 may not be correctly classified. For this reason the Snyder method employs nitromethane as a dipole indicator. However, it is known and has been found experimentally [15,18] that the alcohols not only show hydrogen-bond activity, but possess strong dipole properties, and therefore all the "polar" interactions are well represented by this type of probe. For this reason, as the correspondence between the trend of  $\Delta C$  and those of other polarity indicators shows [2,3], the "polarity order" of different liquid phase obtained with either systems fairly corresponds, and this justifies the use of the easily calculated  $\Delta C$  values. Furthermore, some of the polarity indicators listed above cannot be applied to capillary columns:  $K_c$  cannot be calculated as it depends on a knowledge of  $V_g$  values; other indicators (RP, Snyder's selectivity parameters, McReynold's constants) require a knowledge of the  $\Delta I$  values with respect of squalane, which cannot be used at temperature above 120°C. Another problem connected with the determination of these values is the choice of the polarity probes: the boiling points of the McReynolds and Snyder probes are low and therefore the retention times at column temperatures above 120°C are so short to be subject to appreciable errors that impair the accuracy of the calculation. The polarity indicators suitable up to 120°C are the sum of the first five McReynolds' probes,  $\sum_{MR}^5$ , the sum of the Rorschneider's probes,  $\sum^R$  and Snyder's selectivity parameter.  $\Delta C$  can be used up to the maximum allowable temperature of the columns.

From the theoretical point of view, the  $\Delta C$  value expresses the difference between purely dispersion interactions, well represented by the behaviour of

inert solutes such as alkanes, that are solubilized in every stationary phase, polar or non-polar, with the same mechanism which requires the creation in the phase of a cavity of suitable size to accommodate the solute molecule, the reorganization of solvent molecules around the cavity and the introduction of solute into the cavity. In theory with completely non-polar phases, the interaction mechanism of alcohols should be the same, except for the different volume of the molecule due to the -OH group. The cavity required to accommodate a *n*-alcohol molecule with *Z* carbon atoms is therefore larger than that suitable to contain the *n*-alkanes with the same *Z* value. Therefore, the plots of the retention values of *n*-alkanes and of *n*-alcohols as a function of *Z* cannot be coincident and a minimum  $\Delta C$  value should be observed also for the hypothetical absolute non-polar phase for which the name of "zerolane" was suggested [20]. In practice, owing to the hydrogen bonding dipole/dipole and dipole/induced dipole effects, possible also in non-polar columns due to the Si-O-Si bonds of the support, of the column walls or of the silanizing agents, if used, and of the silicon type liquid phases, the  $\Delta C$  value of the real non-polar phases is greater than the theoretical minimum  $\Delta C$  value. As an example, squalane, which is considered to be the standard non-polar probe, shows a minimum  $\Delta C$  value of about 1.5. It has been found that some stationary phases have a polarity smaller than that of squalane: some porous polymer beads (Porapak or Chromosorb century series) have  $\sum_{MR}^5$  and  $\sum_R^5$  values well below zero, the Chromosorb 106 and the Porapak Q being the less polar members of the two series of products, and showing at 200°C  $\sum_{MR}^5$  values of -121 and -82 and  $\sum_R^5$  values of -154 and -86, respectively [21]. In the same series of experiments it was also found that the synthetic reference phase C<sub>87</sub>H<sub>176</sub> apolane [22] has at 200°C an average  $\sum_{MR}^5$  value of 70, and a  $\sum_R^5$  value of about 66, being therefore more polar than squalane itself. On the contrary, the linear isomer of squalane, *n*-triacontane, shows at 80°C a negative  $\sum_R^5$  value of -76, and a  $\Delta C$  of 1.47 being therefore less polar than squalane [23].

In a systematic investigation of the application of the  $\Delta C$ , this parameter was used for studying the

polarity at 120°C of thirty liquid phases, six Porapak types and some polar and non-polar wide bore bonded phase capillary columns [4]. It was also used for the characterization of graphite- and carbon-layer capillary columns [24–26] and the determination of relative polarity of modified cyclodextrin stationary phases [27]. It was observed that the  $\Delta C$  value may change with changing temperature of the column, its value being a measure of the relative importance of the dispersion and polar effect on the solute-solvent interaction. Therefore, in the present paper we describe the dependence on temperature of the  $\Delta C$  value of packed columns filled with twenty-two different liquid phases of various polarity and of ten polar and non-polar narrow bore bonded phase or graphite layer capillary columns.

## 2. Experimental

The  $\Delta C$  value of the packed columns was measured by injecting samples of *n*-alkanes (C<sub>4</sub>-C<sub>12</sub>) and *n*-alkanols (C<sub>2</sub>-C<sub>8</sub>). The columns were prepared with a concentration of 20% of liquid phase on Chromosorb W AW (80–100 mesh), in order to permit the comparison with values published previously [2,3] and to reduce the interfacial and adsorption effects on the solid support. In Table 1, the liquid phases used in the experiments are listed. The values for Pluronic phases at temperatures ranging from 100 to 120°C were calculated by using the data published by McReynolds [5], in order to evaluate the applicability of the classification method to literature data the values obtained experimentally were compared with the same literature source. As previously found at constant temperature [3] the best fitting between experimental and literature data was obtained by using liquid phases of definite chemical composition (e.g. esters); columns prepared with silicone polymers or with hydrocarbons mixtures (e.g., Apiezon) show an appreciable fluctuation of the  $\Delta C$  values, owing to the different distribution of molecular masses in the various commercial products. Varian (Palo Alto, CA, USA) Model 3700 and 1220 gas chromatographs, equipped with thermal conductivity detectors, were used to test the packed columns. The analyses were performed on stainless steel columns having 1/8 in. and 1/4 in. O.D., with a

Table 1  
 $\Delta C$  value measured at various temperatures on packed columns with different liquid phases

Column	Symbol	Temperature (°C)					$\delta\Delta C/\delta T \times 10^3$
		80	100	120	140	160	
<i>n</i> -C <sub>30</sub>	C30	1.47					
Squalane1 20%	Squal1	1.54					
Squalane2 15%	Squal1		1.96	1.97		1.98	0.50
Apolane 15%	Apol			2.01		2.03	0.50
Squalane MC 20%	SqualMC	2.33	2.33				0.00
Apiezon L1 20%	ApiezL1	2.42			2.38		-0.67
Apiezon L MC 20%	ApiezLMC			2.32		2.37	1.25
SE 52	SE 52			2.93		2.80	-3.25
SE 30	SE 30			2.93		2.78	-3.75
Diisodecyl phthalate	DIDP			3.88	3.80		-4.00
Dioctyl phthalate	DOP			3.97	3.93		-2.00
Di-2-ethylhexyl sebacate	D2ET S		3.76	3.66			-5.00
Dioctyl sebacate	DOS		3.74	3.62			-6.00
Di-2-ethylhexyl adipate	D2ET A		3.94	3.82			-6.00
Castorwax	Castor			4.28	4.18		-5.00
Hallcomid M18	H M18		4.76	4.60			-8.00
Pluronic L81	P L81		5.11	4.94			-8.50
Neopentyl glycol adipate	NPG A			5.98	6.04		3.00
Pluronic P85	P P85		5.73	5.61			-6.00
Pluronic P65	P P65		5.72	5.71			-0.50
Pluronic F88	P F88		6.37	6.31			-3.00
Pluronic F68	P F68		6.41	6.35			-3.00
Carbowax 20M	C20M			7.07		7.06	-0.25
DEG adipate	DEG A			7.70	7.74		2.00
DEG succinate	DEG S			9.66	9.94		14.00

The change of  $\Delta C$  due to a variation of temperature of 1°C,  $\delta\Delta C/\delta T$ , is also shown.

length of 3 m; helium was used as the carrier gas, at a flow-rate of 30 cm<sup>3</sup> min<sup>-1</sup> (1 in. = 2.54 cm).

The capillary columns used were narrow-bore open-tubular columns with of 30 m × 0.32 mm I.D.. (a) Bonded-phase columns: polydimethylsiloxane 0.25 μm film (SPB-1); polyethylenglycol 0.25 μm film (Supelcowax-10 or WAX); poly(50% *n*-octyl–50% methylsiloxane) 0.25 μm film (SPB-octyl) from Supelco, Bellefonte, PA, USA; 70% cyanopropyl-polysilphenyl-siloxane 0.25 μm film (BPX-70) from SGE International, Ringwood, Australia; poly(5% diphenyl–95% dimethylsiloxane) 0.25 μm film (DB-5); polydimethylsiloxane 0.25 μm film (DB-1) from J&W Scientific, Folsom, CA, USA. (b) Carbon layer columns: 15% FFAP on graphitized carbon black 1.4 μm (CLOT) from Supelco with; 16% FFAP on graphitized carbon black 0.3 μm (CL-U) and 1% FFAP on graphitized carbon black 0.7 μm (CL-A) obtained by courtesy of the Istituto di Scienze Chimiche, University of Urbino, Italy.

The fused-silica columns were installed in a Varian Model 3600 gas chromatograph equipped with a capillary split-splitless injector and a flame ionization detector (FID). Helium was used as the carrier gas. The carbon number range of *n*-alkanes and *n*-alkanols used in order to calculate the  $\Delta C$  values was increased to C<sub>22</sub> and C<sub>13</sub>, respectively.

The  $\Delta C$  was graphically measured from experimental  $V_g$  and  $t'_R$  values, by measuring the horizontal distance between the two straight lines having the equations

$$\ln V_{gP} = a_P + b_P Z \quad (1)$$

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

obtained by plotting  $\ln V_g$  as a function of the number of carbon atoms,  $Z$ , for *n*-alkanes (P) and *n*-alkanols (OH). When the  $\Delta C$  of capillary columns is measured the adjusted retention times,  $t'_R$ , are used

instead of  $V_g$ , because the determination of specific retention volume in quite difficult as the total amount of liquid phase in the capillary column is unknown.  $\Delta C$  can also be calculated mathematically, with the equation

$$\Delta C = (a_{OH} - a_P) / [(b_{OH} + b_P) / 2] = \Delta a / b^\circ \quad (3)$$

where  $b^\circ$  is the average slope value [2]. As the two lines show in general a fairly parallel behaviour,  $b_{OH}$  and  $b_P$  have the same value; in this instance, and if the difference between  $a_{OH}$  and  $a_P$  values is small the “mathematical”  $\Delta C$  well approximates the “graphical” one. It has been suggested that the  $\Delta C$  could be calculated with the equation:

$$\Delta C = (\ln V_{gOH_Z} - \ln V_{gP_Z}) / b \quad (4)$$

where the alcohol and alkane  $OH_Z$  and  $P_Z$  have the same number of carbon atoms. In other word, instead of a horizontal line, a vertical line is chosen and one may think to inject only one alcohol and one alkane

with the same  $Z$  and obtain the  $\Delta C$  value. In practice, the  $t'_R$  value can be used instead of  $V_g$ . The use of Eq. (4) is only possible in a few instances, and Eq. (3) also has some limitations, as illustrated in Fig. 1, which shows the experimental  $t'_R$  values obtained at 60, 80, 100, 120°C with a BPX-70 column. When the column polarity is high, the shift between the plots of  $n$ -alkanes and those of  $n$ -alkanols is great and compounds of the two series with the same  $Z$  value can seldom be analysed at the same temperature. As shown by the A arrow in Fig. 1, the difference of the retention times is so great that the precision of their measurement quite differs, introducing an uncertainty in the calculation. In the majority of cases, the vertical line should be drawn between experimental values and largely extrapolated ones (arrow B), thus increasing the error of the determination.

The extrapolation problem [28] can also influence the results obtained with Eq. (3). Whereas the slope,  $b$ , can be calculated with great accuracy, the intercept,  $a$ , is subjected to changes due to the choice of

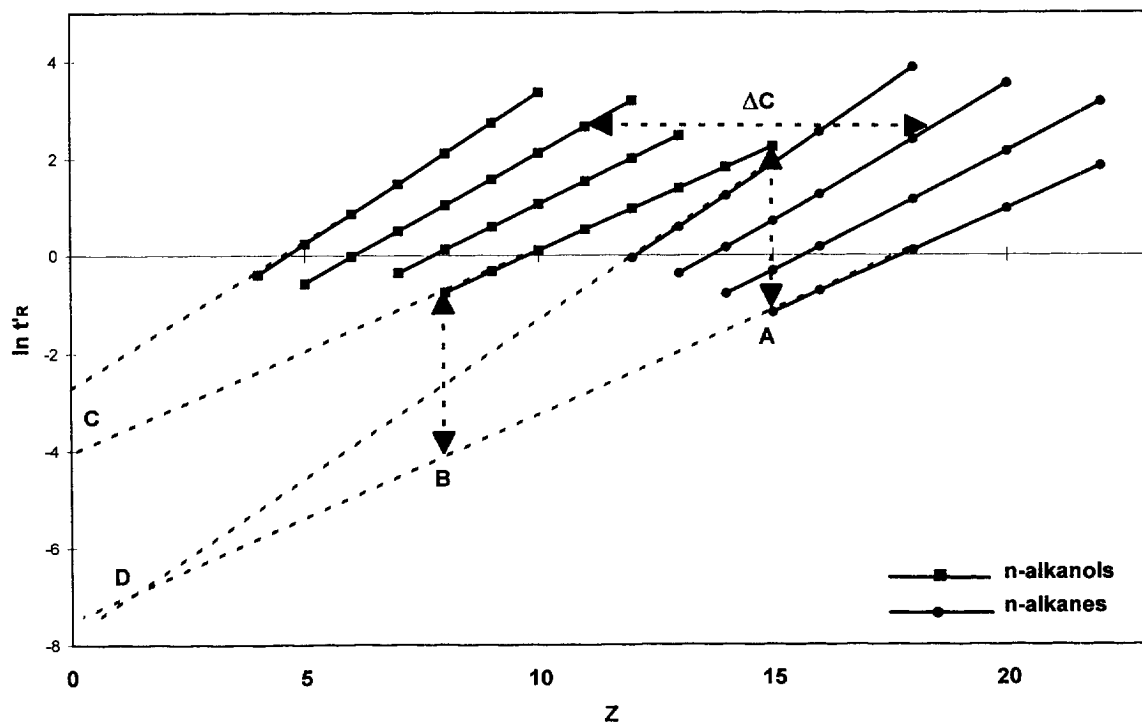


Fig. 1. Plot of  $\ln t'_R$  at various temperatures for  $n$ -alkanes and  $n$ -alkanols as a function of the number of carbon atoms of the probes,  $Z$ . Experimental values for BPX-70 column. For explanation of the points A, B, C, D and  $\Delta C$  see Section 2 Section 3.

the  $Z$  values of alkanes and alkanols and to the same problems involved in the determination of the Kováts' coefficient [3,10,11], i.e., relatively large variations due to small change of slope, precision of experimental data or regression procedure. In some instances, as shown by the dotted lines in Fig. 1, the convergence of the plots leads to close values of  $a$  (point C) for different plots leads to close values of  $a$  (point C) for different temperatures or to very small contribution of the  $n$ -alkanes term to the  $\Delta a$  value of Eq. (3). The "vertical" method (Eq. (4)) or the use of Eq. (3) are therefore suitable for non-polar or low polar phases, when the distance between the lines for alkanes and alkanols is small.

On the contrary, the application of the  $\Delta C$  calculation method corresponding to the definition, i.e., "the difference in apparent carbon number of linear alkanes and alcohols with the same retention", indicated by the horizontal arrow in Fig. 1, does not suffer from the above listed drawbacks. In fact: (a) the use of  $n$ -alkanes and  $n$ -alkanols with similar retention ranges as probes results in a similar accuracy of the  $V_g$  or  $t'_R$  values; (b) the injection of few terms of the two series eluting in the same retention times range permits us to check if the two lines are parallel in the temperature range of interest without too great extrapolation; (c) the errors due to the calculation of the intercept value are avoided.

The length of the horizontal line ( $\Delta C$  in Fig. 1) can be measured graphically or by solving a system of Eqs. (1) and (2) for the two series with an equation  $\ln V_g = \text{constant}$  where the best choice of the value of the constant is the average retention of the members of the two reference series used for the calibration. Again,  $t'_R$  values can be used instead of  $V_g$ .

### 3. Results and discussion

Table 1 shows the values of  $\Delta C$  at various temperatures obtained on packed columns. Some of the liquid phases tested are nowadays replaced by silicone polymers modified with a proper amount of polar groups, but were investigated because they have a reproducible chemical composition and the polarity indicators are not influenced by molecular mass distribution, amount of specific groups bonded to the polysiloxane backbone, chain branching etc. It

is therefore possible to compare the experimental data with previously published values. As a general rule, the  $\Delta C$  values for packed columns remain constant or decrease with temperature. The variation of  $\Delta C$  for one degree of temperature increase,  $\delta\Delta C/\delta T$ , is shown in the last column of Table 1 and in Fig. 1. By taking into account the uncertainty due to experimental variation of retention times, temperature and flow-rate, columns showing  $\delta\Delta C/\delta T$  values between  $2 \times 10^{-3}$  and  $-2 \times 10^{-3}$  can be classified as having a polarity independent on temperature.

The change of  $\Delta C$  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. When  $\Delta C$  decreases with increasing temperature (negative values in Fig. 2), the distance between the two plots decreases. It has been shown [19] that the contribution from polar interactions depends weakly on temperature, whereas the cavity–dispersion interaction becomes less favorable for solute transfer at higher temperatures; the change of  $\Delta C$  is therefore due mainly to the shift of the  $n$ -alkanes plot, as discussed in detail below, for capillary columns.

Different  $\Delta C$  values were found for low-polarity phases as squalane itself. This is probably due to the influence of the support. If the liquid phase is non-polar, the effect of the silanol, Si–OH, and siloxane, Si–O–Si, bonds of the support can play an important role in the interaction; moreover, when adsorption contributes to the retention, for non-polar phases the dominant contribution is at the support–liquid interface and for polar ones at the gas–liquid interface [19]. For this reason, phases of low polarity show  $\Delta C$  values strongly dependent on the column preparation, deactivation of the support, etc., and values obtained in different experimental conditions may differ considerably (see Table 1). The lowest  $\Delta C$  value (1.54) for Squalane1 was obtained with columns prepared with 20% of liquid phase on flux-calcinated diatomite support Chromosorb W, AW, having a surface area of  $1 \text{ m}^2/\text{g}$  and a tailing factor of about 90% [29]. The value 2.33 was calculated by using the data published by McReynolds

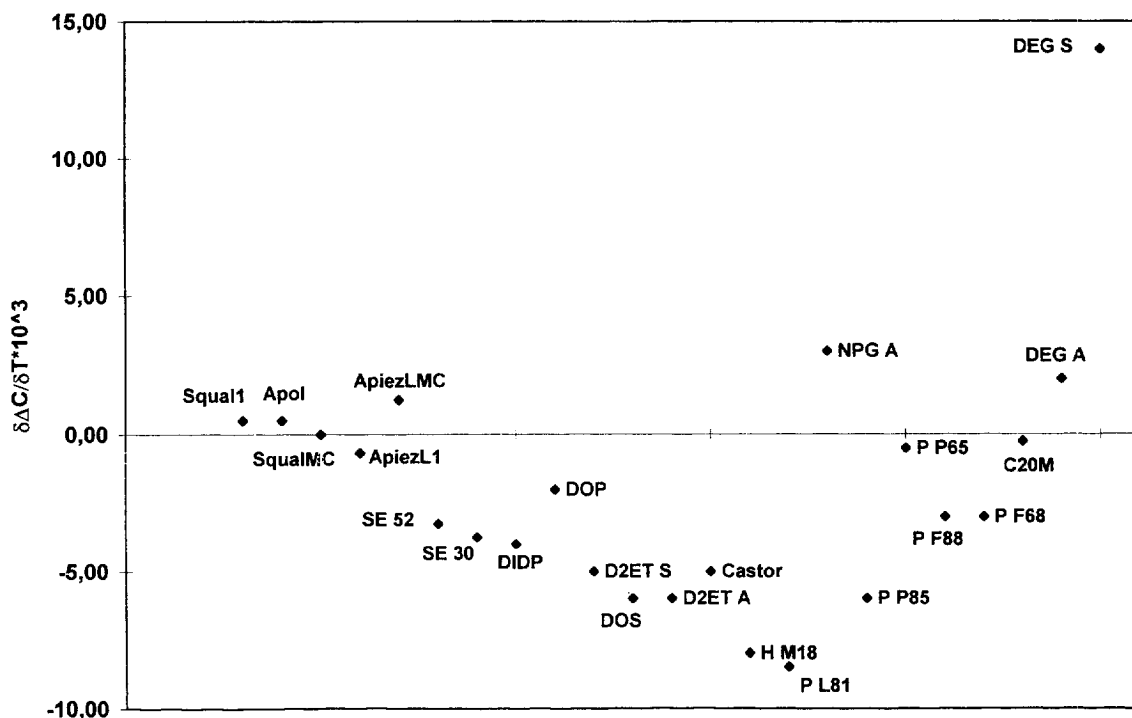


Fig. 2. Values of the change of  $\Delta C$  when the column temperature changes by  $1^\circ\text{C}$ ,  $\delta\Delta C/\delta T$ , for the various packed columns shown in Table 1.

(Squalane2) [6] which used as support the Johns Manville's filter aid Celite 545, more active and with a greater surface area, and added 0.5% of Polytergent J-300 wetting agent, thus increasing the polarity of the stationary phase. An effect of the amount of the liquid phase i.e., of the coverage of the support was also observed; the column Squalane2 in Table 1, prepared with the same support of Squalane1 but with less liquid (15% instead of 20%), shows a  $\Delta C$  value slightly greater owing to the greater adsorption and interfacial effects. The  $\Delta C$  value of about 2 for Apolane and that of 1.47 for *n*-triacontane confirms that these phases are slightly more polar and respectively less polar than squalane, as found previously [21,23].

For polar phases and compounds, the predominant effect is the interaction with the liquid phase. In addition, Si–OH and Si–O–Si groups of the support or of the capillary column inner wall are neutralized being involved in hydrogen bonding with the corresponding groups of the phase. For this reason, polar compounds as the polyglycols are used as deactivat-

ing agents in adsorption type columns [25,26]. Therefore, the effect of the adsorption and gas–solid phenomena on the behaviour of polar phases is small with respect of solution interactions and the overall  $\Delta C$  is only slightly influenced by the choice of the support. A significative variation from the general behaviour was observed for the DEGS column, whose  $\Delta C$  was calculated with the McReynolds' data [6]. The strong increase with increasing temperature of  $\Delta C$  for this column can be explained by the fact that interfacial adsorption plays a dominant role in the retention of compounds on this phase, mainly for hydrocarbons. For those compounds which are retained by a mixed mechanism the relative contribution from adsorption mechanism decrease with increasing temperature. This contribute for tridecane is 66.3% at  $81.2^\circ\text{C}$  and 26.9% at  $121.2^\circ\text{C}$  whereas in the same temperature range the adsorption contribute changes from 14.7 to 66% for heptan-1-ol [19]. This means that with increasing temperature the distance between the *n*-alkanols and *n*-alkanes plots increases, leading to a greater  $\Delta C$  value.

Table 2  
 $\Delta C$  values measured at various temperatures on some capillary columns

T (°C)	CL-A	Octyl (a)	Octyl (c)	DB-1 (3 $\mu$ m)	DB-1 (0.25 $\mu$ m)	SPB1	DB-5	CLOT	CL-U	BPX-70 (a)	BPX-70 (b)	WAX (a)	WAX (b)
50		2.23	2.53										
60	1.80	2.19	2.50	–	2.55	2.69	2.73	6.00	6.53	7.27	7.33	7.51	7.67
80	1.69	2.20	2.50	–	2.56	2.70	2.73	6.07	6.65	7.50	7.51	7.52	7.66
100	1.63	2.22	2.51	2.44	2.55	2.69	2.72	6.12	6.77	7.73	7.74	7.52	7.66
120	1.52	2.24	2.54	2.43	2.55	2.70	2.73	6.19	6.87	7.97	7.98	7.53	7.67
140	1.45	2.26	2.56	2.44	2.55	2.69	2.73	6.27	6.95	8.21	8.24	7.52	7.67
160	1.37	2.29	2.59	2.45	2.56	2.70	2.72	6.33	7.08	8.45	8.47	7.52	7.68
180	1.31	2.34	2.64	2.44	2.55	2.70	2.73	6.40	7.18	8.69	8.67	7.51	7.67
200	1.22	2.39	2.69	–	–	2.70	2.71	6.46	7.30	8.94	–	7.52	–
$\delta\Delta C/\delta T \times 10^3$	–4.10	2.20(d)	2.20(d)	0.10	0.00	0.00	0.00	3.30	5.40	11.90	11.50	0.00	0.00

The change of  $\Delta C$  due to a variation of temperature of 1°C,  $\delta\Delta C/\delta T$ , is also shown.

(a) New column.

(b) After six months of continuous use.

(c) After analysis of chlorophenols.

(d) For the SPB-octyl column the  $\delta\Delta C/\delta T$  was measured in the range 140–200°C.

A more detailed investigation, in a wider temperature range, was carried out on capillary columns. Table 2 and Fig. 3 show the  $\Delta C$  values of the capillary columns at temperatures ranging from 60 to 200°C. The  $\delta\Delta C/\delta T$  values calculated in the same temperature interval as it was found that, except for the SPB-octyl column, the dependence of  $\Delta C$  on temperature follows a straight line, are also shown in Table 2. The  $\delta\Delta C/\delta T$  value for SPB-octyl column was calculated in the 140–200°C range. The columns are listed from left to right in order of increasing  $\Delta C$  at the lowest temperature, 60°C. The values for polydimethylsiloxane, poly(5% diphenyl–95% dimethylsiloxane) and polyglycol columns (DB-1, SPB-1, DB-5 and Supelcowax-10) remain constant over the entire temperature range tested. The constant value of the polarity of pure polydimethylsiloxane and polyglycol columns in a wide temperature range is important because these columns are often used for the preliminary screening of unknown samples in order to obtain the separation of polar and non-polar compounds, to have an indication of the number of components of the mixture and to identify tentatively some of them by using tabulated values of the retention index on the two liquid phases. The poly(5% diphenyl–95% dimethylsiloxane) DB-5 column is also widely used for the analysis and identification of polychlorinated biphenyls (PCBs). The constant polarity assures that the identification

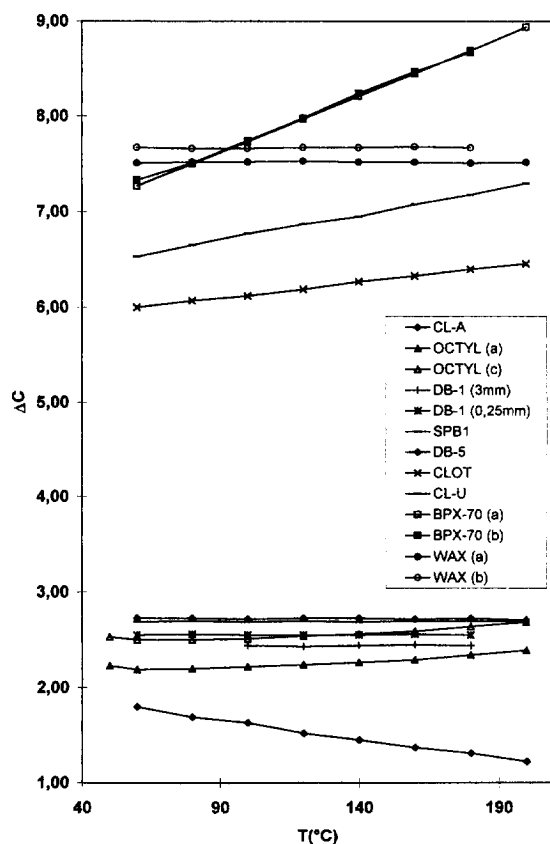


Fig. 3. Dependence of  $\Delta C$  on temperature for the capillary columns listed in Table 2.



carried out at a given temperature does not change when changing or programming the column temperature. Furthermore, the separation of a complex mixture can be obtained by using polar and non-polar columns of different length connected in series, in order to tune the overall polarity of the system [30–35]. The prediction of the retention values of the compounds analysed and the determination of the best polar/non-polar ratio of the composite column are rather independent on temperature, owing to the constant  $\Delta C$  of the two liquid phases. The comparison of DB-1 columns with different thickness of the phase layer confirms the results obtained with packed columns containing 15 and 20% of squalane. The greater amount of liquid phase increases the relative importance of gas–liquid partition phenomena between the solutes and the bonded polymer with respect of surface and gas–solid adsorption. The  $\Delta C$  value is therefore smaller for non-polar phases with greater layer thickness.

The  $\Delta C$  of other bonded-phase gas–liquid columns and of the graphite layer with large amount of polyglycol increases with temperature in a regular way, except for SPB-octyl, which shows a curvature better observed with enlarged vertical scale in Fig. 4. The CL-A column (1% FFAP on 0.7  $\mu\text{m}$  of graphit-

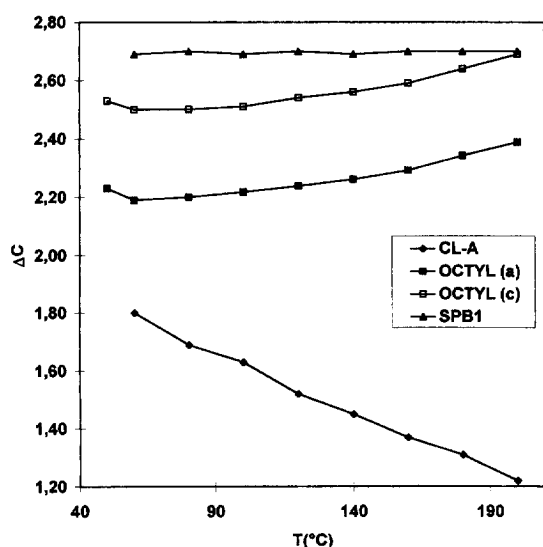


Fig. 4. Enlarged portion of Fig. 3, to show the constant values of  $\Delta C$  for the SPB-1 column and the change with temperature of the column CL-A, of a new and of an aged SPB-octyl column.

ized carbon black) shows a negative slope as a function of temperature. This behaviour may depend on the prevailing effect of the carbon layer due the small amount of modifying liquid phase, according to the negative slope of the temperature dependence of  $\Delta C$  previously observed [25,26] for carbon black columns deactivated with FFAP amounts less than 6.5%. The carbon-layer columns with higher amount of liquid modifier (CLOT and CL-U of this paper and a column with 44% of FFAP) show an increase of  $\Delta C$  due to the influence of the liquid polar phase.

With the above shown exceptions, the majority of the capillary columns tested show an increase of  $\Delta C$  values with temperature. This behaviour is due to a greater change of non-polar or dispersion interactions when temperature increases, with respect of hydrogen bonds and other polar effects. The *n*-alkanes plot shifts towards lower retention values more quickly than that of *n*-alkanols. This behaviour is not due to a different slope, because the values of Table 3 show that the *n*-alkanes and *n*-alkanols plots remain parallel at every temperature, but depends on the overall retention of the entire non-polar reference series. This should be indicated by the values of the intercept *a* of Eq. (1); however, the extrapolation to  $Z=0$  of the plots is subject to uncertainty that can conceal the regular dependence on temperature; moreover, for some polar columns, the plots for alkanols have a crossing point at  $Z>0$  (see point D in Fig. 1). Therefore, the dependence of the retention values on temperature is illustrated by showing the vertical distance between the *n*-alkanes and *n*-alkanols plots for a temperature change of 20°C,  $\Delta \ln t'_R$ , measured within the range of *Z* experimental values, where the linear regression has the greatest accuracy. The values of the  $\Delta \ln t'_R$  show (Fig. 5) that, for the same temperature change, the shift of *n*-alkanes and *n*-alkanols parallel plots is the same for DB-1 and WAX columns (no change of  $\Delta C$  values with temperature) and is greater for *n*-alkanes plot for the BPX-70 column, whose  $\Delta C$  shows the greatest increase with temperature among all the columns tested. This means that for the BPX-70 column, temperature changes have the greatest effect on the dispersion interaction, whereas the polar effects are less temperature-dependent.

Table 2 also shows the effect of the ageing of two polar columns (BPX-70 and Supelcowax-10). After

Table 3

Slope of the plots of  $\ln t'_R$  of *n*-alkanes and *n*-alkanols as a function of *Z*, measured at various temperatures on the packed (above) and capillary (below) columns listed in Table 1 Table 2

Column	Symbol	Temperature (°C)							
		100		120		140		160	
		$b_p$	$b_{OH}$	$b_p$	$b_{OH}$	$b_p$	$b_{OH}$	$b_p$	$b_{OH}$
Squalane	Squal	0.757	0.776	0.851	0.845				
Apiezon L	Apiez			0.681	0.682			0.562	0.578
SE 52	SE 52			0.608	0.611			0.495	0.517
SE 30	SE 30			0.603	0.610			0.488	0.514
Diisodecyl phthalate	DIDP			0.687	0.703	0.620	0.643		
Diocetyl phthalate	DOP			0.692	0.703	0.618	0.649		
Di-2-ethylhexyl sebacate	D2ET S	0.763	0.768	0.695	0.725				
Diocetyl sebacate	DOS	0.763	0.768	0.696	0.705				
Di-2-ethylhexyl adipate	D2ET A	0.763	0.766	0.694	0.704				
Castorwax	Castor			0.673	0.689	0.612	0.631		
Hallcomid M18	H M18	0.758	0.817	0.692	0.704				
Pluronic L81	P L81	0.713	0.709	0.652	0.647				
Neopentyl glycol adipate	NPG A			0.583	0.601	0.537	0.545		
Pluronic P85	P P85	0.700	0.685	0.649	0.631				
Pluronic F88	P F88	0.660	0.643	0.597	0.603				
Pluronic F68	P F68	0.660	0.645	0.605	0.588				
Carbowax 20M	C20M			0.568	0.565			0.448	0.479
DEG adipate	DEG A			0.542	0.536	0.489	0.489		
DEG succinate	DEG S			0.477	0.459	0.420	0.435		
CL-A	CL-A	1.267	1.219	1.170	1.113	1.076	1.032	0.982	0.931
DB-5	DB-5	0.619	0.625	0.553	0.560	0.462	0.487	0.487	0.511
SPB-1	SPB-1	0.588	0.592	0.513	0.521	0.454	0.460	0.374	0.385
DB-1	DB-1	0.602	0.613	0.518	0.538	0.450	0.471	0.399	0.415
CLOT	CLOT	0.638	0.621	0.563	0.546	0.504	0.489	0.448	0.436
CL-U	CL-U	0.608	0.578	0.533	0.512	0.469	0.451	0.409	0.399
Supelcowax-10 (b)	WAX (b)	0.531	0.543	0.471	0.484	0.417	0.427	0.369	0.378
BPX-70 (b)	BPX(b)	0.499	0.472	0.436	0.424	0.400	0.387	0.336	0.302

(b) Values measured after six months of continuous use.

six months of continuous use, the  $\Delta C$  values of these columns increased: for the BPX-70 column the change was due to a slight decrease of the retention of *n*-alkanes, whereas that of the *n*-alkanols was not affected; for the Supelcowax-10 column, a slight decrease of the retention of *n*-alkanes was accompanied by a greater increase of the retention of *n*-alkanols. In both instances, the slope of the alkanes and alkanols plots remains the same and no appreciable change of efficiency was observed. The change of  $\Delta C$  values are also an indication of the effects of some samples on the performance of the columns. It has been found that samples containing relatively large amounts of chloronaphthalenes and chloro-

phenols can heavily damage some columns. Large injections of pentachlorophenol completely destroyed the efficiency of polyglycol columns. The two series of data for SPB-octyl column in Table 2 show the effect on this column of replicate injections of sample containing chlorophenols. In this instance, the increase of  $\Delta C$  was due to an increase of the retention of alkanols and a decrease of that of alkanes, without changing the slope of the plots.

#### 4. Conclusions

The calculation of  $\Delta C$  as a polarity indicator does

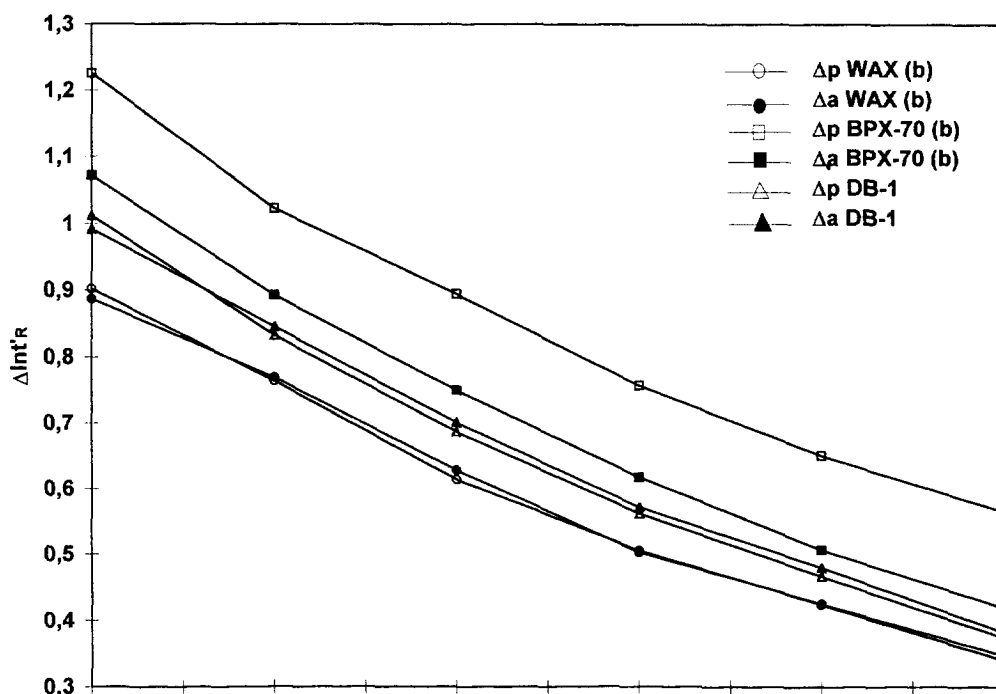


Fig. 5. Values of  $\Delta \ln t'_R$ , i.e., the vertical distance between the parallel plots of *n*-alkanols and *n*-alkanes at the various temperatures for the DB-1, BPX-70 and WAX columns. The slope values of the plots are shown in Table 3.

not depend on the use of reference phases and can easily be made by using only *n*-alkanes and *n*-alkanols. The obtained values can be used to compare the behaviour of different stationary phases with respect of polar and non-polar solutes. If the  $\Delta C$  does not change with temperature, the elution order of all compounds, independent on their polarity, remains unchanged at different isotherms and in programmed temperature analyses: identification of peaks carried out at any temperature is not impaired when changing the analysis parameters.

The change of  $\Delta C$  with temperature or with ageing of the column is a measure of the rate of decrease in polar interactions (measured by the behaviour of alkanols) compared to the rate of decrease in dispersive interaction (available to both alkanols and alkanes). Both interactions decreases as temperature increases and the rate of decrease will vary from one stationary phase to another; if the dispersive interactions decrease at a lower rate with respect to polar interaction, a negative  $\Delta C$  trend is

expected, if the dispersive interaction decrease at a greater rate than polar ones, positive trend will be observed.

When the  $\Delta C$  values changes with changing temperature or with ageing of the column, care should be taken to confirm the identification of the component of complex polar/non-polar mixtures. The determination of the  $\Delta C$  values at regular intervals during the life of a column along with a measure of its number of theoretical plates can verify if the performance of the stationary phase remains unchanged or is subjected to variation due to the analysis of some reactive compounds.

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