Prediction of the resolution of capillary columns in different conditions of inlet pressure and temperature

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Abstract

A procedure previously described for the prediction of the plate height of capillary columns operated at different inlet pressure of the carrier gas and at various column temperatures by using few retention data measured under isobaric conditions was modified and improved in order to permit the prediction of the retention times and of the peak widths at various heights. It is therefore possible to calculate the ratio, δ, between the peak width at different heights and the peak width at half height, whose value is used to predict the resolution at different height of two closely eluting peaks. It was found that the δ values do not depend on temperature and inlet pressure and are a characteristic of the used column; they can therefore be used in order to calculate the resolution in any temperature and inlet pressure condition. The method was used to predict the retention time, the peak width and the resolution of polar and non-polar compounds (alkanes, alkenes, chloroalkanes, alcohols, ketones) on capillary columns of different length and polarity by using as the starting data retention and width values measured in three isobaric runs only.
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1. Introduction

Several calculation methods have been suggested in order to predict retention times and peak widths in temperature programmed gas chromatography [1–3]. When both the retention time and the width of a peak are available, also the resolution of adjacent peaks can be calculated [4–7]. Many proposed methods are based on the assumption that for increasing the speed of the analysis and permit the elution of high-molecular weight compounds the increase of the column temperature is the best and almost the unique solution. However, a too high temperature may cause the decomposition of some compounds, decrease the efficiency of the column and change of the relative retention of peaks of different polarity, with possible interference or inversion of the elution order, requiring a new identification procedure when the analysis conditions are changed. These problems are not encountered if the decrease of the retention times is obtained by increasing the inlet pressure of the column in isother-

mal conditions. The use of high carrier gas flow rates was in fact the first technique used in order to decrease the gas chromatographic retention of compounds with great molecular mass [8–14] because the stationary phases available at the beginning of gas chromatography did not tolerate high temperatures. New stationary phases with increased thermal stability and low vapour pressure and suitable temperature programming devices caused pressure programming to be neglected for many years because the mechanical and pneumatic manifolds used for this task were complicate or inaccurate and high flow rate in packed columns required very high inlet pressure and large gas consumption; moreover, the increase of the flow rate decreased quickly the efficiency of the packed columns by shifting the plate height values toward the right side of the Van Deemter plot, rapidly increasing due to the contribution of the mass transfer terms. Today, available instruments can monitor and control in a reproducible manner the pressure at the column inlet during the analysis, and the use of capillary columns having a broad minimum and a slow increase of plate height values with increasing carrier gas velocity leads to results equivalent in some respects to those of increasing temperature, as foreseen by Purnell [15]. However, the range of compounds

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which can be analysed by increasing the flow rate at the maximum pressure values allowed by the existing equipment is small if compared with the range covered by the maximum temperature range permitted by the high temperature stationary phases now available. Notwithstanding this, the simultaneous use of temperature programming and high flow rate shortens the total analysis time and decreases the maximum temperature necessary for the elution of the heaviest compounds. This decreases the decomposition of temperature sensitive compounds and reduces the bleeding of the stationary phase and the column ageing. The prediction of the retention times and peak resolution during simultaneous temperature and pressure programming is rather complex. Few papers were published on the theoretical prediction of the effect of pressure increase on the column efficiency, mainly regarding fast chromatography applications [16–18].

In a previously published paper [19] it was described a calculation method for the evaluation of the efficiency of capillary columns which permits to predict the plate height obtained at any inlet pressure of the carrier gas by using as the input data the retention times, t_R, and the peak widths at half height, $b_{1/2}$, of a mixture of polar and non-polar compounds measured in three isobaric runs carried out at different inlet pressure. In order to check the validity of using the inlet pressure increase instead of temperature programming for reducing the time of analysis without loss of efficiency it is necessary to measure or calculate the resolving power of the column at various inlet pressure and column temperature values. With a method capable to predict the t_R and the $b_{1/2}$ of all the peaks of the analysed mixture at any inlet pressure and column temperature, it is possible to evaluate the resolution of closely eluting peaks and select the best analytical parameters which simultaneously offer suitable resolution and fast analysis, without the negative effect connected to an excess of temperature.

The use of three series of data measured at the lowest, at the highest and at an intermediate value of the used pressure range yields a fair approximation of the calculated values with the experimental ones. It has been found that, at a given temperature and by changing the inlet pressure, the $b_{1/2}$ values of compounds with similar polarity depend linearly on the values of their t_R. It is therefore possible to predict the t_R and the $b_{1/2}$ of all the peaks of the analysed mixture at any inlet pressure and temperature and at the same time to evaluate the peak resolution.

Furthermore, the elution order of compounds of different polarity does not change when the analysis time is reduced by increasing the inlet pressure at a constant temperature, whereas the change of temperature often modifies the relative retention of closely eluting peaks, due to the different effect on the partition coefficients of the compounds. This phenomenon may cause the co-elution or the inversion of some peaks and require a new identification of the eluted compounds when the temperature is changed. The method described here, which is implemented with respect of that previously published [19] permits to evaluate the behaviour of the column and to select the conditions necessary to obtain a suitable resolution of the analysed mixture.

2. Theory

The $b_{1/2}$ and the t_R values of the peaks of the analysed compounds and the plate height value of the used column at various temperatures and inlet pressures can be calculated by starting from the $b_{1/2}$ and t_R values measured in three isobaric runs [19]. By using the calculated plate height values, the method evaluates the total number of plates in the column and calculates the t_R and the $b_{1/2}$ of the peaks at any pressure in isothermal conditions. By repeating the procedure at various temperature, one can evaluate the performance of the column in a great range of experimental conditions. The height equivalent to a theoretical plate, as defined by the Golay equation [20–23], is not the same along the entire column length, L, but if one supposes that it remains constant in a short tract of column length covered by the eluting compound in a given time interval, then the number of theoretical plates, N, calculated with the formula [24]:

$$N = 5.54 \left(\frac{t_R}{b_{1/2}} \right)^2 \tag{1}$$

where t_R is the gross retention time and $b_{1/2}$ the peak width at half height, is given by:

$$N = \sum_{j=1}^{n} N_j = \sum_{j=1}^{n} \frac{\Delta L_j}{h_j} \tag{2}$$

where n is the number of the short tracts of length ΔL_j in which the column has been divided and where the number of theoretical plates, N_j, and the corresponding plate height, h_j, have been calculated [19,21]. The h_j values are calculated with the following equation:

$$h_j = \frac{2D_g}{u_{cg,j}} + \frac{(1 + 6k'(P_j) + 11k'(P_j)^2)r^2}{24D_g(1 + k'(P_j))^2} u_{cg,j} + \frac{2k'(P_j)d_f^2}{3D_s(1 + k'(P_j))^2} u_{cg,j} \tag{3}$$

where D_g and D_s are the diffusion coefficients in the gas and stationary phases, respectively, d_f the thickness of the stationary phase layer and r the internal radius of the column, $u_{cg,j}$ the carrier gas linear velocity, k' the capacity factor and P_j the pressure in the ΔL_j interval. When the diffusion coefficients have been obtained, Eq. (2) can be applied in any pressure and temperature condition and it is possible to predict through an iterative calculation procedure the number of theoretical plates for any isobaric run. Then, by using Eq. (1), one can obtain the $b_{1/2}$ value of the peaks taken as Gaussian curves.

The resolution of two closely spaced peaks is expressed by the classical formula which relates the distance between the apexes of the two peaks (Δt_R) to the base width [25]:

$$R_s = \frac{2(t_{R2} - t_{R1})}{w_{b1} + w_{b2}} = \frac{2\,\Delta t_R}{w_{b1} + w_{b2}} \tag{4}$$

where t_{R1} and t_{R2} are the retention times of the two closely spaced peaks and w_{b1} and w_{b2} are the corresponding width at the peak base. If the tailing is small and both peaks can be considered as Gaussian distribution curves, a value of $R_s = 1.0$ means that the distance Δt_R between the peak apexes is equal to 4σ (4σ resolution) and about 95% separation of the peak areas is achieved. Baseline separation requires a $R_s = 1.5$ value (6σ resolution). Since the direct measurement of the base width is difficult because it, if carried out graphically, involves drawing the tangents to the inflection points, for Gaussian peaks its value can be deducted from the $b_{1/2}$ values measured by the data system, which also calculates σ values. Since peak width at various height is a function of σ, for Gaussian peaks the width at the base, w_b, can be calculated from the $b_{1/2}$ value with the following equation [25]:

$$w_b = \frac{4}{2\sqrt{2\ln 2}} b_{1/2} = 1.699 b_{1/2} \tag{5}$$

However, often the peaks are not symmetrical and show appreciable tailing: therefore the determination of the base width and the calculation of the resolution with Eq. (4) may be difficult. A method which can be accepted from the practical point of view is to evaluate the resolution not at the baseline but at a sufficient height above the baseline, e.g. at $(1/x)$th fraction of the total peak height, where the shape of the peaks is near Gaussian and the valley between two adjacent peaks is deep enough to permit a separation suitable for qualitative identification and tolerable accuracy in the determination of the peak area for quantitative analysis. The method used for the calculation of the $b_{1/2}$ value can be easily modified in order to obtain the peak width at any height and the resolution at this height, R_x, can be calculated by using the ratio, δ_x, between the width at $(1/x)$th of the peak height, $b_{1/x}$, and the width at half height, $b_{1/2}$.

$$b_{1/x} = \delta_x b_{1/2} \tag{6}$$

If the R_x value is considered as acceptable, the δ_x value of Eq. (6) must be calculated at $(1/x)$th of the peak height. The following procedure can be used to evaluate the R_x value:

$$R_x = \frac{2(t_{R,i+1} - t_{R,i})}{\delta_x(b_{1/2,i+1} + b_{1/2,i})} \tag{7}$$

where t_{Ri} and $b_{1/2i}$ are respectively the gross retention time and the peak width at half height of the ith peak, t_{Ri+1} and $b_{1/2i+1}$ are the corresponding values for the peak eluted after the ith one.

The behaviour of the $b_{1/2}$ values, as a function of t_R at different inlet pressure and column temperature, can be well

described by a straight line [18,26,27]:

$$b_{1/2,i} = mt_{R,i} + q \tag{8}$$

where m is the slope and q the intercept. Therefore, by using this equation, it is possible to calculate the peak width at half height of any compound at any pressure and retention time in isothermal conditions.

In order to evaluate the resolution of a given peak, i, from the peak eluted just before, $i - 1$, and after it, $i + 1$, the following equations can be written:

$$R_{xi+1,i} = \frac{2(t_{R,i+1} - t_{R,i})}{\delta_x(b_{1/2,i+1} + b_{1/2,i})} \tag{9}$$

$$R_{xi,i-1} = \frac{2(t_{R,i} - t_{R,i-1})}{\delta_x(b_{1/2,i} + b_{1/2,i-1})} \tag{10}$$

If one establish the condition that the resolution R_x must be greater than unity in isothermal conditions, the following equations are obtained:

$$t_{R,i+1} > \frac{1/\delta_x + m}{1/\delta_x - m} t_{R,i} + \frac{2q}{1/\delta_x - m} \tag{11}$$

$$t_{R,i-1} < \frac{1/\delta_x - m}{1/\delta_x + m} t_{R,i} - \frac{2q}{1/\delta_x + m} \tag{12}$$

It is therefore possible to calculate the minimum and maximum values that the retention time of a peak eluted near to that of interest must have so that the resolution R_x is greater than unity.

3. Experimental

The determination of the retention times and peak widths at half height of reference mixtures containing non-polar and polar compounds was made by using three capillary columns with a length of 30 m $\times$ 0.32 mm i.d., phase thickness 0.25 μm: a non-polar poly(dimethylsiloxane) DB-1 (J&W) and two polar poly(ethyleneglycol) columns: Supelcowax-10 (Supelco) and CP WAX 52CB (Chrompack). A medium-polarity column poly(diphenyldimethylsiloxane) DB-17 (J&W) with a length of 15 m $\times$ 0.32 mm i.d., phase thickness 0.25 μm, was also used.

The columns were installed in a Varian model 3800 gas chromatograph (Varian, Palo Alto, CA, USA) equipped with a split–splitless injector and a flame ionisation detector. Helium was used as the carrier gas. The split ratio was 1/20. The column temperature was checked with an independent thermocouple with an accuracy of 0.1 °C. The inlet pressure of the column was controlled and measured by the electronic hardware of the gas chromatograph with an accuracy of ± 0.1 psig (1 Pa $= 1.45038 \times 10^{-4}$ psig) and checked with a mercury manometer directly connected to the injector septum through a thin needle. Throughout the text the inlet pressure values are reported in psig which is the unit used

Table 1

Column DB-1 (30 m × 0.32 mm i.d., 0.25 μm phase thickness). Comparison between the experimental values of the peak width at half height(s) of some linear alkanes and 1-alcohols, $b_{1/2}$ exp, and those calculated with the described method, $b_{1/2}$ cal. The relative percent errors between experimental and calculated values E_{rel} (%) $= 100(b_{1/2}\,\text{exp} - b_{1/2}\,\text{cal})/b_{1/2}\,\text{exp}$ is also shown

P (psig)	C10			C11			C12			C13			C14			C15			C16			C17		
	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)
n-Alkanes																								
$T = 100\,^\circ$C																								
7.5	2.32	2.32	−0.03	3.43	3.37	1.87	5.61	5.63	−0.34	9.71	9.68	0.39	17.63	17.35	1.56	31.82	31.82	0.00						
17.5	1.02	1.03	−1.45	1.63	1.60	1.46	2.76	2.76	−0.05	5.11	5.10	0.14	9.59	9.63	−0.37	18.13	18.21	−0.46						
25.0	0.86	0.86	0.34	1.36	1.37	−0.79	2.40	2.37	1.32	4.48	4.45	0.73	8.59	8.49	1.24	16.22	16.15	0.41						
$T = 130\,^\circ$C																								
7.5	1.93	1.94	−0.52	2.19	2.21	−1.02	2.79	2.80	−0.23	3.83	3.83	0.16	5.60	5.57	0.51	18.65	8.67	−0.29	13.94	13.87	0.52	23.04	22.78	1.13
17.5	0.69	0.70	−0.40	0.86	0.86	−0.07	1.16	1.17	−0.19	1.72	1.72	0.21	2.72	2.71	0.44	4.44	4.44	0.16	7.55	7.46	1.21	12.50	12.34	1.26
25.0	0.53	0.52	0.21	0.68	0.68	0.56	0.95	0.94	0.40	1.43	1.43	0.50	2.31	2.31	0.20	3.87	3.83	0.92	6.49	6.52	−0.34	11.04	10.82	1.99
$T = 160\,^\circ$C																								
7.5	1.64	1.66	−0.94	1.86	1.86	−0.29	2.15	2.15	0.04	2.55	2.55	0.02	3.04	3.08	−1.26	13.95	3.98	−0.64	5.22	5.23	−0.23	7.64	7.60	0.54
17.5	0.59	0.59	0.02	0.66	0.66	0.05	0.75	0.76	−0.74	0.92	0.92	0.10	1.20	1.20	−0.40	1.61	1.63	−1.06	2.36	2.34	0.87	3.51	3.48	0.99
25.0	0.44	0.44	−1.011	0.50	0.50	0.32	0.57	0.57	0.53	0.70	0.70	1.12	0.96	0.95	1.47	1.32	1.31	0.30	1.98	1.95	1.67	2.94	2.91	0.92

P (psig)	C8OH			C9OH			C10OH			C11OH			C12OH			C13OH			C14OH			C15OH		
	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)
1-Alcohols																								
$T = 100\,^\circ$C																								
7.5	2.86	2.80	2.05	4.50	4.49	0.28	7.41	7.32	1.18	12.87	12.62	1.98	23.74	23.51	0.98									
17.5	1.23	1.23	0.19	2.05	2.03	0.97	3.66	3.64	0.54	6.89	6.79	1.46	13.04	12.91	1.00									
25.0	1.02	1.02	−0.37	1.72	1.71	0.72	3.12	3.15	−0.89	5.96	6.01	−0.74	11.61	11.43	1.52									
$T = 130\,^\circ$C																								
7.5	2.08	2.11	−1.59	2.54	2.56	−0.87	3.29	3.31	−0.44	4.60	4.61	−0.17	7.03	7.04	−0.12	11.22	11.21	0.02	18.35	18.31	0.27			
17.5	0.77	0.77	−0.39	0.98	0.98	0.30	1.38	1.39	−0.89	2.10	2.10	−0.06	3.46	3.44	0.62	5.73	5.69	0.72	9.76	9.67	0.85			
25.0	0.59	0.59	0.03	0.77	0.77	0.01	1.13	1.14	−0.15	1.77	1.77	0.03	2.98	2.95	1.19	4.99	4.93	1.26	8.47	8.45	0.24			
$T = 160\,^\circ$C																								
7.5	1.85	1.85	−0.02	2.09	2.09	−0.23	2.39	2.39	0.08	2.88	2.87	0.34	3.61	3.65	−1.10	14.76	4.80	−0.93	6.66	6.66	0.01	9.30	9.43	−1.38
17.5	0.63	0.63	−0.04	0.71	0.71	−0.01	0.83	0.83	−0.16	1.06	1.07	−0.15	1.41	1.41	0.04	1.97	1.98	−0.42	2.93	2.91	0.69	4.38	4.43	−0.99
25.0	0.46	0.46	0.11	0.52	0.52	0.12	0.63	0.62	0.75	0.82	0.82	0.11	1.11	1.11	0.36	1.63	1.61	1.48	2.40	2.40	−0.32	3.70	3.74	−1.03

for controlling and checking the gas chromatograph pressure and is therefore exactly known. In the calculation the pressure values measured by the gas chromatograph's software in psig were converted in cgs units (dynes/cm^2). The correlation between the pressure and the carrier flow rate on the used columns is shown below in Table 7.

The samples containing several terms of the homologous series of *n*-alkanes and of straight chain 1-alcohols (indicated for sake of simplicity in the following text, in the tables and in the captions of the figures as C10, C11, C12 … or C10OH, C11OH, C12OH …, respectively) and of some alkenes, chloroalkanes and ketones were prepared with standard solutions in dichloromethane at a concentration of 10 µg/ml for each compound. The injected amount was 1 µl and the retention times were measured with an accuracy of ±0.001 min by means of a Varian Star Data System. The analyses were carried out at temperatures between 100 and 160 °C in the inlet pressure range 7.5–30 psig at 2.5 psig intervals.

4. Results and discussion

The parameters that must be known for the application of the calculation method are: the atmospheric pressure, the dimensions of the column, the nature of the carrier gas and its viscosity, the column temperature, the pressure at the column inlet, the retention time, the peak width at half height [19]. For the following calculations the experimental $b_{1/2}$ and t_R values used were those measured at three inlet pressures (the highest, the lowest and an intermediate value of the investigated pressure range) and at various temperatures because in a previously published research it has been found that three data yield an accuracy very close to that obtained by using a greater amount of experimental data [19]. The selected data were input to the program made by applying Eqs. (1)–(3) shown above in Section 2, in order to calculate for each of the injected compounds the behaviour of the plate height as a function of the inlet pressure. As the independent variables the inlet pressure and the temperature were used, because they can be set and exactly measured,

Table 2

Column DB-17 (15 m × 0.32 mm i.d., 0.25 µm phase thickness). Comparison between the experimental values of the peak width at half height(s) of some linear alkanes and 1-alcohols, $b_{1/2}$ exp, and those calculated with the described method, $b_{1/2}$ cal. The relative percent errors between experimental and calculated values E_{rel} (%) = $100(b_{1/2} \exp - b_{1/2} \text{cal})/b_{1/2} \exp$ is also shown

P (psig)	C13			C15			C17			C20		
	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)
n-Alkanes												
T = 100 °C												
7.5	1.74	1.71	2.14	5.12	5.05	1.39	16.77	16.51	1.54			
17.5	1.18	1.18	−0.46	3.42	3.50	−2.35	11.59	11.58	0.13			
25.0	1.08	1.07	1.01	3.20	3.17	0.94	10.53	10.51	0.17			
T = 130 °C												
7.5	0.75	0.76	−0.74	1.46	1.46	1.12	3.78	3.74	1.01	16.92	16.79	0.79
17.5	0.55	0.55	−0.38	1.03	1.04	−0.84	2.53	2.56	−1.23	11.83	11.82	0.13
25.0	0.52	0.51	2.46	0.98	0.95	2.91	2.37	2.32	2.00	10.91	10.77	1.28
T = 160 °C												
7.5				0.68	0.68	−0.09	1.23	1.24	−0.75	3.92	3.89	0.75
17.5				0.49	0.49	1.08	0.87	0.87	0.29	2.73	2.74	−0.07
25.0				0.46	0.45	2.87	0.82	0.80	2.93	2.52	2.50	0.59

P (psig)	C8OH			C10OH			C12OH			C14OH			C15OH		
	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)
1-Alcohols															
T = 100 °C															
7.5	0.94	0.95	−0.95	2.45	2.43	0.79	8.05	7.87	2.18	28.37	27.57	2.80			
17.5	0.62	0.62	0.80	1.61	1.61	−0.28	5.26	5.32	−1.26	18.30	18.84	−2.95			
25.0	0.55	0.55	0.21	1.44	1.45	−0.48	4.95	4.79	3.27	17.54	16.95	3.41			
T = 130 °C															
7.5				0.97	0.97	−0.43	2.17	2.14	1.12	5.72	5.66	1.04	9.78	9.73	0.45
17.5				0.63	0.62	0.62	1.36	1.37	−1.00	3.80	3.77	0.71	6.26	6.24	0.39
25.0				0.56	0.55	0.59	1.25	1.22	2.22	3.41	3.40	0.38	5.80	5.52	1.33
T = 160 °C															
7.5				0.58	0.59	−2.09	0.89	0.88	1.40	1.68	1.70	−0.87	2.54	2.54	0.20
17.5				0.37	0.37	−1.20	0.56	0.57	−2.57	1.12	1.13	−0.62	1.66	1.69	−1.47
25.0				0.34	0.33	2.50	0.53	0.52	1.81	1.03	1.02	1.12	1.54	1.52	1.22

Table 3
Column Supelcowax-10 (30 m × 0.32 mm i.d., 0.25 μm phase thickness). Comparison between the experimental values of the peak width at half height(s) of some linear alkanes and 1-alcohols, $b_{1/2}$ exp, and those calculated with the described method, $b_{1/2}$ cal. The relative percent errors between experimental and calculated values E_{rel} (%) = $100(b_{1/2}\exp - b_{1/2}\text{cal})/b_{1/2}\exp$ is also shown

P (psig)	C11			C13			C15		
	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)
n-Alkanes									
$T = 100\,°C$									
7.5	2.81	2.85	−1.54	5.88	5.77	−1.56	11.66	11.82	−1.36
17.5	1.46	1.45	0.46	3.28	3.29	−0.40	7.20	7.21	−0.25
25.0	1.15	1.19	−3.89	2.68	2.75	−2.72	6.02	6.08	−1.05
$T = 130\,°C$									
7.5	1.79	1.82	−1.72	2.90	2.92	−0.94	5.15	5.20	−1.07
17.5	0.90	0.91	−0.87	1.56	1.58	−0.97	2.97	2.97	0.09
25.0	0.73	0.75	−2.37	1.29	1.31	−1.28	2.41	2.48	−2.88
$T = 160\,°C$									
7.5	1.36	1.37	−0.79	1.84	1.85	−0.71	2.71	2.72	−0.12
17.5	0.71	0.71	0.54	0.96	0.96	−0.27	1.51	1.52	−0.99
25.0	0.60	0.60	1.10	0.81	0.80	1.15	1.33	1.28	3.79
	C6OH			C8OH			C10OH		
	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)	$b_{1/2}$ exp	$b_{1/2}$ cal	E_{rel} (%)
1-Alcohols									
$T = 100\,°C$									
7.5	7.93	8.01	−1.03	16.64	16.76	−0.72	40.82	40.72	0.25
17.5	4.50	4.47	0.83	10.14	10.14	−0.01	25.12	25.04	0.33
25.0	3.61	3.72	−2.89	8.44	8.54	−1.19	21.26	21.19	0.33
$T = 130\,°C$									
7.5	3.57	3.61	−1.03	6.51	6.56	−0.69	12.60	12.62	−0.19
17.5	1.94	1.94	0.32	3.81	3.80	0.49	7.77	7.70	0.84
25.0	1.58	1.60	−1.58	3.12	3.18	−1.82	6.40	6.49	−1.48
$T = 160\,°C$									
7.5	2.19	2.20	−0.81	3.33	3.33	0.02	5.55	5.53	0.25
17.5	1.10	1.11	−0.43	1.81	1.81	−0.11	3.19	3.18	0.38
25.0	0.92	0.91	0.25	1.55	1.50	2.89	2.71	2.66	1.87

whereas the flow rate is a derived value calculated by using the parameters of the column, the viscosity of the carrier gas, the pressure measured at the injector and the temperature. For the same reason the inlet pressure values are reported in psig which is the unit used for controlling and checking the gas chromatograph pressure. Below in Table 7 the correlation between the pressure and the carrier flow rate on the used columns is shown.

The Star Data System yields the values of the peak width at half height with an approximation of 0.1 s, not enough accurate for the calculations; an auxiliary calculation program was therefore written which, using the raw data stored in the Star files, calculates the peak width at various height ($b_{1/x}$) with an approximation of 0.06 s, increasing the accuracy of the final calculation.

The auxiliary calculation program can be summarised as:

(1) selection of the initial time t_i and final time t_f of the selected peak;
(2) construction of the baseline as a straight line from t_i to t_f with equation $z = \alpha t + \beta$;
(3) subtraction of the calculated baseline value from the peak signal in the Δt range (t_f–t_i): $y^* = y - z$;
(4) search of the maximum value of the peak signal in the Δt range: y^*_{max} and calculation of the corresponding t_R;
(5) for $y^*_x = y^*_{max}/x$ search of two points to the left and to the right of y^*_{max} such that $y^*(t_k) < y^*_x < y^*(t_{k+1})$ with $t_{k+1} < t_R$ and $y^*(t_j) > y^*_x > y^*(t_{j+1})$ with $t_j > t_R$;
(6) construction of two straight lines: A_1 through the points $(t_k, y^*(t_k))$; $(t_{k+1}, y^*(t_{k+1}))$; and A_2 through the points $(t_i, y^*(t_j))$; $(t_{j+1}, y^*(t_{j+1}))$;
(7) calculation on the straight line A_1 of the time value, t_1, where the signal is equal to y^*_x;
(8) calculation on the straight line A_2 of the time value, t_2, where the signal is equal to y^*_x;
(9) therefore the width at $1/x$ of the peak height is: $b_{1/x} = t_2 - t_1$.

Tables 1–3 show, for some *n*-alkanes and 1-alcohols analysed on DB-1, DB-17 and Supelcowax-10 columns, respectively, the comparison between the values of the $b_{1/2}$ exp, which is the peak width at half height

Table 4

Column DB-1 (30 m × 0.32 mm i.d., 0.25 μm phase thickness). Comparison between the experimental values of the retention times (min) of some linear alkanes and 1-alcohols, t_R exp, and those calculated with the described method, t_R cal. The relative percent errors between experimental and calculated values, E_{rel} (%) $= 100(t_R$ exp $- t_R$ cal$)/t_R$ exp, is also shown

P (psig)	C10			C11			C12			C13			C14			C15			C16			C17		
	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)
n-Alkanes																								
$T = 100\,°C$																								
7.5	4.953	4.940	0.26	7.345	7.320	0.34	11.864	11.835	0.24	20.364	20.338	0.13	38.353	36.347	0.02	68.195	68.195	0.00						
17.5	2.212	2.205	0.32	3.277	3.263	0.42	5.292	5.267	0.48	9.085	9.045	0.44	16.197	16.157	0.25	29.526	29.462	0.22						
25.0	1.588	1.587	0.08	2.352	2.345	0.30	3.793	3.780	0.34	6.508	6.488	0.30	11.604	11.587	0.15	21.144	21.145	0.00						
$T = 130\,°C$																								
7.5	3.473	3.477	−0.11	4.238	4.242	−0.091	5.552	5.552	0.01	7.795	7.800	−0.06	11.617	11.620	−0.03	18.119	18.130	−0.06	29.143	29.162	−0.06	47.768	47.800	−0.07
17.5	1.548	1.550	−0.13	1.887	1.890	−0.16	2.467	2.472	−0.19	3.458	3.470	−0.35	5.153	5.165	−0.23	8.037	8.057	−0.24	12.931	12.958	−0.21	21.213	21.250	−0.17
25.0	1.118	1.117	0.12	1.363	1.360	0.22	1.783	1.777	0.36	2.502	2.493	0.35	3.723	3.708	0.39	5.803	5.783	0.34	9.332	9.302	0.33	15.293	15.258	0.23
$T = 160\,°C$																								
7.5	3.037	3.038	−0.04	3.335	3.335	0.00	3.807	3.807	0.01	4.550	4.548	0.04	5.723	5.718	0.08	7.563	7.562	0.02	10.449	10.447	0.02	14.958	14.955	0.02
17.5	1.358	1.358	−0.02	1.492	1.490	0.13	1.702	1.700	0.12	2.033	2.030	0.15	2.555	2.550	0.20	3.377	3.370	0.21	4.662	4.652	0.22	6.670	6.655	0.22
25.0	0.983	0.980	0.31	1.078	1.075	0.28	1.230	1.227	0.27	1.468	1.462	0.43	1.843	1.837	0.34	2.432	2.425	0.29	3.353	3.347	0.19	4.797	4.785	0.25

P (psig)	C8OH			C9OH			C10OH			C11OH			C12OH			C13OH			C14OH			C15OH		
	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)
1-Alcohols																								
$T = 100\,°C$																								
7.5	6.013	5.992	0.35	9.407	9.375	0.34	15.845	15.812	0.21	27.986	27.967	0.07	50.867	50.877	−0.02									
17.5	2.683	2.673	0.36	4.197	4.183	0.33	7.063	7.033	0.42	12.476	12.432	0.36	22.665	22.617	0.21									
25.0	1.927	1.922	0.28	3.010	3.007	0.11	5.063	5.047	0.32	8.940	8.915	0.28	16.253	16.218	0.21									
$T = 130\,°C$																								
7.5	3.818	3.823	−0.14	4.848	4.850	−0.04	6.618	6.623	−0.08	9.654	9.658	−0.04	14.836	14.850	−0.09	23.673	23.678	−0.02	38.701	38.747	−0.12			
17.5	1.702	1.705	−0.18	2.157	2.162	−0.22	2.938	2.947	−0.29	4.282	4.295	−0.30	6.580	6.602	−0.33	10.509	10.528	−0.18	17.190	17.225	−0.20			
25.0	1.228	1.227	0.11	1.558	1.555	0.19	2.125	2.118	0.31	3.095	3.085	0.32	4.757	4.740	0.36	7.585	7.560	0.33	12.396	12.368	0.22			
$T = 160\,°C$																								
7.5	3.177	3.177	0.01	3.563	3.563	−0.01	4.175	4.173	0.04	5.143	5.138	0.09	6.677	6.672	0.08	9.088	9.087	0.01	12.873	12.855	0.14	18.795	18.790	0.03
17.5	1.420	1.420	0.00	1.593	1.592	0.08	1.867	1.863	0.20	2.298	2.293	0.20	2.980	2.973	0.22	4.052	4.045	0.17	5.735	5.723	0.20	8.372	8.355	0.20
25.0	1.028	1.025	0.29	1.152	1.148	0.32	1.348	1.343	0.35	1.658	1.652	0.38	2.147	2.140	0.33	2.917	2.908	0.30	4.127	4.117	0.25	6.022	6.005	0.28

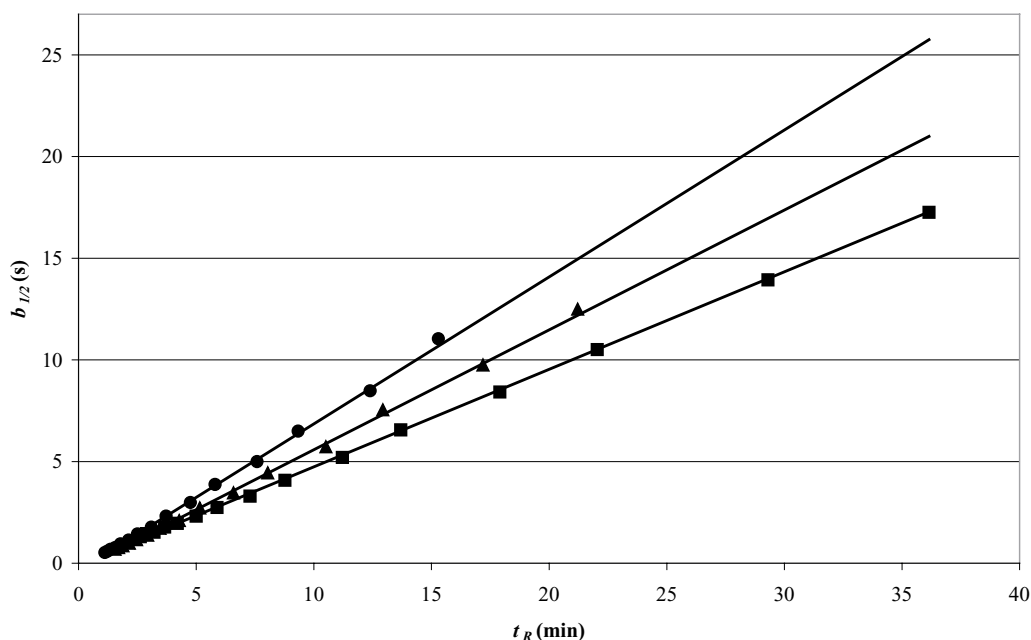S. Vezzani et al. / J. Chromatogr. A 1026 (2004) 201–221

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Fig. 1. Comparison between the experimental, $b_{1/2}$ exp, and calculated, $b_{1/2}$ cal, values of peak width at half height, as a function of t_R on column DB-1 (30 m × 0.32 mm i.d., 0.25 μm phase thickness) at 130 °C. Black squares, experimental values at 10 psig; black triangles, experimental values at 17.5 psig; black circles, experimental values at 25 psig; full lines, calculated peak width, $b_{1/2}$ cal.

determined with the auxiliary calculation program at the three temperatures and the three pressures tested, and the values of $b_{1/2}$ cal, predicted with the calculation method described above in Section 2. The relative percent errors between experimental and calculated values, E_{rel} (%) $= 100(b_{1/2}$ cal $- b_{1/2}$ exp$)/b_{1/2}$ exp, are also reported.

Tables 4–6 show the comparison between the values of the t_R exp and the values of t_R cal and relative percent errors between experimental and calculated values. The compounds belonging to the n-alkanes and 1-alcohols homologous series, used in order to evaluate the behaviour of the three columns, have different chain length ranges because of the
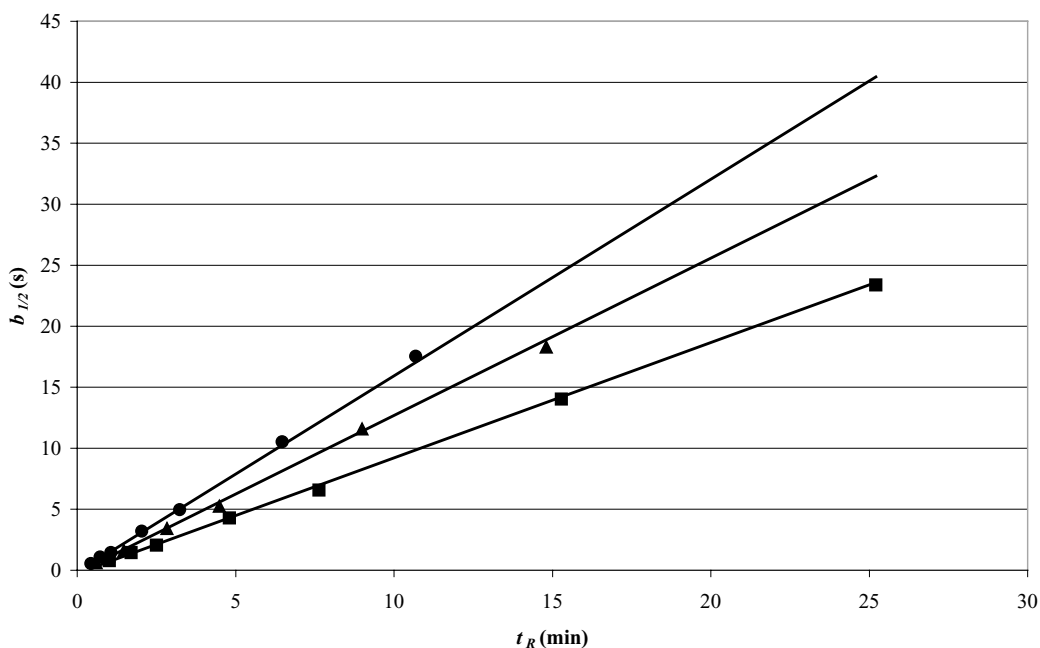

Fig. 2. Comparison between the experimental, $b_{1/2}$ exp, and calculated, $b_{1/2}$ cal, values of peak width at half height, as a function of t_R on column DB-17 (15 m × 0.32 mm i.d., 0.25 μm phase thickness) at 130 °C. Black squares, experimental values at 10 psig; black triangles, experimental values at 17.5 psig; black circles, experimental values at 25 psig; full lines, calculated peak width, $b_{1/2}$ cal.

Table 5
Column DB-17 (15 m × 0.32 mm i.d., 0.25 μm phase thickness). Comparison between the experimental values of the retention times (min) of some linear alkanes and 1-alcohols, t_R exp, and those calculated with the described method, t_R cal. The relative percent errors between experimental and calculated values, E_{rel} (%) = 100(t_R exp − t_R cal)/t_R exp, is also shown

P (psig)	C13			C15			C17			C20		
	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)
n-Alkanes												
T = 100 °C												
7.5	2.265	2.247	0.81	6.417	6.362	0.86	20.351	20.203	0.73			
17.5	1.003	1.003	−0.03	2.830	2.837	−0.24	8.987	9.002	−0.16			
25.0	0.722	0.723	0.18	2.038	2.042	−0.18	6.470	6.473	−0.05			
T = 130 °C												
7.5	1.132	1.133	0.12	2.155	2.157	−0.08	5.028	5.035	−0.14	21.239	21.298	−0.28
17.5	0.507	0.507	0.07	0.962	0.963	−0.14	2.235	2.240	−0.22	9.447	9.457	−0.10
25.0	0.363	0.365	0.55	0.693	0.693	−0.05	1.610	1.610	0.00	6.767	6.785	−0.27
T = 160 °C												
7.5				1.167	1.158	0.74	1.942	1.933	0.45	5.517	5.515	0.04
17.5				0.515	0.517	−0.32	0.860	0.860	0.00	2.455	2.455	0.00
25.0				0.372	0.372	0.09	0.620	0.620	0.00	1.765	1.765	0.00

P (psig)	C8OH			C10OH			C12OH			C14OH			C15OH		
	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)
1-Alcohols															
T = 100 °C															
7.5	1.348	1.338	0.72	3.338	3.308	0.89	10.192	10.135	0.56	33.535	33.332	0.61			
17.5	0.597	0.598	−0.22	1.473	1.477	−0.25	4.488	4.515	−0.60	14.803	14.852	0.33			
25.0	0.432	0.432	0.08	1.063	1.063	−0.03	3.233	3.247	−0.42	10.682	10.680	0.02			
T = 130 °C															
7.5				1.428	1.428	−0.02	3.022	3.025	−0.10	7.543	7.552	−0.11	12.281	12.308	−0.22
17.5				0.638	0.638	−0.05	1.347	1.348	−0.10	3.353	3.358	−0.16	5.463	5.468	−0.10
25.0				0.460	0.460	0.00	0.970	0.970	0.00	2.412	2.412	0.01	3.923	3.925	−0.05
T = 160 °C															
7.5				0.952	0.943	0.91	1.430	1.422	0.58	2.593	2.587	0.24	3.695	3.690	0.14
17.5				0.418	0.420	−0.48	0.632	0.632	0.05	1.150	1.152	−0.15	1.640	1.642	−0.10
25.0				0.302	0.302	0.11	0.455	0.455	0.00	0.828	0.828	−0.04	1.182	1.182	0.03

different polarity of the columns: owing to the increased retention of 1-alcohols with respect of *n*-alkanes on the polar columns, the use of the same reference mixture on all the columns and at all pressures and temperatures would result in too great retention times of some compounds. Both $b_{1/2}$ and t_R calculated values well fit the experimental data.

Fig. 1 shows the behaviour of the $b_{1/2}$ values of *n*-alkanes and 1-alcohols as a function of the retention time at 130 °C and at three pressure values (10–17.5–25 psig) on the non-polar column DB-1. The points indicated with different symbols are the measured values of the $b_{1/2}$ exp, whereas the lines show the trend of the $b_{1/2}$ cal. The experimental data lie on the corresponding calculated line. This fact confirms that the precision of the calculation method is satisfactory and the linear behaviour of the plots shows that at half height the shape of the peaks of both polar and not polar compounds is very close to that predicted by a Gaussian distribution curve. The same behaviour is shown for DB-17 and Supelcowax-10 columns in the plots of Figs. 2 and 3, respectively. Table 7 shows the slope and intercept values of Eq. (8) obtained at different inlet pressures on the three

columns. In this table the carrier flow rate in the various condition is also reported. By using Eq. (8) with the data of Table 7 one can obtain the plot at the highest and at the lowest pressure used with the Supelcowax-10 and DB-1 columns and calculate the $b_{1/2}$ values in this pressure range as shown in Fig. 4 at 130 °C. Within the pressure range considered in this work, the $b_{1/2}$ values at any temperature depend linearly on t_R (see Eq. (8)) and its change with pressure depends on the used columns. This is shown in Fig. 4 by the distance between the lines corresponding to the highest (25 psig) and the lowest (7.5 psig) inlet pressure, which is greater for Supelcowax-10. The change of pressure can be used in order to evaluate and optimise the separation of a given pair of closely eluting peaks, as it influences the retention, more on the polar than on the non-polar column, where the elution time is mainly dependent on dispersion forces and on the molecular mass and vapour pressure of the compounds.

With the data measured and calculated as shown above, it is possible to calculate the resolution between any given pair of adjacent peaks. The measurement of the resolution at
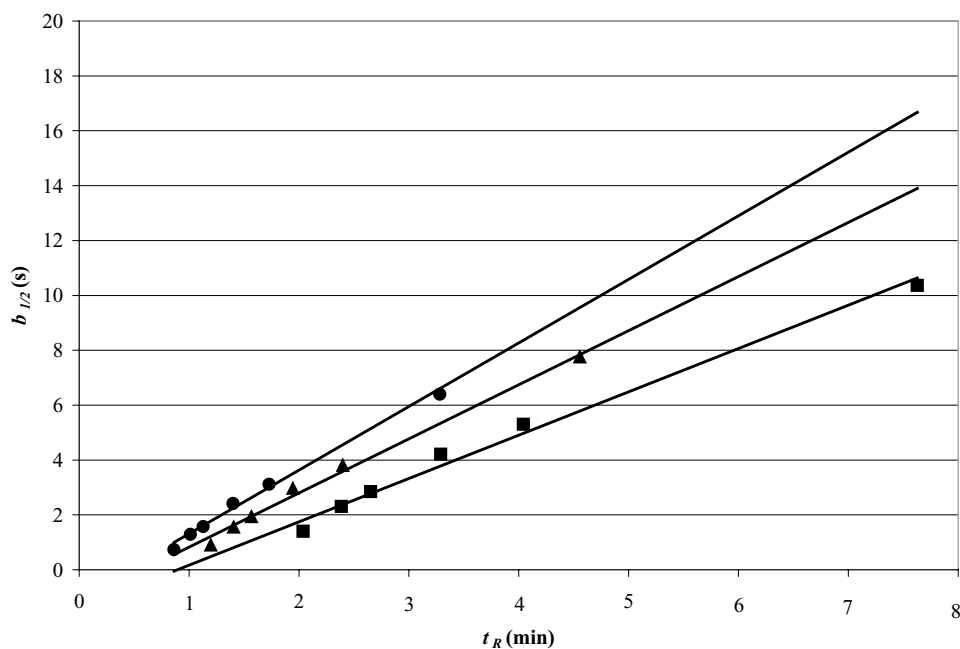
Fig. 3. Comparison between the experimental, $b_{1/2}$ exp, and calculated, $b_{1/2}$ cal, values of peak width at half height, as a function of t_R on column Supelcowax-10 (30 m × 0.32 mm i.d., 0.25 μm phase thickness) at 130 °C. Black squares, experimental values at 10 psig; black triangles, experimental values at 17.5 psig; black circles, experimental values at 25 psig; full lines, calculated peak width, $b_{1/2}$ cal.

the baseline is difficult, as discussed previously in Section 2, as the manual choice of the peak start and of the peak end carried out by the operator on the chromatogram displayed on the computer screen depends on personal interpretation and is influenced by the baseline noise value and by the

scale expansion used for the plot. Therefore, as the choice of the width at the baseline is subjected to errors, the resolution of two adjacent peaks can be measured at a suitable fraction $(1/x)$th of the peak height. It can be accepted that if two peaks are resolved at $(1/10)$th of their height the

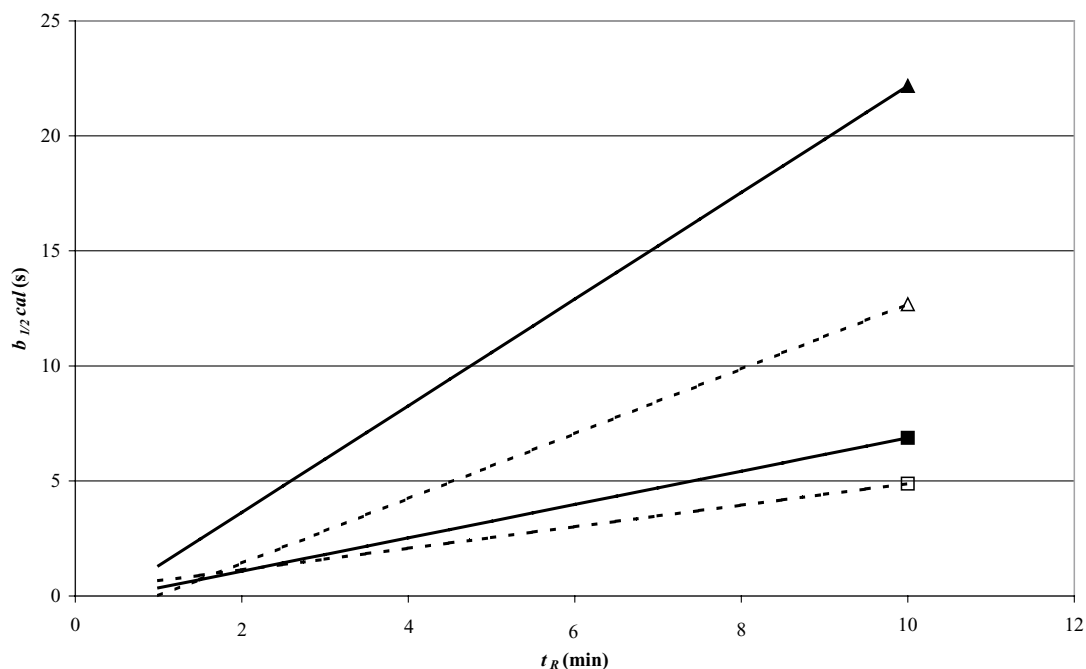
Fig. 4. Behaviour of the calculated peak width values, $b_{1/2}$ cal, as a function of the retention time, t_R, within the tested inlet pressure range at 130 °C. Black symbols and full lines, highest pressure (25 psig); white symbols and dashed lines, lowest pressure (7.5 psig). Squares, DB-1 column; triangles, Supelcowax-10 column.

Table 6
Column Supelcowax-10 (30 m × 0.32 mm i.d., 0.25 μm phase thickness). Comparison between the experimental values of the retention times (min) of some linear alkanes and 1-alcohols, t_R exp, and those calculated with the described method, t_R cal. The relative percent errors between experimental and calculated values, E_{rel} (%) = $100(t_R$ exp − t_R cal)/t_R exp, is also shown

P (psig)	C11			C13			C15		
	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)
n-Alkanes									
$T = 100\,°C$									
7.5	2.890	2.895	−0.17	4.165	4.185	−0.48	8.112	8.172	−0.74
17.5	1.293	1.292	0.08	1.877	1.873	0.21	3.873	3.687	0.16
25.0	0.928	0.928	0.00	1.347	1.350	−0.22	2.642	2.647	−0.19
$T = 130\,°C$									
7.5	2.890	2.695	−0.19	3.150	3.155	−0.16	4.343	4.352	−0.21
17.5	1.197	1.200	−0.25	1.405	1.405	0.00	1.945	1.942	0.15
25.0	0.863	0.863	0.00	1.012	1.012	0.00	1.400	1.398	0.14
$T = 160\,°C$									
7.5	2.672	2.673	−0.04	2.867	2.868	−0.03	3.308	3.313	−0.15
17.5	1.193	1.193	0.00	1.280	1.280	0.00	1.478	1.480	−0.14
25.0	0.865	0.860	0.58	0.928	0.923	0.54	1.070	1.067	0.28
	C6OH			C8OH			C10OH		
	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)	t_R exp	t_R cal	E_{rel} (%)
1-Alcohols									
$T = 100\,°C$									
7.5	5.235	5.258	−0.44	11.579	11.640	−0.53	30.983	31.002	−0.06
17.5	2.365	2.357	0.34	5.267	5.240	0.51	14.103	14.040	0.45
25.0	1.698	1.700	−0.12	3.787	3.792	−0.13	10.164	10.198	−0.33
$T = 130\,°C$									
7.5	3.512	3.515	−0.09	5.360	5.360	0.00	10.135	10.133	0.02
17.5	1.567	1.565	0.13	2.398	2.392	0.25	4.555	4.538	0.37
25.0	1.128	1.127	0.09	1.728	1.728	0.00	3.282	3.275	0.21
$T = 160\,°C$									
7.5	3.003	3.003	0.00	3.647	3.647	0.00	5.098	5.100	−0.04
17.5	1.340	1.342	−0.15	1.632	1.632	0.00	2.285	2.285	0.00
25.0	0.975	0.971	0.41	1.185	1.177	0.68	1.658	1.650	0.48

separation (R_{10}) is good enough to permit qualitative identification and a tolerable accuracy in the quantitative determination. It should be noted that the determination of the tailing factor of a peak is conventionally carried out at (1/10)th of the peak height. The choice of (1/10)th of the height offers a resolution between the peak areas of about 97%, greater than the 95% obtained by the 4σ resolution, which yields a separation at $1/e^2 = 1/7.4$ of the peak height. By using the auxiliary calculation method shown above the peak width at (1/10)th of the height, $b_{1/10}$, can be calculated and the ratio δ_{10} obtained with the following relationship:

$$b_{1/10} = \delta_{10}b_{1/2} \tag{13}$$

It has been found that the δ_{10} value is the same at different temperatures and carrier gas pressures and only depends on the used column (Tables 8–10); in this instance both the DB-1 and the Supelcowax-10 columns show a δ_{10} value very close to 2, whereas the DB-17 column shows a δ_{10} value of 1.9. It is possible to calculate the δ_x value at other and smaller fractions of the peak height. As an example, in Tables 8–10 the δ_{20} values are shown, i.e. the ratios between

the peak width at (1/20)th of the height and the $b_{1/2}$. With the columns used, the δ_{20} values are less reproducible than the δ_{10} ones, as shown by the standard deviation values reported in the legends of the figures, and depend on the compound: this is due to the different tailing of the *n*-alkanes and 1-alcohols peaks, correlated to the interaction with the siloxane and silanolic groups of the silica column wall. The choice of the δ_{10} values seems to be suitable in the majority of practical applications but, in some instances, other and more restrictive values can be selected if the δ_x value is the same for all the peaks of the analysed mixture. As an example, Table 11 shows the values of this parameter calculated for various kinds of compounds (alkanes, alkenes, chloroalkanes, alcohols, ketones) on a polar CP WAX 52CB column, different from those reported in Tables 8–10. Both the δ_{10} and the δ_{20} values of all the compounds are near constant, independent on the inlet pressure and temperature, with average values of 1.83 ± 0.04 and 2.11 ± 0.06, respectively, close to the corresponding values theoretically calculated for a peak with perfect Gaussian shape ($\delta_{10} = 1.823$ and $\delta_{20} = 2.079$). This favourable result means that

Table 7
Values of the slope, m, and intercept, q, of Eq. (4) at different pressure and temperature values on column DB-1 and Supelcowax-10 (30 m × 0.32 mm i.d., 0.25 µm phase thickness) and DB-17 (15 m × 0.32 mm i.d., 0.25 µm phase thickness). The values of the carrier gas flow rate, ϕ, at the various temperature and pressure values are also shown

P (psig)	$T = 100\,^\circ$C			$T = 130\,^\circ$C			$T = 160\,^\circ$C		
	ϕ (ml/min)	q	m	ϕ (ml/min)	q	m	ϕ (ml/min)	q	m
Column DB-1									
7.5	1.2	−0.107	0.475	1.0	0.195	0.469	0.9	0.306	0.464
10.0	1.7	−0.356	0.495	1.5	−0.066	0.480	1.3	0.059	0.472
12.5	2.2	−0.459	0.530	2.0	−0.198	0.509	1.7	−0.057	0.490
15.0	2.8	−0.511	0.573	2.5	−0.274	0.547	2.2	−0.135	0.515
17.5	3.7	−0.536	0.619	3.1	−0.315	0.588	2.7	−0.181	0.546
20.0	4.2	−0.547	0.667	3.7	−0.343	0.634	3.3	−0.212	0.581
22.5	5.0	−0.556	0.719	4.4	−0.360	0.679	3.9	−0.233	0.618
25.0	5.8	−0.558	0.770	5.1	−0.371	0.724	4.5	−0.246	0.655
Column Supelcowax-10									
7.5	1.2	0.426	0.318	1.0	−1.393	1.408	0.9	−1.614	2.638
10.0	1.7	0.364	0.428	1.5	−1.406	1.579	1.3	−1.680	2.493
12.5	2.2	0.216	0.561	2.0	−1.312	1.714	1.7	−1.723	2.327
15.0	2.8	0.168	1.677	2.5	−1.261	1.872	2.2	−1.889	2.238
17.5	3.7	0.045	1.800	3.1	−1.145	1.972	2.7	−2.047	2.096
20.0	4.2	0.005	1.921	3.7	−1.108	2.105	3.3	−2.177	1.933
22.5	5.0	0.064	2.024	4.4	−1.089	2.255	3.9	−2.409	1.785
25.0	5.8	0.090	2.125	5.1	−0.999	2.317	4.5	−2.956	1.685
Column DB-17									
7.5	2.4	−0.153	0.828	2.1	−0.237	0.802	1.9	−0.145	0.731
10.0	3.4	−0.151	0.946	3.0	−0.250	0.911	2.6	−0.140	0.830
12.5	4.5	−0.149	1.073	3.9	−0.253	1.023	3.5	−0.137	0.935
15.0	5.7	−0.143	1.173	5.0	−0.251	1.133	4.4	−0.129	1.042
17.5	7.0	−0.136	1.290	6.1	−0.250	1.251	5.4	−0.109	1.149
20.0	8.4	−0.133	1.398	7.4	−0.248	1.364	6.5	−0.092	1.253
22.5	9.9	−0.126	1.502	8.7	−0.249	1.474	7.7	−0.089	1.356
25.0	11.6	−0.120	1.611	10.1	−0.250	1.585	9.0	−0.085	1.463

the peaks of all the compounds eluted from this column are very symmetrical, resembling a Gaussian distribution curve for almost (19/20)th of their height, and therefore the resolution can be correctly calculated at a level of the peak height closer to the baseline. The values of δ_{20} measured on the DB-1, Supelcowax-10 and DB-17 columns scatter more than the δ_{10} ones, showing that the shape of the peaks eluted from these columns is less symmetrical and depends on the

Table 8
Values of the ratios, δ_{10} and δ_{20}, between the peak width at (1/10)th and (1/20)th of the peak height, $b_{1/10}$ and $b_{1/20}$, and the peak width at half height, $b_{1/2}$, of some n-alkanes and 1-alcohols on the DB-1 column at various inlet pressure and temperature

P (psig)	T (°C)	C10	C8OH	C11	C9OH	C12	C10OH	C13	C11OH	C14	C12OH	Average
δ_{10}												
7.5	100	2.02	1.92	2.03	1.98	2.09	1.94	2.09	2.08	2.15	2.17	2.05
	160	1.99	1.97	2.13	2.01	2.13	2.12	2.06	2.05	2.11	2.15	2.07
17.5	100	2.03	2.01	1.99	2.02	2.08	2.01	2.05	2.03	2.08	2.02	2.03
	160	1.95	2.05	2.02	2.05	2.12	2.08	2.11	2.05	1.98	2.07	2.05
25	100	2.07	1.96	1.99	2.03	2.03	2.04	2.04	2.04	2.04	2.06	2.03
	160	2.13	2.13	2.10	2.12	2.09	2.06	2.09	2.05	2.00	1.99	2.08
δ_{20}												
7.5	100	2.60	2.45	2.75	2.53	2.87	2.52	2.76	2.85	3.14	2.80	2.73
	160	2.30	2.20	2.42	2.83	2.44	2.76	2.25	2.76	2.45	2.93	2.53
17.5	100	2.38	2.27	2.37	2.23	2.22	2.31	2.57	2.53	2.59	2.36	2.38
	160	2.13	2.47	2.37	2.62	2.50	2.77	2.64	2.84	2.65	3.00	2.60
25	100	2.34	2.24	2.31	2.34	2.35	2.35	2.45	2.47	2.49	2.61	2.40
	160	2.66	2.64	2.91	2.70	2.70	2.81	2.91	2.77	2.82	2.70	2.76

Average of all the δ_{10} values = 2.05 ± 0.06; average of all the δ_{20} values = 2.57 ± 0.23.

Table 9
Values of the ratios, δ_{10} and δ_{20}, between the peak width at (1/10)th and (1/20)th of the peak height, $b_{1/10}$ and $b_{1/20}$, and the peak width at half height, $b_{1/2}$, of some n-alkanes and 1-alcohols on the DB-17 column at various inlet pressure and temperature

P (psig)	T (°C)	C8OH	C13	C10OH	C15	C12OH	C17	C14OH	C15OH	Average
δ_{10}										
7.5	100	2.04	1.89	1.95	1.72	1.91				1.90
	160	1.92	1.81	1.91	1.91	1.88	1.85	1.97	1.97	1.90
17.5	100	1.99	1.81	1.89	1.84	1.82	1.81	1.91	2.03	1.89
	160	1.89	1.86	1.83	1.89	1.88	1.86	1.92	1.90	1.88
25	100	1.91	1.90	1.89	1.80	1.82	1.89	1.88	1.92	1.88
	160	1.88	1.89	1.93	1.84	1.83	1.87	1.94	1.89	1.88
δ_{20}										
7.5	100	2.57	2.10	2.34	1.91	2.33				2.25
	160	2.29	2.04	2.16	2.24	2.25	2.07	2.43	2.47	2.24
17.5	100	2.34	2.06	2.18	2.10	2.07	1.99	2.22	2.53	2.19
	160	2.18	2.01	1.93	2.10	2.15	2.01	2.26	2.24	2.11
25	100	2.27	1.98	2.17	2.08	2.01	2.22	2.21	2.61	2.19
	160	2.13	2.11	2.10	2.10	2.14	2.01	2.33	2.17	2.14

Average of all the δ_{10} values = 1.89 ± 0.06; average of all the δ_{20} values = 2.18 ± 0.16.

compound; this difference is enhanced if the peak width is measured nearer to the baseline. If one requires a 6σ resolution, the δ value should be calculated at $1/e^{4.5}$ i.e. at (1/90)th of the peak height, where the baseline slope and noise make it impossible the correct determination of the peak width, also if the described auxiliary calculation program is used.

Measurements carried out on peaks of different compounds separated on other columns, have shown that in the majority of cases the δ_{10} values are constant and reproducible. Therefore, if the resolution at (1/10)th of the peak height is considered great enough in order to permit the identification of the compounds and a reasonably correct quantitative determination, the following equation can be used for the calculation of the R_{10} value:

$$R_{10} = \frac{2(t_{R,i+1} - t_{R,i})}{\delta_{10}(b_{1/2,i+1} + b_{1/2,i})} \tag{14}$$

An example of the application of the procedure is shown in Fig. 5. The pairs of peaks indicated with A, B and C show the separation of 1-butanol and 1-chloro-heptane at 100 °C and 30, 15 and 10 psig, respectively, on the CP WAX 52 CB column. The experimental $b_{1/2}$ and t_R values were measured by the data system, the accuracy of the values of $b_{1/2}$ enhanced and the $b_{1/10}$ values obtained with the auxiliary

Table 10
Values of the ratios, δ_{10} and δ_{20}, between the peak width at (1/10)th and (1/20)th of the peak height, $b_{1/10}$ and $b_{1/20}$, and the peak width at half height, $b_{1/2}$, of some n-alkanes and 1-alcohols on the Supelcowax-10 column at various inlet pressure and temperature

P (psig)	T (°C)	C11	C13	C6OH	C15	C8OH	C10OH	Average
δ_{10}								
7.5	100	2.03	1.97	2.10	1.90	1.97	2.00	2.00
	160	2.00	1.97	2.01	1.99	2.00	2.01	2.00
17.5	100	1.99	1.99	1.99	1.99	2.00	1.99	1.99
	160	2.08	2.03	2.01	1.99	2.02	2.01	2.02
25	100	1.99	2.02	2.00	2.02	2.03	1.98	2.01
	160	2.01	1.99	2.01	2.01	1.98	2.01	2.00
δ_{20}								
7.5	100	2.67	2.61	2.38	2.30	2.39	2.33	2.45
	160	2.36	2.33	2.26	2.29	2.34	2.24	2.30
17.5	100	2.63	2.37	2.50	2.23	2.26	2.30	2.38
	160	2.45	2.37	2.30	2.35	2.35	2.23	2.34
25	100	2.73	2.41	2.35	2.30	2.24	2.24	2.38
	160	2.47	2.09	2.16	2.11	2.37	2.38	2.26

Average of all the δ_{10} values = 2.00 ± 0.03; average of all the δ_{20} values = 2.35 ± 0.14.

Table 11
Values of the ratio, δ_{10}, between the peak width at (1/10)th of the peak height, $b_{1/10}$, and the peak width at half height, $b_{1/2}$, of different compounds on the CP WAX 52CB column at various inlet pressure and temperature

P (psig)	T (°C)	1-Nonene	1-Decene	1-Butanol	1-Chloroheptane	Dodecane	1-Chlorobenzene	2-Nonanone	1-Chlorodecane	2-Decanone	Hexadecane	1-Nonanol	Heptadecane	Average
δ_{10}														
10	100	1.90	1.82	1.95	1.84	1.91	1.89	1.84	1.82	1.83	1.82	1.83	1.82	1.86
	140	1.77	1.83	1.84	1.77	1.86	1.77	1.84	1.81	1.86	1.87	1.87	1.83	1.83
15	100	1.83	1.86	1.83	1.89	1.87	1.80	1.82	1.83	1.83	1.83	1.87	1.81	1.84
	140	1.80	1.79	1.81	1.77	1.83	1.86	1.88	1.87	1.83	1.84	1.81	1.80	1.82
20	100		1.86	1.86	1.78	1.83	1.89	1.83	1.84	1.83	1.83	1.81	1.80	1.83
	140							1.75	1.79	1.85	1.78	1.87	1.83	1.81
δ_{20}														
10	100	2.12	2.10	2.38	2.09	2.13	2.10	2.10	2.08	2.10	2.09	2.10	2.07	2.12
	140	2.03	2.17	2.18	2.03	2.02	2.15	2.08	2.11	2.16	2.15	2.17	2.10	2.11
15	100	2.04	2.20	2.06	2.16	2.17	2.06	2.08	2.10	2.09	2.09	2.13	2.08	2.11
	140	1.99	2.01	2.04	2.05	2.06	2.17	2.17	2.13	2.12	2.10	2.14	2.07	2.09
20	100		2.18	2.19	2.08	2.13	2.19	2.08	2.08	2.10	2.10	2.12	2.08	2.12
	140							2.07	2.02	2.17	2.06	2.18	2.11	2.10

Average of all the δ_{10} values $= 1.83 \pm 0.04$; average of all the δ_{20} values $= 2.11 \pm 0.06$.

Table 12
Comparison between the values of the experimental resolution, R_{10} exp, of all the pair of consecutive peak eluted on column DB-1 and the R_{10} cal and the R_{10} int obtained with the Eq. (14) by using the δ_{10} values of each column and the $b_{1/2}$ and t_R values obtained in different ways (see text)

T (°C)	P (psig)	C9OH–C11			C12–C9OH			C10OH–C12			C13–C10OH			C11OH–C13			C14–C11OH			C12OH–C14		
		R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int
100	7.5	15.21	15.31	15.59	14.22	14.23	14.60	17.90	17.98	18.02	15.45	15.59	15.63	19.75	20.03	19.64	16.06	16.37	16.17	20.54	20.82	20.64
	10.0	15.99	16.06	16.44	14.66	14.74	15.02	18.39	18.40	18.26	15.65	15.71	15.62	19.94	19.91	19.43	16.00	16.09	15.88	20.29	20.40	20.14
	12.5	16.13	15.98	16.39	14.64	14.52	14.70	17.88	17.95	17.69	15.25	15.16	15.00	18.93	19.03	18.52	15.25	15.26	15.05	19.49	19.32	19.02
	15.0	15.49	15.49	15.90	14.13	13.94	14.03	17.28	17.13	16.80	14.41	14.34	14.14	17.98	17.86	17.37	14.30	14.26	14.07	18.13	18.02	17.72
	17.5	14.65	14.82	15.22	13.34	13.25	13.27	16.17	16.18	15.81	13.51	13.48	13.26	16.55	16.68	16.22	13.22	13.28	13.12	16.73	16.78	16.49
	20.0	14.01	14.07	14.44	12.69	12.53	12.51	15.19	15.23	14.85	12.71	12.63	12.41	15.46	15.57	15.15	12.43	12.38	12.23	15.70	15.63	15.35
	22.5	13.05	13.29	13.64	11.82	11.77	11.72	14.16	14.28	13.90	11.68	11.83	11.59	14.54	14.51	14.12	11.50	11.52	11.39	14.52	14.54	14.28
	25.0	12.51	12.59	12.89	11.12	11.11	11.01	13.47	13.44	13.05	11.13	11.11	10.87	13.63	13.59	13.22	10.71	10.79	10.66	13.47	13.61	13.36
160	7.5	3.38	3.38	3.43	3.37	3.36	3.46	4.74	4.73	4.87	4.44	4.44	4.61	6.39	6.37	6.61	5.73	5.70	5.87	8.40	8.30	8.57
	10.0	3.85	3.86	3.91	3.78	3.81	3.88	5.36	5.39	5.46	4.95	5.00	5.07	7.13	7.20	7.29	6.24	6.32	6.36	9.10	9.17	9.23
	12.5	4.06	4.12	4.18	4.09	4.07	4.13	5.72	5.73	5.77	5.33	5.32	5.34	7.59	7.55	7.58	6.54	6.61	6.61	9.49	9.50	9.45
	15.0	4.21	4.26	4.37	4.27	4.26	4.34	5.91	5.93	5.97	5.44	5.50	5.49	7.77	7.75	7.73	6.69	6.72	6.70	9.68	9.60	9.49
	17.5	4.32	4.35	4.51	4.38	4.33	4.42	6.09	6.01	6.04	5.55	5.57	5.53	7.83	7.78	7.71	6.66	6.63	6.58	9.55	9.50	9.34
	20.0	4.36	4.37	4.55	4.30	4.30	4.39	6.03	5.95	5.98	5.49	5.52	5.46	7.72	7.66	7.57	6.53	6.50	6.44	9.35	9.27	9.08
	22.5	4.25	4.29	4.52	4.25	4.29	4.33	5.91	5.85	5.87	5.34	5.43	5.35	7.51	7.50	7.39	6.24	6.32	6.25	8.88	8.97	8.76
	25.0	4.27	4.24	4.45	4.19	4.22	4.31	5.76	5.73	5.73	5.27	5.25	5.15	7.29	7.33	7.19	6.07	6.12	6.04	8.58	8.63	8.40

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Table 13

Comparison between the values of the experimental resolution, R_{10} exp, of all the pair of consecutive peak eluted on column DB-17 and the R_{10} cal and the R_{10} int obtained with the Eq. (14) by using the δ_{10} values of each column and the $b_{1/2}$ and t_R values obtained in different ways (see text)

| T (°C)	P (psig)	Pair of compounds																				
		C8OH–C13			C10OH–C13			C15–C10OH			C12OH–C15			C17–C12OH			C14OH–C17			C15OH–C14OH		
		R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int
100	7.5	21.66	21.68	22.08	16.26	16.31	16.07	25.83	25.93	25.51	18.20	18.54	18.08	25.99	26.22	25.87	18.55	18.91	18.98			
	10.0	19.53	19.23	19.68	14.54	14.54	14.29	23.11	22.93	22.49	16.50	16.40	15.88	23.60	23.06	22.70	16.85	16.64	16.63			
	12.5	17.52	17.45	17.48	13.14	13.20	12.67	20.70	20.75	19.88	14.77	14.85	14.02	21.03	20.80	20.03	15.12	15.04	14.68			
	15.0	15.78	15.64	16.23	11.79	11.76	11.68	18.38	18.49	18.27	13.26	13.23	12.86	18.55	18.49	18.35	13.57	13.38	13.44			
	17.5	14.33	14.29	14.74	10.71	10.75	10.63	17.13	16.88	16.63	12.13	12.08	11.70	16.96	16.86	16.69	12.35	12.21	12.22			
	20.0	13.16	13.14	13.60	9.85	9.91	9.84	15.55	15.53	15.36	11.05	11.11	10.79	15.61	15.49	15.41	11.06	11.23	11.28			
	22.5	12.21	12.27	12.73	9.18	9.19	9.17	14.47	14.40	14.31	10.18	10.31	10.05	14.35	14.38	14.35	10.20	10.42	10.50			
	25.0	11.30	11.45	11.85	8.58	8.57	8.56	13.33	13.44	13.37	9.31	9.61	9.37	13.27	13.39	13.39	9.53	9.73	9.79			
160	7.5							10.85	10.74	11.10	10.64	10.73	10.70	15.37	15.38	15.26	14.20	14.13	13.92	16.56	16.54	16.43
	10.0							9.84	9.62	10.03	9.70	9.52	9.48	13.87	13.68	13.54	12.75	12.63	12.35	14.87	14.90	14.53
	12.5							8.90	8.59	9.07	8.81	8.58	8.63	12.34	12.23	12.18	11.34	11.27	11.04	13.40	13.36	12.94
	15.0							7.85	7.71	8.09	7.83	7.69	7.79	11.07	11.02	11.03	10.20	10.18	9.98	12.17	12.11	11.67
	17.5							7.16	7.15	7.39	7.07	6.89	6.98	10.11	10.04	10.07	9.24	9.27	9.09	11.17	11.05	10.60
	20.0							6.41	6.56	6.68	6.36	6.35	6.48	9.15	9.24	9.31	8.46	8.50	8.36	10.18	10.20	9.77
	22.5							6.00	6.11	6.22	5.87	5.90	6.04	8.41	8.49	8.58	7.73	7.90	7.78	9.34	9.44	9.03
	25.0							5.58	5.74	5.81	5.35	5.49	5.63	7.78	7.98	8.04	7.13	7.28	7.15	8.73	8.82	8.40
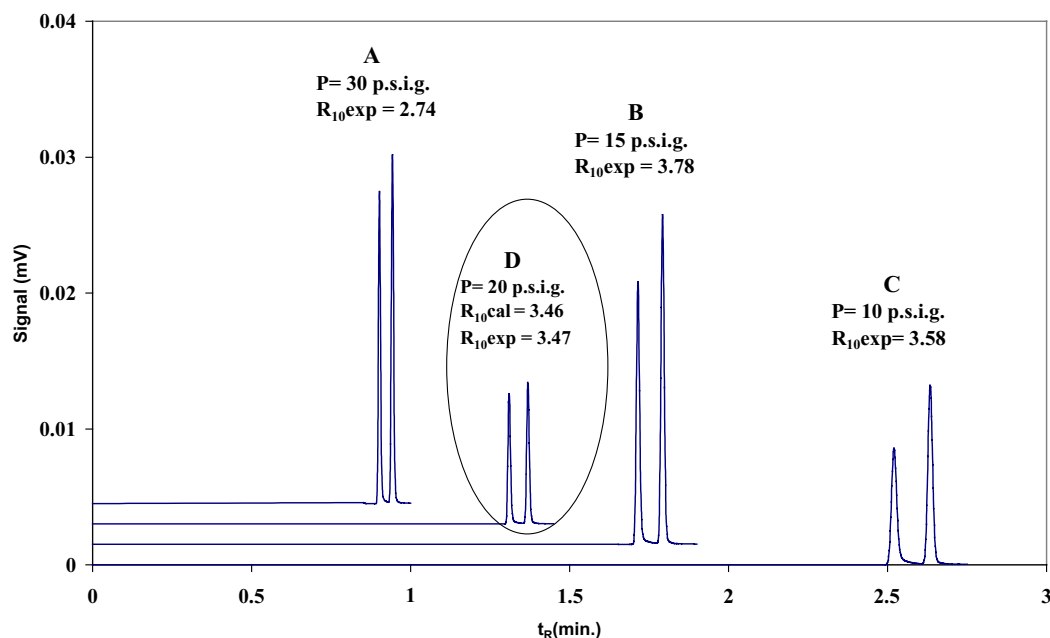
Fig. 5. Chromatogram of two closely eluting peaks (1-butanol and 1-chloro-heptane) on the CPWAX 52CB column (30 m × 0.32 mm i.d., 0.25 μm phase thickness) at different pressures: A, 30 psig; B, 15 psig; C, 10 psig; and D, 20 psig. Temperature 100 °C. The resolution of chromatogram D was predicted (R_{10} cal = 3.46) by using the data measured in runs A, B and C and checked experimentally (R_{10} exp = 3.47).

program shown above. The application of Eqs. (13) and (14) yields the δ_{10} and the R_{10}. The $b_{1/2}$ and t_R values were then calculated at another inlet pressure (20 psig). By using the same δ_{10} value used above (1.83), which is a constant for the given column, the R_{10} cal at 100 °C and 20 psig was obtained (3.46). The analysis carried out in these conditions (pair of peaks indicated with D in Fig. 5) yield an experimental value of R_{10} exp equal to 3.47, very close to the calculated one.

The calculation was repeated for the other columns and Tables 12–14 show at various pressure and at the lowest and the highest temperature of the investigated range the resolution of all the pair of consecutively eluted peaks at (1/10)th of the peak height calculated with the Eq. (14) by using the δ_{10} values of each column (Eq. (13) and Tables 8–10) and the $b_{1/2}$ and t_R values obtained in different ways.
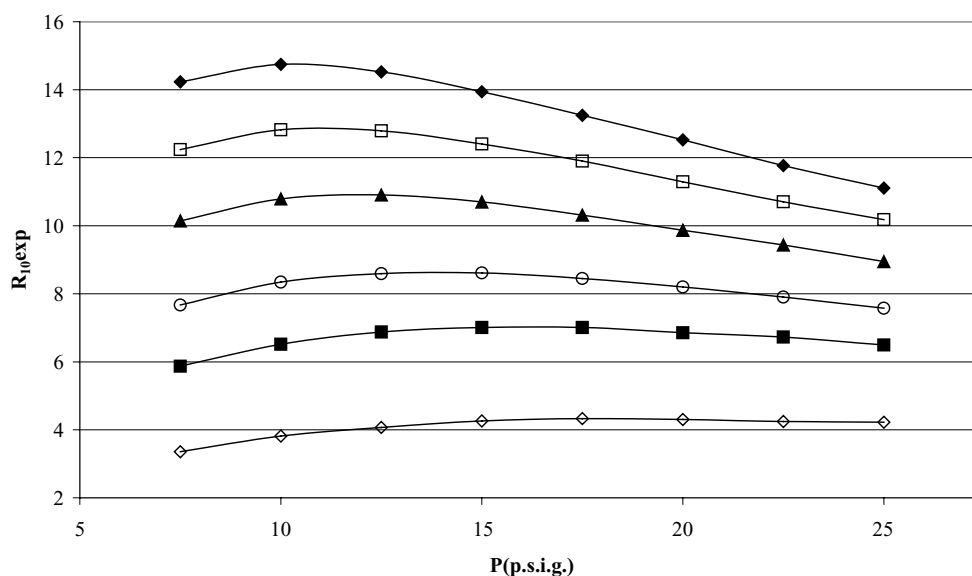
Fig. 6. Example of the behaviour of the resolution of two closely eluting peaks (C12 and C9OH) measured on the DB-1 column as a function of inlet pressure at different temperatures. Black rhombs, 100 °C; white squares, 110 °C; black triangles, 120 °C; white circles, 130 °C; black squares, 140 °C; white rhombs, 160 °C.

Table 14

Comparison between the values of the experimental resolution, R_{10} exp, of all the pair of consecutive peak eluted on column Supelcowax-10 and the R_{10} cal and R_{10} int obtained with the Eq. (14) by using the δ_{10} values of each column and the $b_{1/2}$ and t_R values obtained in different ways (see text)

T (°C)	P (psig)	Pair of compounds											
		C6OH–C13			C15–C6OH			C8OH–C15			C10OH–C8OH		
		R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int	R_{10} exp	R_{10} cal	R_{10} int
100	7.5	4.72	4.67	4.84	8.81	8.81	9.42	7.35	7.28	7.72	20.26	20.21	20.36
	10.0	4.40	4.45	4.46	8.13	8.22	8.69	6.69	6.71	7.13	18.65	18.57	18.81
	12.5	4.12	4.19	4.18	7.58	7.65	8.08	6.16	6.21	6.61	17.14	17.15	17.32
	15.0	3.91	3.95	3.92	7.05	7.14	7.55	5.73	5.78	6.19	16.00	15.97	16.16
	17.5	3.76	3.74	3.76	6.71	6.73	7.19	5.52	5.44	5.86	15.03	15.01	15.18
	20.0	3.60	3.54	3.56	6.38	6.37	6.79	5.16	5.15	5.52	14.10	14.20	14.27
	22.5	3.46	3.39	3.34	6.16	6.06	6.36	4.97	4.91	5.22	13.45	13.52	13.51
	25.0	3.35	3.25	3.15	5.88	5.80	6.03	4.75	4.70	4.96	12.88	12.93	12.85
160	7.5	2.03	2.00	2.03	3.74	3.78	3.93	3.37	3.31	3.44	9.81	9.84	9.88
	10.0	1.95	2.01	1.99	3.60	3.66	3.76	3.21	3.19	3.31	9.38	9.39	9.44
	12.5	1.90	1.93	1.92	3.46	3.48	3.61	3.11	3.05	3.18	8.87	8.85	8.91
	15.0	1.89	1.85	1.87	3.48	3.33	3.51	2.92	2.86	3.03	8.39	8.33	8.41
	17.5	1.75	1.79	1.77	3.17	3.15	3.27	2.79	2.73	2.85	7.85	7.87	7.86
	20.0	1.75	1.72	1.70	2.98	2.98	3.10	2.64	2.58	2.72	7.57	7.47	7.54
	22.5	1.55	1.59	1.54	2.92	2.90	3.00	2.45	2.46	2.57	7.09	7.12	7.10
	25.0	1.63	1.67	1.62	2.54	2.62	2.68	2.40	2.37	2.46	6.66	6.82	6.73

R_{10} exp was calculated by using the experimental values of $b_{1/2}$ and t_R, measured at any pressure and temperature listed in the table.

R_{10} cal was calculated by using the $b_{1/2}$ and t_R values obtained from the plate height values and from the total number of plates in the column calculated by starting from three pressure and temperature values only, as explained at the beginning of Section 2 and in the comments to Eqs. (1)–(3). These values differ from the experimental R_{10} exp less than 2% for DB-1 column, less than 3% for the DB-17 and the Supelcowax-10 columns.

R_{10} int was calculated by using the $b_{1/2}$ and t_R values obtained by interpolation of the straight lines of Eq. (8) whose intercepts, q, and slopes, m, are listed in Table 7.
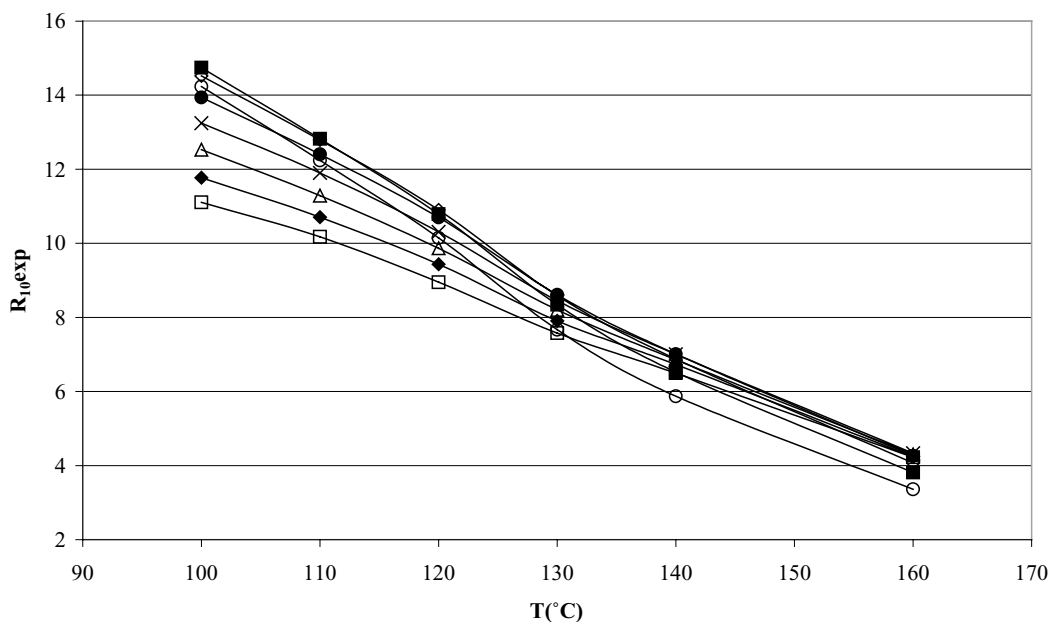

Fig. 7. Example of the behaviour of the resolution of two closely eluting peaks (C12 and C9OH) measured on the DB-1 column as a function of temperature at different pressure values. White squares, 25 psig; black rhombs, 22.5 psig; white triangles, 20 psig; cross, 17.5 psig; black circles, 15 psig; white rhombs, 12.5 psig; black squares, 10 psig; white circles, 7.5 psig.
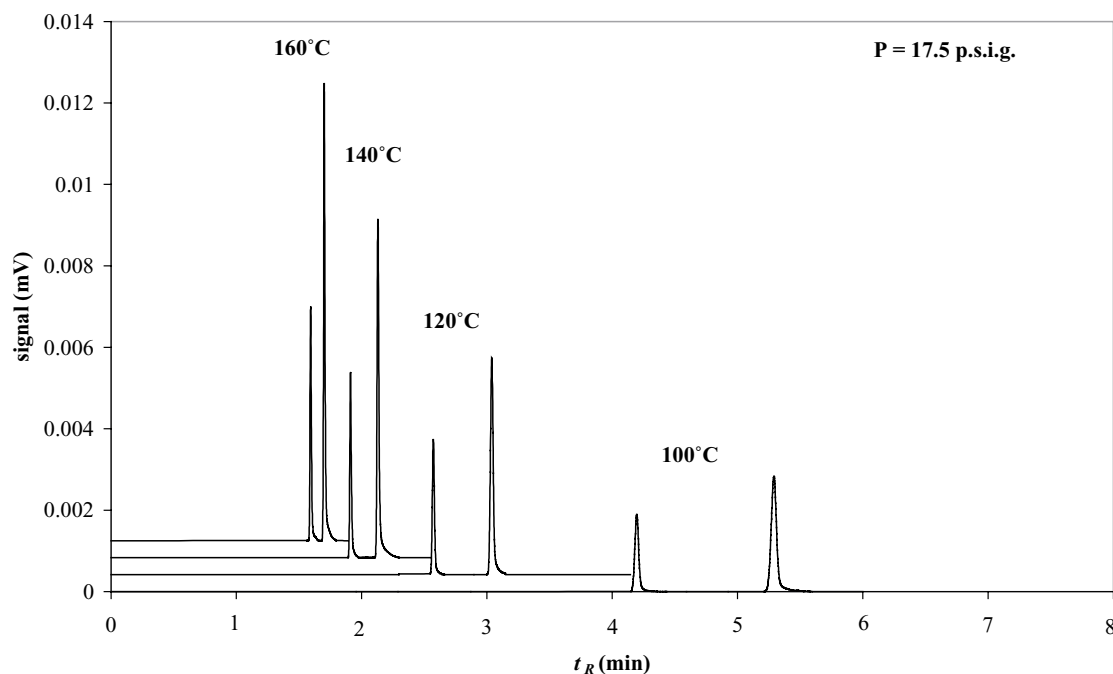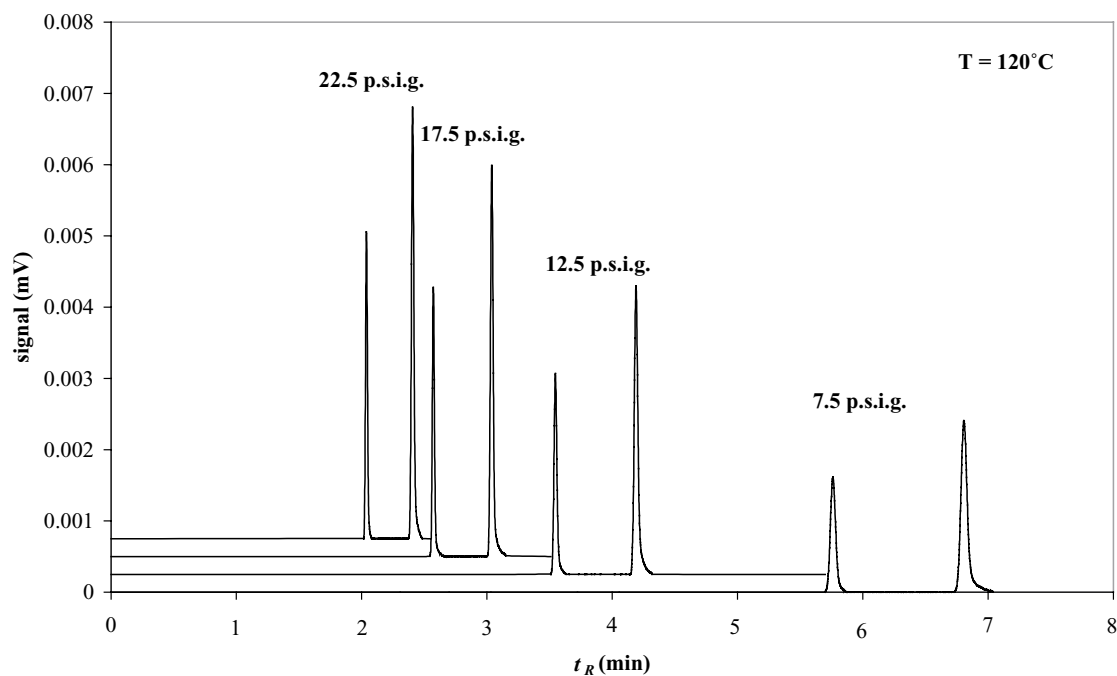
Fig. 8. Chromatogram of two closely eluting peaks (C12 and C9OH) on the DB-1 column (30 m × 0.32 mm i.d., 0.25 μm phase thickness) at different temperatures. Inlet pressure 17.5 psig.

These values differ from the experimental R_{10} exp less than 5% for the DB-1 and DB-17 columns and less than 6% for the Supelcowax-10 column.

The method used for the calculation of R_{10} int yields less accurate results than that used for the determination of R_{10} cal; however, it must be taken into account that the

determination of R_{10} cal requires that all the compounds of the analysed mixture are injected at three different temperatures and at three pressures (if the effects of the two analytical parameters have to be considered in the prediction of the most favourable conditions which offer suitable resolution and short analysis time). On the

Fig. 9. Chromatogram of two closely eluting peaks (C12 and C9OH) on the DB-1 column (30 m × 0.32 mm i.d., 0.25 μm phase thickness) at different pressure values. Temperature 120 °C.

contrary, the method used for the calculation of R_{10} int permits to predict the peak width and calculate the resolution of compounds not included in the three previous isobaric runs if their t_R is known or can be deducted from literature value or by interpolation of homologous series retention data, owing to the knowledge of the linear correlation between $b_{1/2}$ and t_R and of the δ_{10} value of the used column.

The great number of experimental data obtained at various pressure and temperature values in order to verify the validity of the proposed method for the calculation and prediction of the resolution, also permitted to evaluate the different influence of the change of pressure and of temperature on the resolution. With the same decrease of retention time, the resolution decreases much more with increasing temperature than with increasing pressure, as shown by Fig. 6 where the change of the experimental R_{10} exp values as a function of pressure at different temperatures is shown to be much greater than the change as a function of temperature at different pressures (Fig. 7). The plots of Fig. 6 on the DB-1 column as a function of pressure at various temperatures show a maximum. As the resolution is proportional to the total number of plates of the column and the increase of pressure corresponds to an increase of the carrier gas flow rate, Fig. 6 can be correlated with the more familiar representation of the Van Deemter Jones equation. The maximum at various temperatures is shifted toward higher pressure values, according with the shift of the optimum value of the plate height towards high flow rates as the temperature increases.

An example of the different influence of pressure and temperature on the resolution is shown in Figs. 8 and 9 where the chromatograms of two closely eluting peaks (C12 and C9OH) on the DB-1 column are compared as a function of temperature at 17.5 psig (Fig. 8) and as a function of pressure at 120 °C (Fig. 9). The separation between the peaks in Fig. 9 is greater. This behaviour if confirmed by the plots of Fig. 10 where the resolution between the C15 and the C10OH, calculated with Eq. (14), is shown at three temperatures (100, 130, 160 °C) and at three pressures (7.5, 17.5 and 25 psig). In order to compare the behaviour in all the above listed conditions of the same two compounds belonging to the n-alkanes and 1-alcohols series, it was necessary to select peaks contained in all the chromatograms, notwithstanding the range of temperature and pressure and the different polarity of the columns caused a strong difference in the behaviour of the two series of compound. As a consequence, the resolution values between the above mentioned compounds shown in Fig. 10 are great, as their two peaks are not eluted closely in all conditions. Furthermore, as the peak indicated with "$i + 1$" in Eq. (14) is the n-alkane C15 for all the columns and conditions, negative values of R_{10} exp
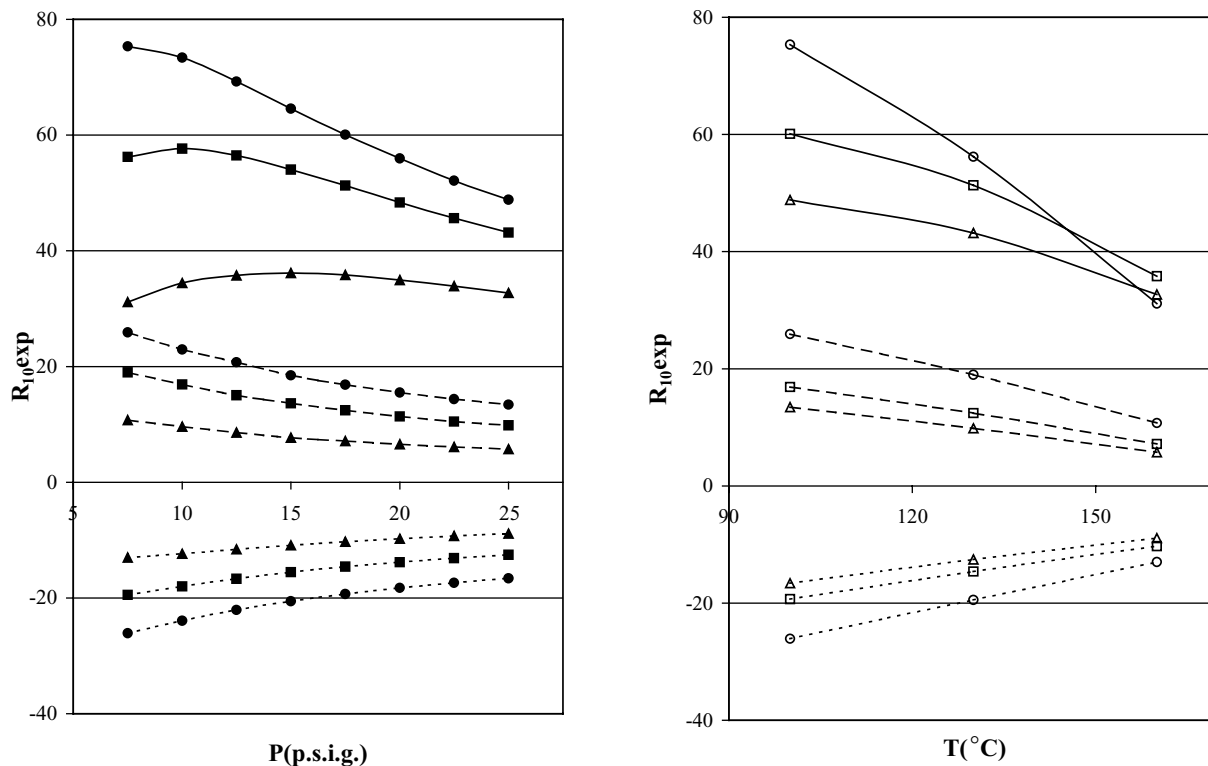

Fig. 10. Comparison of the resolution on DB-1 (full lines), DB-17 (dashed lines) and Supelcowax-10 (dotted lines) columns as a function of pressure at different temperatures (left) and as a function of temperature at different pressures (right). Black circles, 100 °C; black squares, 130 °C; black triangles, 160 °C; white circles, 7.5 psig; white squares, 17.5 psig; white triangles, 25 psig.

are obtained on the polar Supelcowax-10 column, where the C10OH is eluted after the C15.

5. Conclusions

The method described, implemented with an auxiliary program for the calculation of the peak width at any height of the peaks, permits to evaluate the behaviour of the column and to select the conditions necessary to obtain a suitable resolution of the analysed mixture at different values of the peak height in isobaric analyses carried out at different inlet pressures and column temperatures. If the separation of two closely eluting peaks show a valley deep more than the 90% of their height, the resolution at (1/10)th of the peak height is sufficient for qualitative identification and fair enough for approximate quantitative evaluation. Therefore, the prediction of experimental conditions which permit the resolution of all the components of the analysed mixture at (1/10)th of the height of their peaks or more is sufficient for practical purposes.

It has been found that at a given temperature and by changing the inlet pressure, the dependence of the peak width at half height on the retention time is near linear and that the width at (1/10)th of the peak height in the majority of cases is proportional to the width at half height and that the ratio δ_{10} between these two values is a constant depending on the used columns and independent on temperature and carrier gas pressure. This ratio can be used in order to predict the resolution at (1/10)th of the peak width. The calculated values correspond very well with those experimentally measured at any inlet pressure. If the shape of the peaks is similar to a Gaussian distribution curve and the ratio between the peak width at half height and the peak width at a smaller fraction of the height is a constant independent on pressure and temperature, the resolution can be calculated at smaller values of the peak height. The possibility of obtaining at all the retention times the values of the resolution for all the compounds when the data of three isobaric runs only are available, decreases the time spent and the number of preliminary runs necessary in order to select the best conditions for the isothermal separation of all the compounds contained in the sample, whose total time can be reduced by increasing the inlet pressure. This is mainly important when it is not possible to program or increase too much the column temperature due to thermal instability of some compounds.

Acknowledgements

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