



Prediction of the plate height of capillary columns operated at any inlet pressure of the carrier gas by using few retention data measured under isobaric conditions

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Abstract

Programming inlet pressure in gas chromatography permits to decrease the analysis time without changing the elution order of compounds of different polarity whose relative retention changes with changing temperature. The choice of the best values of the inlet pressure and flow-rate of the carrier gas often requires many preliminary analyses with different parameters to be carried out. A method for the prediction of the separation by starting from few experimental data measured in isothermal and isobaric conditions decreases the time required for the optimisation of the analysis. The efficiency of the separation depends on the change of the theoretical plate height at various pressures and temperatures, due to pressure drop along the column. By calculation of the diffusion coefficients of the analysed compounds into the mobile and stationary phase it is possible to evaluate the column efficiency and predict the number of theoretical plates at any inlet pressure. A procedure for the prediction of the plate height of a capillary column at any inlet pressure of the carrier gas and column temperature by using retention data of polar and non-polar compounds (1-alcohols and linear alkanes) obtained in few isobaric runs is described.

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1. Introduction

The use of high carrier gas flow-rates was the early technique used in order to decrease the gas chromatographic retention of compounds with high molecular mass, mainly because the stationary phases available at the beginning of gas chromatography did not tolerate high temperatures. An increase

of the molecular mass range of the analysed compounds was also achieved by increasing the inlet pressure of the column during the analysis and therefore programming the flow-rate of the carrier gas. The availability of high-temperature stationary phases and the introduction of temperature-programming devices caused this technique to be abandoned for many years for two main reasons: the available mechanical devices for pressure programming were complicated or inaccurate and the high flow-rate in packed columns required very high inlet pressure and a large gas consumption; moreover, the increase of

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the flow-rate quickly decreased the efficiency of the packed columns by shifting the plate height values toward the climbing right side of the Van Deemter plot. However, some attempts were made to take advantage of the change of inlet pressure during the analysis by keeping constant the temperature of the column during the pressure change or by programming both the temperature and the flow-rate during the analysis.

The first application of this method, which provides a fairly large flexibility in the solution of separation problems [1], was proposed by Lipsky et al. [2], and then by Wolff and Wolff [3,4] who applied a step programming of the carrier gas inlet pressure. Valussi and Cofleri [5,6] reported the results obtained by using a linearly programmed carrier gas flow-rate in the analysis of natural fatty acid samples. Morgantini [7] proposed the term 'programmed flow gas chromatography', describing a device for the linear programming of the carrier gas flow-rate.

As stated by Purnell in 1962 [8], pressure programming "would certainly lead to results equivalent in many respects to those of temperature programming, and if a reasonably efficient column having a broad minimum of plots of plate height versus u were employed, flow changes of up to an order of magnitude might be employed in a single run without much loss of efficiency". Other papers describing both practical applications and theoretical aspects of pressure programming were published [9–20]. Recent works were published on the correlation between plate height and flow-rate in regimes of high pressure drop (up to 100 p.s.i.g.) in fast gas chromatography [21,22].

At the beginning, the applications of pressure programming were made with self-constructed equipment or by modification of standard gas chromatographs. In the years 1964–1965 the first commercial pressure programming units became available, but their development was partly abandoned because of the impossibility of monitoring exactly the flow-rate change during pressure programming. Today, instead, some instruments equipped with electronic devices are able to monitor and control, in a reproducible manner, the change of pressure at the column inlet during the analysis. The main advantages and disadvantages of pressure programming were summarised in previously published papers [1,23,24].

The standard sequence followed in order to optimise the gas chromatographic separation of a complex mixture of compounds is to select the stationary phase and start the analysis series at high temperature to be sure that the heaviest compounds are all eluted from the column, then decrease and program the temperature in order to separate the lightest components. This should be done at the beginning with the 'optimum' flow-rate corresponding to the minimum of the Van Deemter equation (plate height versus carrier gas velocity), plotted by starting from retention time and peak width measured at various flow-rates. The minimum of the plot may be found by graphical approximation or by using a least-square curve fitting [25]. When the separation and the identification of the components of a very complex mixture is obtained at a given temperature, the traditional method of decreasing the analysis time is to increase the temperature programming rate. However, when components of different polarity are present, whose partition coefficients depend in a different way on temperature, any change of temperature programming rate may modify the elution order and require a new identification. The reduction of analysis time by increasing the flow-rate has the advantage of maintaining the elution order unchanged.

Notwithstanding the evolution of the instrumentation, which permits to obtain good reproducibility, two problems which were responsible for the minor diffusion of pressure programming with respect of temperature programming still reduce the general applicability of the method in practical analysis: often the initial flow-rate is higher than the optimum value corresponding to the minimum of the Van Deemter curve and pressure programming may further decrease the column efficiency for the latest eluting peaks. If the critical separations are in the earlier part of the chromatogram, where the flow-rate is still close to the optimum, and if the Van Deemter plot is flat, the reduction in efficiency is not too significant. However, the choice of the optimum pressure and temperature conditions for the separation of a given mixture is rather complicated and requires many preliminary runs, which are time-consuming. Therefore, it seemed interesting to investigate the dependence of the plate height on these parameters in order to find a procedure which permits to predict the behaviour of the columns on

the basis of few experimental data. In this work, we describe the results obtained by focussing attention on the effect of different inlet pressures: further research is in progress to establish the effects of simultaneous pressure and temperature programming.

In papers published previously [24,26,27], some methods were described for the automatic prediction of retention values in pressure- and in temperature-programmed capillary gas chromatography by using as input data the retention times measured under only few isobaric analytical conditions (one for programmed pressure and three for programmed temperature). The comparison of the experimental retention times with those predicted by using the proposed calculation method have shown that, by using only one isobaric run as the source of the input data, satisfactory accuracy in the prediction of programmed pressure analyses with various linear speed and with and without initial isobaric tract can be obtained. However, the method gave no information about the peak width, did not allow to establish if the column was operated in a reasonably good efficiency region and it was not possible to predict if the base widths of two closely eluting peaks were small enough to permit complete or almost sufficient resolution.

The technique practically used to establish if a capillary column is suitable for the separation of a given couple of closely eluting peaks is to start with a carrier flow-rate previously found to be appropriate for the type of analysis required, and calculate the number of theoretical plates by using the retention time and the width of one of the two peaks or, if they are not separated enough to permit the measurement of the width, of another peak eluting near the couple of interest. By changing, step by step, the inlet pressure, the behaviour of the plate height as a function of the flow-rate can be plotted and, by interpolation, the optimum flow-rate, i.e., the linear velocity of the gas which assures the highest column efficiency can be found. If the given pair of closely eluting peaks cannot be separated under these conditions, no further attempt to change the analytical parameters can improve the resolution and therefore the column has to be changed, increasing its length or, better, modifying the polarity of the stationary phase in order to rely more on the selectivity rather than on the efficiency. It is, in fact, known that the

resolution is directly proportional to the ratio of the partition coefficients of two substances, α , but depends on the square root of the number of theoretical plates and therefore a change of phase has a greater effect than an increase in the column length.

The trial-and-error method for the determination of the optimum carrier gas velocity is time-consuming, as several runs at different flow-rates and temperatures should be carried out. A method which permits to know quickly and with a good approximation the conditions under which the column exhibits the best performance is therefore very useful when the parameters of the gas chromatographic separation of a new sample are selected. The efficiency of the separation depends on the change of the plate height due to pressure drop along the column [28–31]. By calculation of the diffusion coefficients of the analysed compounds into the mobile and stationary phase [32,33] it is possible to evaluate the column efficiency and to predict the retention time and the number of theoretical plates at any inlet pressure and carrier gas flow-rate by using the retention times and the half-height widths of the peaks obtained in a few isobaric runs.

2. Theory

The basic principle of the used calculation method takes into account the fact that the values of the linear carrier gas velocity, of the capacity factor and of the plate height change along the column as a function of the changing pressure at any point from the column inlet to the detector, due to pressure drop along the column. The plate height for every compound is calculated at any point, while it moves throughout the column, with the Golay equation (valid for such a relatively small pressure drop as that found with the length and diameter of the used columns), the diffusion coefficients of which are obtained with a best fit on the total plate number measured experimentally. In any small tract of the column the calculation starts with an initial value of the diffusion coefficient and is repeated for all the tracts until the calculated total plate number approximates the experimental value within a pre-set accuracy. The diffusion coefficients obtained in this way can then be used in order to predict the plate height

at a given temperature for any inlet pressure. The detailed calculation is described below.

The gross retention time t_R of a given compound in a capillary gas chromatographic column under isobaric and isothermal conditions is

$$t_R = t_M(1 + k') \quad (1)$$

where k' is the mean capacity factor and t_M is the gas hold-up time or dead time, which depend on the column temperature and on the head pressure as follows [24]:

$$t_M(T,P) = \frac{32\eta(T)L^2}{3r^2} \cdot \frac{(P_i^3 - P_0^3)}{(P_i^2 - P_0^2)^2} \quad (2)$$

η being the dynamic viscosity of the carrier gas (poise), L the column length (cm), r its internal radius (cm), P_i the absolute pressure at the column inlet and P_0 the absolute pressure at the outlet (p.s.i.g.). The unit p.s.i.g. was used instead of the SI system units because the pressure detector of the used gas chromatograph directly measured the inlet pressure with this unit and therefore the calculations could be made by avoiding the unit conversion.

The dependence on temperature of η is given by:

$$\eta(T) = aT^b \quad (3)$$

where a and b are constants dependent on the nature of the carrier gas.

The capacity factor is correlated with thermodynamic constants by:

$$k'(T,P) = \beta \exp\left(\frac{\Delta G(T,P)}{RT}\right) \quad (4)$$

where β is the phase ratio of the column, i.e., the ratio between the volume of gas phase and that of the liquid phase, ΔG is the standard free solution energy of a compound from the gas phase to the liquid stationary phase, R is the gas constant, T the absolute temperature of the column and P the absolute pressure at a generic point along the column. The free solution energy is given by:

$$-\Delta G = \Delta H - T\Delta S \quad (5)$$

ΔH being the solution enthalpy and ΔS the solution entropy of the system.

The dependence of ΔG on temperature can be taken as linear when the temperature interval is

small, and in this instance the capacity factor can be rewritten [34] as:

$$k'(T) = \beta \exp\left(\frac{A}{T} + B + CT\right) \quad (6)$$

where A , B and C are constant values depending only on the solute–solvent interaction at constant pressure. Simple equations showing the dependence of ΔG on pressure were not available, but, by experimental determination of the ΔG values as a function of inlet pressure, it has been found that, within restricted pressure ranges, the capacity factor can be expressed as a function of the pressure at a generic point along the column by the following formula:

$$k'(P) = \beta \exp(A' \ln P + B') \quad (7)$$

where A' and B' are coefficients depending only on the solute–solvent interaction at a constant temperature and the argument of the exponential can be considered as a variation of the Clausius–Clapeyron equation.

By taking into account the above-listed definitions, it is possible to deduce that, under isothermal conditions, the retention times of a compound obtained in only two isobaric analyses are sufficient in order to predict the retention time of the same compound in any other isobaric analysis. In isobaric runs the elution time t_R can be calculated as follows. If L is the column length and Δt is a small time interval, then the t_R value is given by the sum of n time intervals of length Δt during each of which the compound will be shifted into the column by the distance ΔL . If in each ΔL_j tract the compound velocity is taken as a constant having the following value:

$$u_{e,j} = \frac{\Delta L_j}{\Delta t} \quad (8)$$

then:

$$L = \sum_{j=1}^n \Delta L_j = \sum_{j=1}^n u_{e,j} \Delta t \quad (9)$$

and the velocity of the compound in a column tract ΔL_j is:

$$u_{e,j} = \frac{u_{eg,j}}{(1 + k'(P_j))} \quad (10)$$

where $u_{cg,j}$ is the carrier gas linear velocity and P_j is the pressure in the ΔL_j interval. The relationship of $u_{cg}(P)$ can be calculated by using the following equation of the linear gas velocity [24,35–39]:

$$u_{cg} = -\frac{4r^2}{32\eta} \cdot \frac{dP}{dL} \quad (11)$$

where dP/dL is the change in gas pressure for a change of position dL along the column.

The overall gas velocity along the column can therefore be written as:

$$u_{cg,j} = \frac{\Delta L_{cg,j}}{\Delta t} \quad (12)$$

by solving Eq. (11) the explicit equation of $\Delta L_{cg,j}$ becomes:

$$\Delta L_{cg,j} = L \frac{\left\{ P_j^2 - \left[P_j^3 - \Delta t \cdot \frac{3r^2(P_i^2 - P_0^2)^2}{32L^2\eta} \right]^{\frac{2}{3}} \right\}}{(P_i^2 - P_0^2)} \quad (13)$$

and

$$P_j = \sqrt{P_i^2 - \frac{L_j}{L}(P_i^2 - P_0^2)} \quad (14)$$

$\Delta L_{cg,j}$ is the column tract covered by the carrier gas during the time interval Δt and L_j is the length covered by the carrier gas starting from the column inlet. Being:

$$L = \sum_{j=1}^n \frac{\Delta L_{cg,j}}{(1 + k'(P_j))} \quad (15)$$

from expression 15 one can obtain the value of n by an iterative calculation procedure:

$$t_R = n\Delta t \quad (16)$$

and, if one supposes that the height equivalent to a theoretical plate as defined by the Golay equation [40–43] is not constant along the entire column but only in the tract of length ΔL previously defined, then the number of theoretical plates, N , calculated with the formula [44]:

$$N = 5.54 \cdot \left(\frac{t_R}{b_{1/2}} \right)^2 \quad (17)$$

where $b_{1/2}$ is the peak width at half height, is given by:

$$N = \sum_{j=1}^n N_j = \sum_{j=1}^n \frac{\Delta L_j}{h_j} \quad (18)$$

N_j is the number of theoretical plates in the ΔL_j tract and h_j is the corresponding plate height, given by [41]:

$$h_j = \frac{2D_g}{u_{cg,j}} + \frac{(1 + 6k'(P_j) + 11k'(P_j)^2)r^2}{24D_g(1 + k'(P_j))^2} \cdot u_{cg,j} + \frac{2k'(P_j)d_f^2}{3D_s(1 + k'(P_j))^2} \cdot u_{cg,j} \quad (19)$$

where d_f is the thickness of the stationary phase layer, D_g and D_s are the diffusion coefficients in the gas and stationary phases, respectively. If the peak profile in the chromatogram can be approximated as a Gaussian curve, if the diffusion coefficient in the stationary phase is independent on the pressure and the diffusion coefficient in the gas phase is inversely proportional to the pressure, the diffusion coefficients in both phases of the compounds can be calculated with Eq. (18) using the data measured under isobaric conditions. As Eq. (18) can be applied under any pressure and temperature conditions, when the diffusion coefficients have been obtained, it is possible to calculate through an iterative calculation procedure the number of theoretical plates for any isobaric run. Then, by using Eq. (17), one can obtain the peak width at half height and reconstruct the shape of the peaks, taken as a Gaussian curve, and the entire chromatogram.

3. Experimental

For the determination of the retention times and peak width of reference mixtures containing non-polar and polar compounds a capillary non polar column DB-1 (polydimethylsiloxane) and a polar column Supelcowax-10 (polyglycol), both $30 \text{ m} \times 0.32 \text{ mm I.D.}$, phase thickness $0.25 \text{ } \mu\text{m}$, were used. In order to investigate the dependence of the results on both the column length and on stationary phase, a DB-17 medium-polarity column (50% phenyl-polydimethylsiloxane) $15 \text{ m} \times 0.32 \text{ I.D.}$, phase thickness

0.25 μm , was also used. The columns were installed in a Varian gas chromatograph model 3800 (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 temperature was controlled with an accuracy of $\pm 1^\circ\text{C}$ and the pressure with an accuracy of ± 0.1 p.s.i.g. The inlet pressure of the column was measured both with the electronic hardware of the gas chromatogram and by a mercury manometer directly connected to the injector septum by means of a thin needle. In the calculation, the pressure values measured in p.s.i.g. ($1\text{ Pa} = 1.45038 \times 10^{-4}$ p.s.i.g.), being the gas chromatograph's software output in this unit, were converted in cgs units (dynes/cm^2). 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, etc., or C10OH, C11OH, C12OH, etc., respectively) were prepared with standard solutions at a concentration of 10 $\mu\text{g}/\text{ml}$ 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 parameters which must be known for the application of the calculation method in order to predict the retention time and peak width values at any possible inlet pressure 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 during the preliminary isobaric runs. The results of the different isobaric runs (two or more, and the precision of the final results depend on the number of input data but mainly on the accuracy of their measurement, see below) are evaluated by the data acquisition software and the following values are taken: the retention time, the peak width at half height, the peak area. As the Star Data System yields the values of the peak width with an approximation of 0.1 s, not accurate enough for the following calculations, an auxiliary calculation program was written which reads the raw chromatogram data stored in the Star file, identifies the baseline and the peak apex, calculates the half height value and accurately measures at this point the horizontal distance between the front and the rear

side of the peak. The approximation obtained in this way is 0.06 s and this increases the accuracy of the final calculation. All the data are input to the program made by applying the equations shown 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.

The analyses under isobaric conditions used for the measurement of the initial data and for checking the accuracy of the calculation method were carried out in the inlet pressure range 7.5–25 p.s.i.g. at 2.5-p.s.i.g. intervals, and at temperatures between 100 and 160 $^\circ\text{C}$. The results are reported as a function of pressure instead of using flow-rate. The reason for this choice is that pressure and temperature are the independent variables that can be set and measured on the gas chromatograph and therefore are exactly known, whereas the flow-rate is calculated by using the parameters of the column, the viscosity of the carrier gas, the pressure and the temperature. This calculation is automatically carried out by the built-in program of the Varian 3800 gas chromatograph and was checked using the inlet pressure measured using a mercury manometer connected to the injector and the column temperature measured with a thermocouple connected to the column. Table 1 shows the dependence of the flow-rate on pressure and temperature on DB-1, Supelcowax-10 and DB-17 columns.

4. Calculation procedure

In order to obtain both the retention times and the simulated peak width, it is necessary to estimate the parameters and the quantities which describe these two values. In both instances the following procedure has been followed: the length of the tract of the column covered by a given compound in a constant time interval Δt is evaluated. After *n* time intervals the compound will reach the column outlet and it is therefore possible to evaluate the physical parameters which influence the process. The values that must be known for the application of the model are the pre-set analysis parameters *L*, *r*, *d_f*, *T*, *a*, *b* and the experimental values *t_{Re}*, *P_i*, *P_a*, *b_{1/2}* (all defined below in the Nomenclature). It is also necessary to establish the value of the time interval

Table 1

Flow-rate values (cm^3/min) measured as a function of the inlet pressure (p.s.i.g.) and column temperature ($^{\circ}\text{C}$) on DB-1 and Supelcowax-10 columns ($30\text{ m}\times 0.32\text{ mm}$, $0.25\text{ }\mu\text{m}$ layer thickness) and DB-17 column ($15\text{ m}\times 0.32\text{ mm}$, $0.25\text{ }\mu\text{m}$ layer thickness)

<i>P</i> (p.s.i.g.)	Flow-rate (cm^3/min)											
	100 $^{\circ}\text{C}$		110 $^{\circ}\text{C}$		120 $^{\circ}\text{C}$		130 $^{\circ}\text{C}$		140 $^{\circ}\text{C}$		160 $^{\circ}\text{C}$	
	Supelcowax-10 DB-1	DB-17	Supelcowax-10 DB-1	DB-17	Supelcowax-10 DB-1	DB-17	Supelcowax-10 DB-1	DB-17	Supelcowax-10 DB-1	DB-17	Supelcowax-10 DB-1	DB-17
7.5	1.2	2.4	1.1	2.3	1.1	2.2	1.0	2.1	1.0	2.0	0.9	1.9
10.0	1.7	3.4	1.6	3.2	1.5	3.1	1.5	3.0	1.4	2.8	1.3	2.6
12.5	2.2	4.5	2.1	4.3	2.0	4.1	2.0	3.9	1.9	3.8	1.7	3.5
15.0	2.8	5.7	2.7	5.4	2.6	5.2	2.5	5.0	2.4	4.8	2.2	4.4
17.5	3.7	7.0	3.3	6.7	3.2	6.4	3.1	6.1	2.9	5.9	2.7	5.4
20.0	4.2	8.4	4.0	8.0	3.8	7.7	3.7	7.4	3.5	7.1	3.3	6.5
22.5	5.0	9.9	4.7	9.5	4.5	9.1	4.4	8.7	4.2	8.4	3.9	0.3
25.0	5.8	11.6	5.5	11.1	5.3	10.6	5.1	10.1	4.9	9.7	4.5	9.0

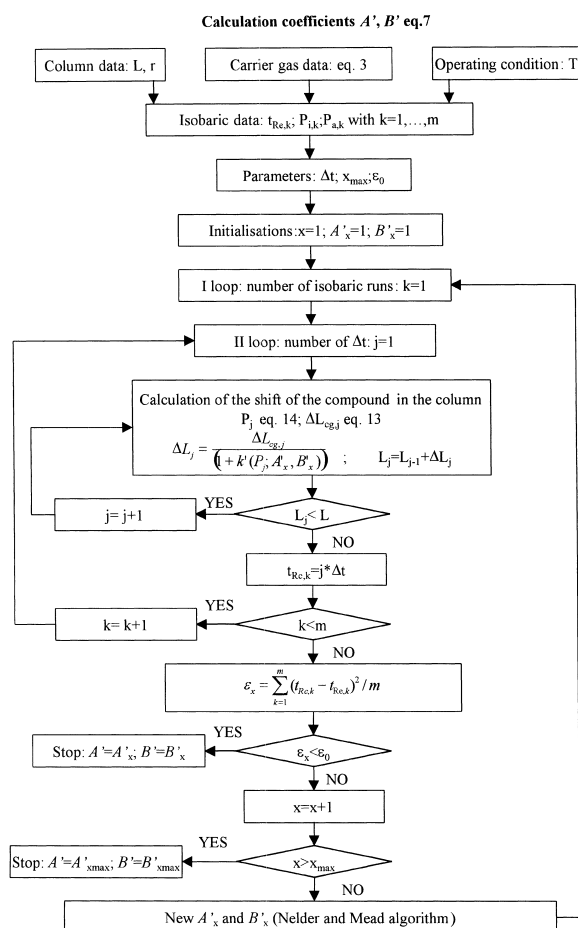


Fig. 1. Flow chart of the program for the calculation of coefficients A' and B' of Eq. (7).

Δt , the maximum number of iterations x_{\max} , the maximum tolerated least-square error ε_0 and the initial guest values of the physical parameters to be calculated. All the above-listed parameters are established a priori or are selected on the basis of preliminary experimental data. In order to obtain the convergence of the calculation with the least-squares method, the following values have been selected: $\Delta t = 0.1$ s (i.e., a value of the same order of magnitude of the uncertainty on the measurement of the retention time by the integration software), $x_{\max} = 100$, as the Nelder and Mead algorithm [45] permits to obtain a fair but relatively slow convergence; ε_0 was taken as the same magnitude as Δt in

order to balance the convergence error with respect of the error in the determination of the absolute physical parameters. The initial value input for the initialisation of the parameters to be calculated (x , A' and B') was taken as equal to 1, satisfactory for the used algorithm. Fig. 1 shows the flow diagram of the calculation procedure for the coefficients A' and B' of Eq. (7). Fig. 2 shows the flow diagram for the determination of D_g and D_s , the diffusion coefficients in the gas and stationary phases, respectively (see Eq. (19)).

5. Results and discussion

Tables 2 and 3 refer to the non-polar column DB-1

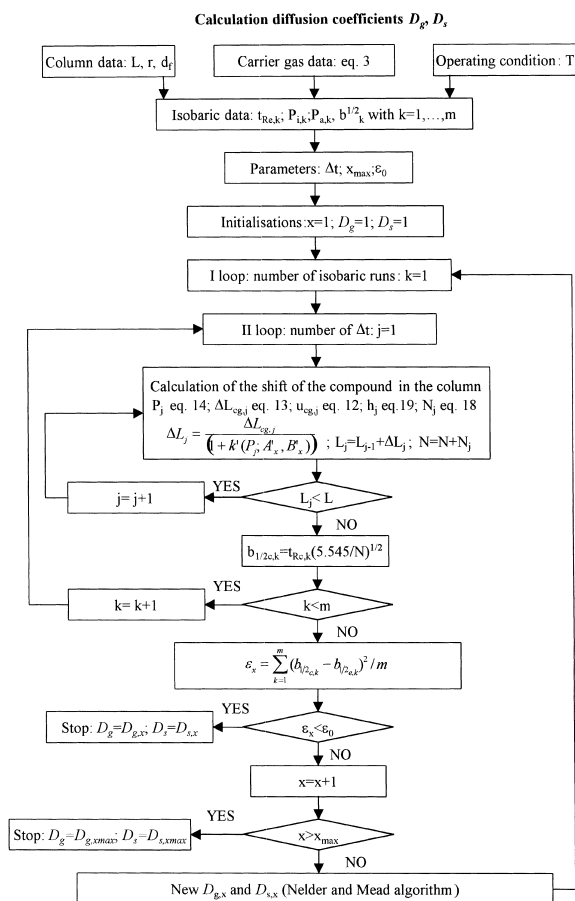


Fig. 2. Flow chart of the program for the calculation of diffusion coefficients D_g and D_s of Eq. (19).

and show, for *n*-alkanes and 1-alcohols, respectively, the comparison between the values of the h_{exp} , which is the plate height determined at any temperature and inlet pressure tested by applying Eq. (17) to the experimental data of the retention time t_{R} and of the peak width at half height $b_{1/2}$, and the values of h_{cal} , calculated with the described procedure. The data reported in these tables were calculated by using as the starting values all the data obtained at 2.5-p.s.i.g. intervals within the tested pressure range. The relative percent errors between experimental and calculated values, $E\% = 100(h_{\text{exp}} - h_{\text{cal}})/h_{\text{exp}}$, are also reported.

When all the available experimental data are used for the calculation, the agreement between h_{exp} and h_{cal} is obviously very good. Whether the calculation carried out with the data measured in few isobaric runs results in correct values of h_{cal} has also been verified. The best pressure values to use for the experimental determination of the starting data and for the application of the calculation method are the highest which permit the resolution of the first peaks of the sample and the lowest which yield a reasonable length of the entire chromatogram. The use of these two series of data (measured in this instance at inlet pressures of 7.5 and 25 p.s.i.g.) yields a fair approximation with the results obtained by using the data measured at all the intermediate pressure values (see Table 4). However, by using two starting values only, any error in the setting of the analysis parameters or in the measurement of the data of one of them may yield incorrect results; therefore the choice of another pressure near the mean value between the two extremes increases the accuracy of the method. Table 5 shows the results obtained by using as the starting data the experimental values of the retention time and of the peak width at half height measured at three inlet pressure (7.5–15–25 p.s.i.g.). Table 6 shows that if the starting data are measured at inlet pressures in a range slightly differing from the widest one (e.g., 7.5–15–22.5 or 10–17.5–25 p.s.i.g.) the method yields results comparable with those obtained by using all the available series of experimental data (eight) or three series of experimental data measured in the widest pressure range. Fig. 3 shows the lines representing the behaviour of the plate height values predicted using the experimental values measured in all the isobaric

runs (full line) and those predicted using the experimental values measured in the three isobaric runs indicated in Table 5 (dashed lines). The lines correspond fairly well and approximate well the experimental points, showing that three series of values are sufficient for a correct prediction. It has been also verified (Table 6) that a slight shift in the pressure range selected towards higher or lower values does not modify appreciably the calculation of the efficiency, as the results depend only on the accuracy in the determination of the inlet pressure and the measurement of retention time and peak width.

The method permits the prediction of the dependence of the plate height on inlet pressure and temperature for any compound. The points in Fig. 4 show, as an example, the behaviour of the experimental plate height of *n*-pentadecane (C15) as a function of inlet pressure of the column at various temperatures. The lines show the calculated trend of the plate height. It can clearly be seen that the theoretical curves well fit the experimental values and that the minimum of the plot shifts toward higher pressure when the temperature increases. The linear alcohols have the same behaviour, and Fig. 5 shows the fitting of calculated curves with experimental plate height for *n*-dodecanol (C12OH) which was selected as an example to show the very close similarity of the behaviour of *n*-alkanes with Z carbon atoms and linear alcohols with a smaller number of carbon atoms (between Z-2 and Z-3), having about the same retention time and peak width. It was observed that, by increasing the length of the carbon atoms chain and therefore the retention time, the position of the minimum is shifted toward smaller pressure values (see values in Tables 2 and 3).

Figs. 4 and 5 show how the efficiency of the column changes when the column temperature increases and how the change of inlet pressure modifies its behaviour. If, at the initial temperature of the runs series (100 °C), the pressure is adjusted in order to obtain the flow-rate corresponding to the minimum of the Van Deemter plot (about 7.5 p.s.i.g.) and the temperature increase to 160 °C is carried out by maintaining this pressure constant, the plate height increases from 0.35 to 0.41 mm on the DB-1 column and from 0.33 to 0.40 mm on the Supelcowax column. The column efficiency decreases

Table 2

Comparison between the experimental values (mm) of the plate height (h_{exp}) of linear alkanes and those calculated (h_{cal}) by using as the starting data the values of the retention times and of peak width at half height measured at temperatures between 100 and 160 °C on a DB-1 column (30 m×0.32 mm, 0.25 μm layer thickness) at eight inlet pressure values; the relative percent errors between experimental and calculated values $E\% = 100(h_{\text{exp}} - h_{\text{cal}})/h_{\text{exp}}$ are shown

<i>P</i> (p.s.i.g.)	C10			C11			C12			C13			C14			C15			C16			C17			
	h_{exp}	h_{cal}	<i>E%</i>	h_{exp}	h_{cal}	<i>E%</i>	h_{exp}	h_{cal}	<i>E%</i>	h_{exp}	h_{cal}	<i>E%</i>	h_{exp}	h_{cal}	<i>E%</i>	h_{exp}	h_{cal}	<i>E%</i>	h_{exp}	h_{cal}	<i>E%</i>	h_{exp}	h_{cal}	<i>E%</i>	
<i>T</i> = 100 °C																									
7.5	0.331	0.333	-0.58	0.328	0.318	3.04	0.336	0.340	-1.18	0.342	0.340	0.53	0.353	0.343	3.06	0.347	0.347	0.00							
10.0	0.298	0.296	0.85	0.299	0.295	1.35	0.325	0.323	0.64	0.347	0.342	1.40	0.365	0.360	1.37	0.378	0.374	1.07							
12.5	0.293	0.293	0.00	0.296	0.304	-2.82	0.339	0.338	0.34	0.364	0.373	-2.41	0.394	0.403	-2.19	0.426	0.426	0.19							
15.0	0.301	0.306	-1.72	0.323	0.328	-1.60	0.361	0.370	-2.31	0.420	0.420	-0.03	0.466	0.463	0.59	0.479	0.495	-3.20							
17.5	0.318	0.329	-3.57	0.370	0.363	2.09	0.408	0.412	-1.07	0.475	0.478	-0.61	0.527	0.534	-1.24	0.566	0.574	-1.37							
20.0	0.359	0.360	-0.42	0.408	0.405	0.82	0.462	0.463	-0.15	0.539	0.545	-1.14	0.603	0.614	-1.85	0.665	0.664	0.19							
22.5	0.400	0.397	0.54	0.467	0.456	2.46	0.529	0.524	1.05	0.638	0.623	2.30	0.718	0.708	1.45	0.788	0.768	2.62							
25.0	0.441	0.438	0.52	0.499	0.510	-2.19	0.600	0.589	1.95	0.712	0.706	0.85	0.824	0.806	2.18	0.884	0.877	0.83							
<i>T</i> = 110 °C																									
7.5	0.369	0.373	-1.07	0.359	0.352	2.07	0.342	0.337	1.50	0.338	0.348	-2.99	0.340	0.352	-3.34	0.360	0.361	-0.46							
10.0	0.322	0.314	2.36	0.317	0.311	2.05	0.318	0.314	1.15	0.341	0.339	0.79	0.357	0.352	1.45	0.380	0.369	2.93							
12.5	0.290	0.292	-0.58	0.303	0.303	0.16	0.318	0.322	-1.17	0.350	0.359	-2.67	0.370	0.381	-3.04	0.396	0.406	-2.67							
15.0	0.290	0.290	-0.05	0.314	0.313	0.11	0.339	0.348	-2.56	0.400	0.398	0.65	0.422	0.429	-1.52	0.447	0.462	-3.31							
17.5	0.307	0.299	2.44	0.341	0.335	1.90	0.382	0.383	-0.31	0.458	0.445	2.90	0.498	0.485	2.60	0.520	0.525	-0.99							
20.0	0.318	0.317	0.37	0.363	0.365	-0.37	0.434	0.428	1.39	0.498	0.504	-1.04	0.555	0.553	0.35	0.602	0.602	0.04							
22.5	0.338	0.340	-0.48	0.396	0.400	-0.96	0.486	0.478	1.48	0.563	0.568	-0.77	0.635	0.627	1.24	0.690	0.685	0.82							
25.0	0.375	0.367	1.95	0.452	0.440	2.77	0.537	0.534	0.56	0.638	0.638	0.09	0.702	0.708	-0.87	0.815	0.774	5.05							
<i>T</i> = 120 °C																									
7.5	0.363	0.362	0.42	0.349	0.347	0.36	0.343	0.341	0.70	0.337	0.333	1.08	0.318	0.318	0.23	0.341	0.338	0.98							
10.0	0.303	0.302	0.32	0.297	0.298	-0.48	0.306	0.307	-0.30	0.312	0.315	-0.85	0.317	0.318	-0.45	0.338	0.346	-2.31							
12.5	0.283	0.282	0.48	0.286	0.285	0.33	0.303	0.307	-1.31	0.322	0.327	-1.31	0.348	0.346	0.67	0.392	0.381	2.79							
15.0	0.278	0.279	-0.24	0.291	0.290	0.50	0.316	0.323	-2.39	0.351	0.356	-1.41	0.394	0.391	0.63	0.421	0.434	-3.02							
17.5	0.289	0.288	0.40	0.306	0.306	-0.11	0.345	0.351	-1.75	0.399	0.397	0.67	0.437	0.447	-2.22	0.490	0.498	-1.60							
20.0	0.303	0.304	-0.34	0.330	0.329	0.28	0.393	0.387	1.52	0.438	0.445	-1.44	0.503	0.511	-1.64	0.566	0.571	-0.77							
22.5	0.324	0.324	-0.08	0.357	0.357	0.14	0.428	0.426	0.40	0.498	0.497	0.22	0.587	0.579	1.45	0.664	0.647	2.63							
25.0	0.351	0.351	-0.13	0.394	0.392	0.33	0.480	0.475	0.96	0.561	0.562	-0.09	0.674	0.663	1.59	0.758	0.741	2.18							

T=130 °C																								
7.5	0.466	0.470	-0.82	0.401	0.409	-1.87	0.380	0.382	-0.48	0.363	0.362	0.44	0.349	0.345	1.07	0.342	0.344	-0.45	0.344	0.340	1.15	0.350	0.341	2.38
10.0	0.371	0.374	-0.89	0.338	0.339	-0.30	0.327	0.329	-0.63	0.325	0.325	-0.10	0.324	0.328	-1.23	0.344	0.339	1.71	0.342	0.347	-1.70	0.342	0.350	-2.37
12.5	0.329	0.329	0.06	0.315	0.311	1.05	0.314	0.314	0.20	0.314	0.323	-2.89	0.333	0.341	-2.44	0.358	0.362	-1.25	0.371	0.382	-3.13	0.373	0.387	-3.95
15.0	0.304	0.308	-1.16	0.303	0.305	-0.44	0.318	0.318	-0.05	0.338	0.340	-0.52	0.370	0.372	-0.61	0.405	0.404	0.02	0.431	0.435	-1.10	0.430	0.443	-2.90
17.5	0.302	0.303	-0.54	0.312	0.311	0.17	0.334	0.334	0.00	0.371	0.367	1.12	0.419	0.413	1.33	0.460	0.456	0.80	0.512	0.498	2.82	0.522	0.507	2.85
20.0	0.309	0.307	0.78	0.320	0.326	-2.11	0.363	0.359	0.91	0.414	0.404	2.31	0.454	0.465	-2.39	0.508	0.519	-2.15	0.589	0.572	2.94	0.581	0.584	-0.55
22.5	0.318	0.317	0.26	0.345	0.347	-0.42	0.397	0.389	1.97	0.460	0.446	3.10	0.531	0.521	1.84	0.587	0.587	-0.04	0.649	0.652	-0.58	0.689	0.667	3.09
25.0	0.332	0.331	0.19	0.373	0.371	0.67	0.424	0.424	0.08	0.494	0.492	0.30	0.580	0.583	-0.39	0.668	0.660	1.17	0.728	0.738	-1.34	0.783	0.756	3.50
T=140 °C																								
7.5	0.446	0.459	-2.85	0.443	0.455	-2.68	0.411	0.421	-2.34	0.388	0.388	0.08	0.376	0.375	0.33	0.370	0.373	-0.94	0.367	0.369	-0.54	0.370	0.366	1.14
10.0	0.368	0.365	0.81	0.372	0.364	2.25	0.349	0.346	0.99	0.345	0.332	3.73	0.341	0.336	1.60	0.362	0.348	3.92	0.361	0.352	2.43	0.354	0.359	-1.42
12.5	0.323	0.321	0.73	0.322	0.323	-0.20	0.315	0.315	-0.06	0.323	0.316	2.12	0.340	0.332	2.23	0.358	0.356	0.63	0.369	0.367	0.55	0.383	0.383	0.00
15.0	0.302	0.300	0.48	0.302	0.305	-0.97	0.297	0.306	-3.09	0.315	0.319	-1.38	0.342	0.348	-1.70	0.378	0.382	-1.11	0.396	0.401	-1.18	0.412	0.426	-3.30
17.5	0.294	0.294	0.06	0.300	0.301	-0.28	0.312	0.310	0.80	0.334	0.335	-0.28	0.376	0.375	0.08	0.418	0.421	-0.58	0.438	0.446	-1.88	0.472	0.480	-1.79
20.0	0.298	0.297	0.49	0.307	0.307	0.06	0.325	0.323	0.64	0.359	0.359	-0.06	0.418	0.411	1.48	0.473	0.468	0.98	0.505	0.501	0.79	0.554	0.544	1.82
22.5	0.305	0.306	-0.26	0.319	0.319	0.05	0.339	0.342	-0.74	0.395	0.388	1.68	0.449	0.452	-0.87	0.533	0.520	2.38	0.566	0.560	1.00	0.626	0.613	2.21
25.0	0.319	0.319	-0.08	0.335	0.335	0.06	0.370	0.366	1.19	0.432	0.423	2.11	0.500	0.499	0.14	0.587	0.579	1.31	0.636	0.627	1.37	0.709	0.689	2.87
T=160 °C																								
7.5	0.439	0.447	-1.81	0.466	0.469	-0.58	0.479	0.479	0.07	0.472	0.472	-0.04	0.424	0.435	-2.70	0.411	0.416	-1.32	0.374	0.376	-0.51	0.392	0.388	1.04
10.0	0.349	0.348	0.25	0.366	0.365	0.09	0.374	0.371	0.62	0.373	0.370	0.88	0.360	0.356	0.99	0.353	0.350	0.76	0.342	0.335	1.92	0.350	0.351	-0.42
12.5	0.306	0.308	-0.78	0.324	0.324	-0.08	0.330	0.329	0.23	0.325	0.330	-1.50	0.333	0.332	0.46	0.331	0.334	-0.81	0.330	0.335	-1.39	0.348	0.335	-1.87
15.0	0.288	0.287	0.32	0.302	0.302	-0.09	0.307	0.306	0.37	0.312	0.310	0.53	0.313	0.325	-3.88	0.326	0.336	-2.94	0.361	0.352	2.68	0.374	0.377	-0.71
17.5	0.281	0.281	0.08	0.296	0.296	-0.16	0.294	0.299	-1.73	0.306	0.306	-0.10	0.329	0.333	-1.20	0.342	0.351	-2.55	0.385	0.380	1.30	0.417	0.411	1.54
20.0	0.283	0.283	0.19	0.299	0.299	0.05	0.301	0.301	-0.20	0.315	0.312	0.92	0.341	0.350	-2.65	0.374	0.375	-0.28	0.411	0.418	-1.81	0.451	0.454	-0.61
22.5	0.292	0.291	0.43	0.315	0.308	2.31	0.308	0.310	-0.75	0.325	0.324	0.29	0.384	0.373	2.89	0.409	0.406	0.91	0.460	0.462	-0.30	0.505	0.504	0.25
25.0	0.296	0.303	-2.65	0.321	0.321	0.08	0.325	0.324	0.32	0.346	0.341	1.37	0.409	0.400	2.26	0.440	0.440	0.02	0.525	0.509	2.94	0.565	0.557	1.34

Table 4

Comparison between the experimental values (mm) of the plate height (h_{exp}) of 1-alcohols and those calculated (h_{cal}) by using as the starting data the values of the retention times and of peak width at half height measured at 130 °C on a DB-1 column (30 m×0.32 mm, 0.25 μm layer thickness) at two inlet pressure values (7.5 and 25 p.s.i.g. isobaric runs)

Compounds	P=7.5 p.s.i.g.			P=10.0 p.s.i.g.			P=12.5 p.s.i.g.			P=15.0 p.s.i.g.			P=17.5 p.s.i.g.			P=20.0 p.s.i.g.			P=22.5 p.s.i.g.			P=25.0 p.s.i.g.		
	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%
C10	0.466	0.469	-0.65	0.371	0.361	2.70	0.329	0.336	-2.13	0.304	0.314	-3.29	0.302	0.314	-3.97	0.309	0.321	-3.88	0.318	0.330	-3.77	0.332	0.343	-3.31
C8OH	0.446	0.448	-0.45	0.380	0.370	2.75	0.320	0.331	-3.44	0.310	0.321	-3.55	0.305	0.316	-3.61	0.308	0.320	-3.90	0.323	0.334	-3.41	0.342	0.353	-3.22
C11	0.401	0.400	0.29	0.338	0.342	-1.05	0.315	0.323	-2.40	0.303	0.313	-3.30	0.312	0.323	-3.53	0.320	0.330	-3.13	0.345	0.357	-3.48	0.373	0.383	-2.68
C9OH	0.411	0.411	0.06	0.353	0.349	1.23	0.310	0.321	-3.55	0.303	0.312	-2.97	0.313	0.324	-3.51	0.322	0.332	-3.11	0.345	0.358	-3.77	0.366	0.379	-3.55
C12	0.380	0.381	-0.22	0.327	0.336	-2.90	0.314	0.317	-0.96	0.318	0.329	-3.46	0.334	0.344	-2.99	0.363	0.376	-3.58	0.397	0.408	-2.77	0.424	0.439	-3.54
C10OH	0.372	0.372	-0.09	0.321	0.330	-2.71	0.305	0.311	-1.97	0.313	0.323	-3.19	0.332	0.342	-3.01	0.361	0.375	-3.88	0.398	0.409	-2.76	0.428	0.442	-3.27
C13	0.363	0.364	-0.33	0.325	0.333	-2.53	0.314	0.318	-1.27	0.338	0.348	-2.96	0.371	0.381	-2.70	0.414	0.429	-3.53	0.460	0.475	-3.21	0.494	0.506	-2.43
C11OH	0.341	0.341	-0.14	0.307	0.315	-2.52	0.305	0.310	-1.64	0.334	0.343	-2.76	0.363	0.377	-3.81	0.399	0.409	-2.51	0.449	0.462	-2.90	0.492	0.505	-2.64
C14	0.349	0.349	-0.14	0.324	0.334	-3.09	0.333	0.338	-1.50	0.370	0.383	-3.38	0.419	0.425	-1.52	0.454	0.468	-3.08	0.531	0.537	-1.18	0.580	0.600	-3.50
C12OH	0.337	0.337	-0.14	0.323	0.321	0.48	0.332	0.336	-1.20	0.370	0.369	0.38	0.416	0.411	1.16	0.462	0.465	-0.55	0.511	0.523	-2.43	0.591	0.587	0.73
C15	0.342	0.342	0.05	0.344	0.338	1.70	0.358	0.363	-1.53	0.405	0.407	-0.43	0.460	0.459	0.16	0.508	0.523	-3.02	0.587	0.593	-0.98	0.668	0.667	0.10
C13OH	0.337	0.338	-0.34	0.332	0.335	-0.81	0.348	0.360	-3.55	0.387	0.390	-0.78	0.447	0.457	-2.32	0.489	0.505	-3.27	0.577	0.593	-2.79	0.651	0.669	-2.72
C16	0.344	0.343	0.20	0.342	0.348	-1.82	0.371	0.381	-2.78	0.431	0.433	-0.38	0.512	0.493	3.71	0.589	0.566	3.96	0.649	0.644	0.75	0.728	0.728	0.04
C14OH	0.338	0.338	0.07	0.340	0.339	0.24	0.364	0.369	-1.47	0.413	0.418	-1.17	0.484	0.476	1.72	0.545	0.546	-0.17	0.631	0.622	1.40	0.702	0.703	-0.18
C17	0.350	0.350	0.10	0.342	0.349	-2.05	0.373	0.385	-3.22	0.430	0.440	-2.33	0.522	0.531	-1.80	0.581	0.598	-2.93	0.689	0.700	-1.54	0.783	0.792	-1.14

Table 5

Comparison between the experimental values (mm) of the plate height (h_{exp}) of 1-alcohols and those calculated (h_{cal}) by using as the starting data the values of the retention times and of peak width at half height measured at 130 °C on a DB-1 column (30 m×0.32 mm, 0.25 μm layer thickness) at three inlet pressure values (7.5–15–25 p.s.i.g., isobaric runs)

Compounds	P=7.5 p.s.i.g.			P=10.0 p.s.i.g.			P=12.5 p.s.i.g.			P=15.0 p.s.i.g.			P=17.5 p.s.i.g.			P=20.0 p.s.i.g.			P=22.5 p.s.i.g.			P=25.0 p.s.i.g.		
	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%
C10	0.466	0.461	1.15	0.371	0.367	1.17	0.329	0.323	1.91	0.304	0.303	0.40	0.302	0.298	1.21	0.309	0.303	2.05	0.318	0.313	1.50	0.332	0.328	1.24
C8OH	0.446	0.442	0.90	0.380	0.370	2.63	0.320	0.314	1.89	0.310	0.300	3.23	0.305	0.295	3.43	0.308	0.301	2.24	0.323	0.314	2.92	0.342	0.330	3.40
C11	0.401	0.397	0.88	0.338	0.329	2.53	0.315	0.302	3.99	0.303	0.296	2.29	0.312	0.303	2.99	0.320	0.317	0.80	0.345	0.337	2.18	0.373	0.362	3.08
C9OH	0.411	0.408	0.80	0.353	0.345	2.27	0.310	0.306	1.17	0.303	0.299	1.47	0.313	0.304	2.80	0.322	0.318	1.11	0.345	0.338	1.90	0.366	0.363	0.91
C12	0.380	0.377	0.78	0.327	0.326	0.24	0.314	0.313	0.37	0.318	0.318	-0.14	0.334	0.336	-0.53	0.363	0.362	0.29	0.397	0.393	0.98	0.424	0.428	-1.05
C10OH	0.372	0.370	0.45	0.321	0.321	-0.04	0.305	0.309	-1.25	0.313	0.316	-0.88	0.332	0.334	-0.73	0.361	0.362	-0.28	0.398	0.396	0.62	0.428	0.433	-1.05
C13	0.363	0.361	0.55	0.325	0.324	0.30	0.314	0.322	-2.41	0.338	0.338	0.11	0.371	0.365	1.70	0.414	0.401	3.18	0.460	0.443	3.80	0.494	0.489	1.06
C11OH	0.341	0.340	0.40	0.307	0.308	-0.37	0.305	0.309	-1.41	0.334	0.329	1.58	0.363	0.359	1.17	0.399	0.398	0.14	0.449	0.444	1.16	0.492	0.493	-0.28
C14	0.349	0.348	0.31	0.324	0.331	-2.23	0.333	0.345	-3.70	0.370	0.377	-2.00	0.419	0.419	-0.09	0.454	0.472	-3.88	0.531	0.529	0.34	0.580	0.591	-1.93
C12OH	0.337	0.337	0.09	0.323	0.319	1.10	0.332	0.333	-0.28	0.370	0.364	1.49	0.416	0.406	2.39	0.462	0.458	0.77	0.511	0.516	-1.05	0.591	0.579	2.10
C15	0.342	0.342	-0.11	0.344	0.338	1.66	0.358	0.363	-1.51	0.405	0.406	-0.33	0.460	0.459	0.27	0.508	0.523	-2.86	0.587	0.592	-0.83	0.668	0.666	0.33
C13OH	0.337	0.336	0.27	0.332	0.329	1.00	0.348	0.351	-0.84	0.387	0.391	-1.12	0.447	0.441	1.25	0.489	0.503	-2.90	0.577	0.571	1.09	0.651	0.643	1.23
C16	0.344	0.344	-0.03	0.342	0.349	-1.91	0.371	0.381	-2.78	0.431	0.432	-0.29	0.512	0.492	3.84	0.589	0.577	2.04	0.649	0.643	0.96	0.728	0.726	0.28
C14OH	0.338	0.338	0.14	0.340	0.337	0.80	0.364	0.366	-0.53	0.413	0.413	-0.01	0.484	0.470	2.98	0.545	0.538	1.21	0.631	0.613	2.83	0.702	0.693	1.28
C17	0.350	0.348	0.70	0.342	0.355	-3.80	0.373	0.385	-3.22	0.430	0.445	-3.49	0.522	0.508	2.60	0.581	0.585	-0.62	0.689	0.667	3.27	0.783	0.754	3.74

Table 6

Comparison between the experimental values (mm) of the plate height (h_{exp}) of 1-alcohols and those calculated (h_{cal}) by using as the starting data the values of the retention times and of peak width at half height measured at 130 °C on a DB-1 column (30 m×0.32 mm, 0.25 μm layer thickness) at three inlet pressure values (7.5–15–22.5 and 10–17.5–22.5 p.s.i.g.) different from those used in the calculation of Table 4

Compounds	P=7.5 p.s.i.g.			P=10.0 p.s.i.g.			P=12.5 p.s.i.g.			P=15.0 p.s.i.g.			P=17.5 p.s.i.g.			P=20.0 p.s.i.g.			P=22.5 p.s.i.g.			P=25.0 p.s.i.g.		
	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%	h_{exp}	h_{cal}	E%
<i>Isobaric runs 7.5–15.0–22.5 p.s.i.g.</i>																								
C10	0.466	0.462	0.81	0.371	0.364	1.81	0.329	0.317	3.55	0.304	0.295	3.05	0.302	0.295	2.32	0.309	0.301	2.59	0.318	0.308	3.14	0.332	0.325	2.11
C8OH	0.446	0.443	0.77	0.380	0.368	3.16	0.320	0.313	2.13	0.310	0.299	3.55	0.305	0.299	1.97	0.308	0.299	3.01	0.323	0.311	3.82	0.342	0.331	3.22
C11	0.401	0.398	0.63	0.338	0.328	3.05	0.315	0.310	1.59	0.303	0.296	2.31	0.312	0.301	3.53	0.320	0.309	3.39	0.345	0.334	3.19	0.373	0.361	3.22
C9OH	0.411	0.409	0.58	0.353	0.345	2.27	0.310	0.303	2.11	0.303	0.294	2.92	0.313	0.305	2.56	0.322	0.311	3.29	0.345	0.335	2.90	0.366	0.354	3.34
C12	0.380	0.378	0.43	0.327	0.323	1.12	0.314	0.306	2.45	0.318	0.309	2.83	0.334	0.324	3.11	0.363	0.352	3.03	0.397	0.385	3.02	0.424	0.408	3.70
C10OH	0.372	0.371	0.22	0.321	0.319	0.57	0.305	0.305	0.09	0.313	0.310	1.04	0.332	0.327	1.60	0.361	0.353	2.34	0.398	0.384	3.52	0.428	0.420	1.91
C13	0.363	0.362	0.35	0.325	0.323	0.65	0.314	0.319	-1.51	0.338	0.334	1.33	0.371	0.359	3.15	0.414	0.400	3.38	0.460	0.448	2.61	0.494	0.479	2.98
C11OH	0.341	0.340	0.24	0.307	0.307	0.00	0.305	0.307	-0.64	0.334	0.325	2.66	0.363	0.354	2.47	0.399	0.393	1.61	0.449	0.436	2.79	0.492	0.485	1.44
C14	0.349	0.348	0.19	0.324	0.330	-1.95	0.333	0.343	-3.13	0.370	0.375	-2.22	0.419	0.416	0.83	0.454	0.467	-2.82	0.531	0.523	1.42	0.580	0.584	-0.78
C12OH	0.337	0.337	-0.13	0.323	0.318	1.39	0.332	0.331	0.40	0.370	0.361	2.44	0.416	0.401	3.52	0.462	0.452	2.06	0.511	0.509	0.35	0.591	0.571	3.46
C15	0.342	0.342	0.08	0.344	0.337	2.11	0.358	0.361	-0.84	0.405	0.403	0.46	0.460	0.455	1.13	0.508	0.518	-1.93	0.587	0.586	0.13	0.668	0.660	1.27
C13OH	0.337	0.337	0.10	0.332	0.328	1.35	0.348	0.348	-0.09	0.387	0.387	-0.11	0.447	0.436	2.39	0.489	0.497	-1.57	0.577	0.563	2.43	0.651	0.634	2.62
C16	0.344	0.344	0.07	0.342	0.349	-1.94	0.371	0.382	-2.91	0.431	0.433	-0.48	0.512	0.493	3.62	0.589	0.566	3.87	0.649	0.645	0.66	0.728	0.728	-0.01
C14OH	0.338	0.337	0.26	0.340	0.339	0.31	0.364	0.369	-1.48	0.413	0.418	-1.25	0.484	0.476	1.60	0.545	0.547	-0.34	0.631	0.623	1.23	0.702	0.705	-0.40
C17	0.350	0.348	0.60	0.342	0.355	-3.78	0.373	0.383	-2.68	0.430	0.444	-3.33	0.522	0.507	2.80	0.581	0.583	-0.39	0.689	0.665	3.50	0.783	0.752	3.98
<i>Isobaric runs 10.0–17.5–25.0 p.s.i.g.</i>																								
C10	0.466	0.480	-3.00	0.371	0.382	-2.96	0.329	0.340	-3.34	0.304	0.313	-2.96	0.302	0.314	-3.97	0.309	0.321	-3.79	0.318	0.330	-3.71	0.332	0.343	-3.42
C8OH	0.446	0.461	-3.36	0.380	0.390	-2.63	0.320	0.332	-3.75	0.310	0.314	-1.29	0.305	0.317	-3.88	0.308	0.317	-2.90	0.323	0.324	-0.44	0.342	0.337	1.47
C11	0.401	0.415	-3.49	0.338	0.350	-3.55	0.315	0.324	-2.86	0.303	0.314	-3.63	0.312	0.322	-3.30	0.320	0.332	-3.75	0.345	0.353	-2.27	0.373	0.375	-0.65
C9OH	0.411	0.425	-3.41	0.353	0.360	-1.98	0.310	0.320	-3.23	0.303	0.315	-3.96	0.313	0.324	-3.38	0.322	0.334	-3.71	0.345	0.351	-1.63	0.366	0.372	-1.73
C12	0.380	0.392	-3.16	0.327	0.338	-3.36	0.314	0.320	-1.91	0.318	0.324	-1.89	0.334	0.347	-3.81	0.363	0.371	-2.25	0.397	0.402	-1.14	0.424	0.436	-2.73
C10OH	0.372	0.383	-2.96	0.321	0.333	-3.74	0.305	0.310	-1.64	0.313	0.325	-3.83	0.332	0.343	-3.31	0.361	0.372	-3.07	0.398	0.404	-1.61	0.428	0.441	-3.05
C13	0.363	0.375	-3.22	0.325	0.330	-1.54	0.314	0.325	-3.50	0.338	0.350	-3.55	0.371	0.383	-3.18	0.414	0.421	-1.60	0.460	0.464	-0.78	0.494	0.511	-3.45
C11OH	0.341	0.350	-2.53	0.307	0.318	-3.49	0.305	0.313	-2.62	0.334	0.339	-1.48	0.363	0.370	-1.80	0.399	0.410	-2.68	0.449	0.455	-1.40	0.494	0.505	-2.71
C14	0.349	0.337	3.44	0.324	0.324	0.11	0.333	0.342	-2.64	0.370	0.377	-2.00	0.419	0.422	-0.81	0.454	0.470	-3.52	0.531	0.539	-1.43	0.580	0.600	-3.45
C12OH	0.337	0.337	0.13	0.323	0.323	0.14	0.332	0.339	-2.04	0.370	0.373	-0.80	0.416	0.417	-0.23	0.462	0.472	-2.11	0.511	0.528	-3.33	0.591	0.597	-0.98
C15	0.342	0.351	-2.69	0.344	0.344	-0.14	0.358	0.368	-2.71	0.405	0.409	-0.99	0.460	0.460	0.01	0.508	0.522	-2.79	0.587	0.590	-0.49	0.668	0.662	0.83
C13OH	0.337	0.336	0.36	0.332	0.332	0.14	0.348	0.356	-2.40	0.387	0.399	-3.18	0.447	0.452	-1.06	0.489	0.505	-3.27	0.577	0.586	-1.53	0.651	0.661	-1.48
C16	0.344	0.332	3.37	0.342	0.344	-0.50	0.371	0.382	-2.92	0.431	0.438	-1.59	0.512	0.503	1.82	0.589	0.580	1.51	0.649	0.663	-2.22	0.728	0.752	-3.29
C14OH	0.338	0.338	0.12	0.340	0.341	-0.25	0.364	0.372	-2.34	0.413	0.423	-2.30	0.484	0.482	0.46	0.545	0.554	-1.56	0.631	0.631	-0.01	0.702	0.714	-1.68
C17	0.350	0.338	3.43	0.342	0.342	-0.13	0.373	0.387	-3.74	0.430	0.445	-3.49	0.522	0.521	0.25	0.581	0.600	-3.27	0.689	0.697	-1.11	0.783	0.793	-1.27

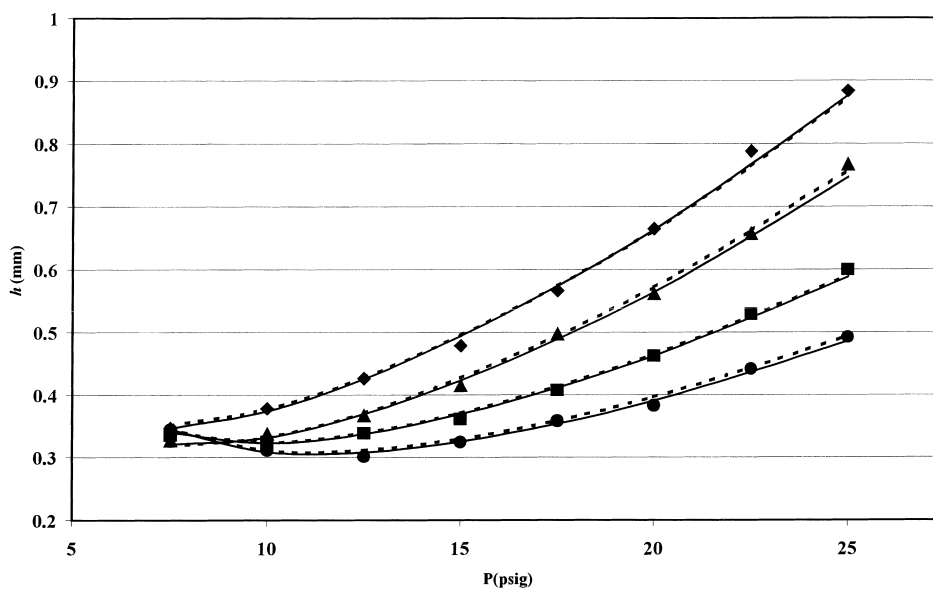


Fig. 3. Comparison between plate height values calculated with eight isobaric runs (full lines) and with the three isobaric runs shown in Table 5 (dashed lines). Temperature, 100 °C. Symbols: black rhombi, C15; black triangles, C12OH; black squares, C12; black circles, C9OH.

owing to the increment of the carrier gas viscosity with increasing temperature, which decreases the flow-rate with respect of the optimum value set at the beginning.

An attempt to solve this problem when complete pressure programming devices were not available was made by using differential flow controllers, simple pneumatic manifolds which maintain the

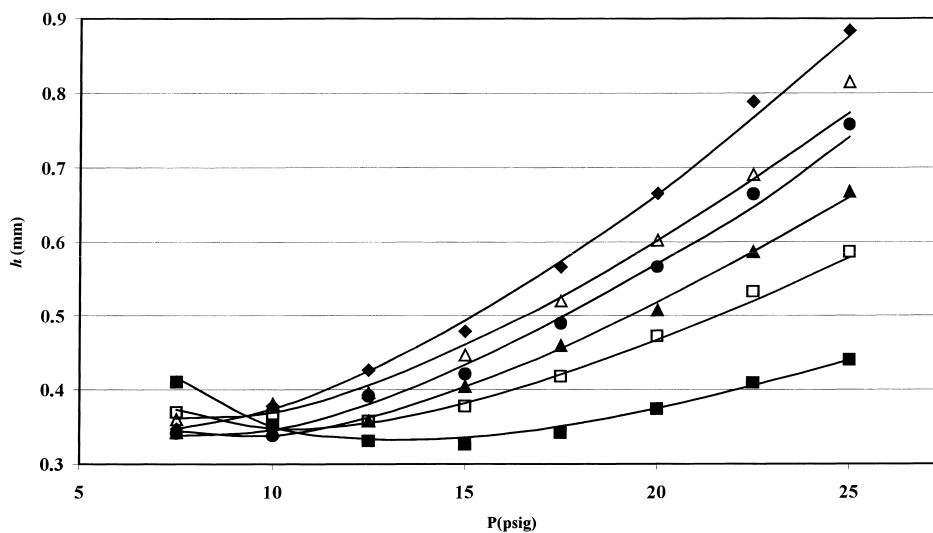


Fig. 4. Behaviour of the experimental (symbols) and calculated (full lines) plate height values for *n*-pentadecane at a function of inlet pressure at various column temperatures. Symbols: black rhombi, 100 °C; white triangles, 110 °C; black circles, 120 °C; black triangles, 130 °C; white squares, 140 °C; black squares, 160 °C.

flow-rate constant during temperature programming by increasing the inlet pressure [46,47]. In order to check if this solution can compensate sufficiently for the decrease of efficiency due to increasing temperature, this procedure was applied to the columns tested in this research. If the pressure-controlling device of the used gas chromatograph is set in order to maintain the flow-rate constant in the temperature range from 100 to 160 °C, the inlet pressure automatically changes from 7.5 to 9.5 p.s.i.g. in the 30 m×0.32 mm columns, and from 7.5 to 9.0 p.s.i.g. in the 15 m×0.32 mm column. At 160 °C the plate height obtained at this pressure (see the line with black squares in Figs. 4 and 5) is still greater than the optimum value indicated by the minimum of the plot. If the inlet pressure is programmed by starting from 7.5 p.s.i.g. in order to reach a value of about 14 p.s.i.g. at 160 °C, the best efficiency of the columns used is maintained throughout the entire temperature-programmed run. Furthermore, as the right-hand tract of the plots obtained at high temperature increases slowly with increasing pressure, the elution of heavy components of the sample can

be accelerated by further pressure increase, with a tolerable loss of column efficiency and without risk of decomposition of temperature-sensitive compounds. The increase of the baseline due to column bleeding at high temperature is also reduced and the column life is enhanced.

In order to verify if the change of the stationary phase and of the column length influences the results, some measurements have been carried out on polar Supelcowax-10 and medium-polar DB-17 columns, 30 and 15 m long, respectively. Table 7 shows the h_{exp} , h_{cal} and $E\%$ values obtained with three isobaric runs (7.5–17.5–25 p.s.i.g.). In the samples analysed on the DB-17 column, heavier terms for the alkanes and alcohols series were added, in order to obtain retention times and peak width values great enough to be measured with the same accuracy of the values measured on the DB-1 and Supelcowax columns. The $E\%$ values calculated for alcohols between C6OH and C10OH and alkanes between C11 and C15 are greater than those obtained for the same compounds on DB-1 and Supelcowax column, whereas the $E\%$ values of the heavier compounds are

Table 7

Comparison between the experimental values (mm) of the plate height (h_{exp}) of 1-alcohols and those calculated (h_{cal}) by using as the starting data the values of the retention times and of peak width at half height measured at 130 °C on the polar column Supelcowax-10 (30 m×0.32 mm, 0.25 µm layer thickness) and on the medium-polar column DB-17 (15 m×0.32 mm, 0.25 µm layer thickness) at three inlet pressure values (7.5–15–25 p.s.i.g.)

Compounds	$P=7.5$ p.s.i.g.			$P=17.5$ p.s.i.g.			$P=25.0$ p.s.i.g.		
	h_{exp}	h_{cal}	$E\%$	h_{exp}	h_{cal}	$E\%$	h_{exp}	h_{cal}	$E\%$
<i>Column: Supelcowax-10</i>									
C11	0.637	0.634	-0.38	0.856	0.884	3.21	1.170	1.178	0.76
C13	1.168	1.174	0.51	1.854	1.853	-0.03	2.448	2.496	1.96
C6OH	1.577	1.580	0.19	2.372	2.334	-1.60	2.993	3.098	3.52
C15	1.936	1.939	0.15	3.520	3.409	-3.15	4.521	4.643	2.69
C8OH	2.258	2.253	-0.21	3.807	3.786	-0.53	5.103	5.108	0.10
C10OH	2.433	2.432	-0.06	4.389	4.446	1.30	6.156	6.058	-1.60
<i>Column: DB-17</i>									
C6OH	0.456	0.438	-3.87	1.271	1.324	4.15	2.352	2.230	-5.19
C11	0.480	0.495	2.95	1.515	1.460	-3.66	2.561	2.453	-4.20
C8OH	0.388	0.398	2.42	1.126	1.158	2.83	1.854	1.920	3.58
C13	0.350	0.360	2.94	0.966	0.996	3.14	1.721	1.654	-3.87
C10OH	0.334	0.329	-1.41	0.798	0.786	-1.56	1.296	1.256	-3.11
C15	0.359	0.360	0.35	0.874	0.881	0.85	1.450	1.417	-2.30
C12OH	0.377	0.372	-1.28	0.885	0.879	-0.63	1.380	1.403	1.65
C17	0.381	0.384	0.91	0.970	0.974	0.42	1.612	1.595	-1.04
C14OH	0.445	0.443	-0.44	0.992	1.002	0.96	1.550	1.568	1.14
C15OH	0.522	0.523	0.21	1.083	1.072	-1.00	1.633	1.611	-1.33
C20	0.484	0.480	-0.84	1.151	1.158	0.63	1.820	1.840	1.13

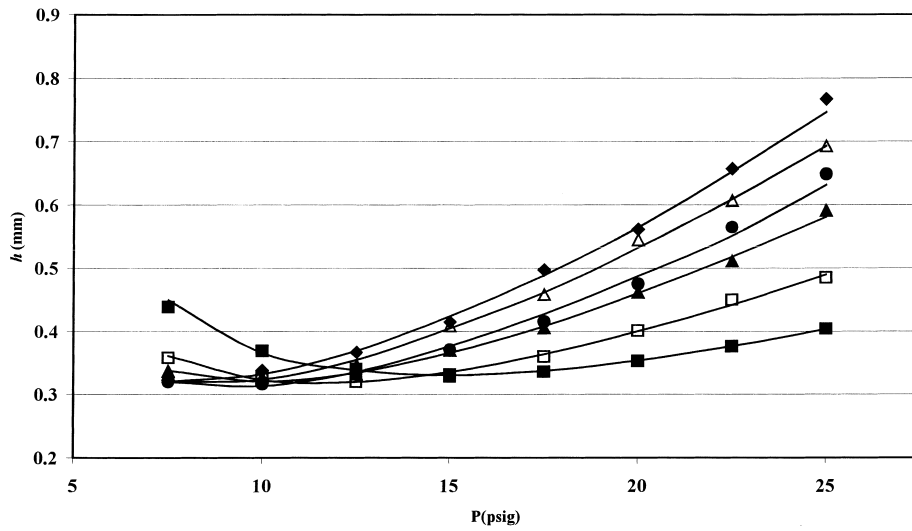


Fig. 5. Behaviour of the experimental (symbols) and calculated (full lines) plate height values for 1-dodecanol at a function of inlet pressure at various column temperatures. Symbols: black rhombi, 100 °C; white triangles, 110 °C; black circles, 120 °C; black triangles, 130 °C; white squares, 140 °C; black squares, 160 °C.

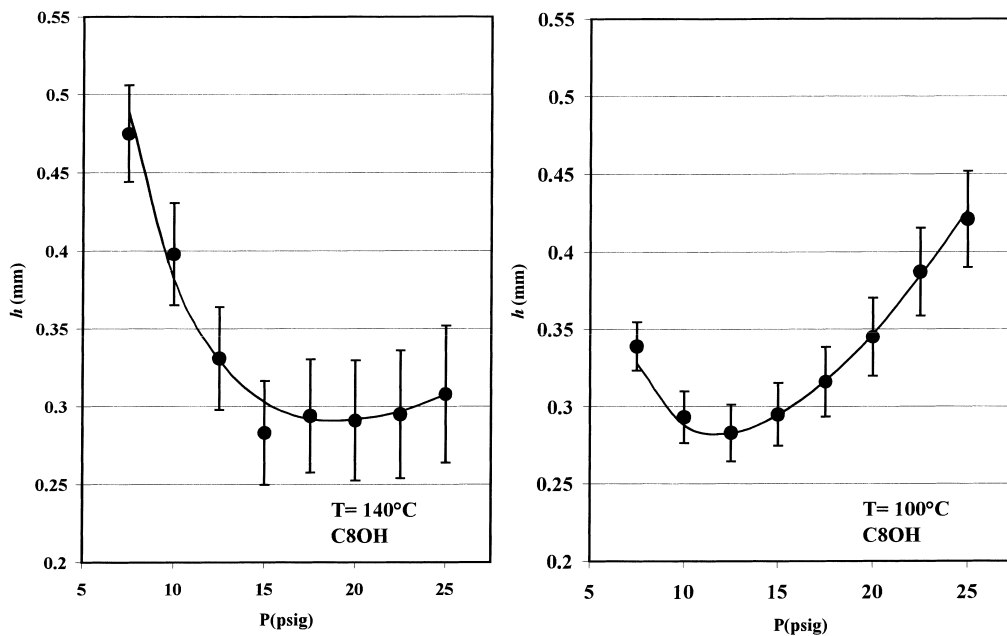


Fig. 6. Fluctuation of the data and errors in the determination of the plate height values by starting from the experimental measurement of the peak width at half height ($b_{1/2}$). The behaviour as a function of inlet pressure is shown at 100 and 140 °C.

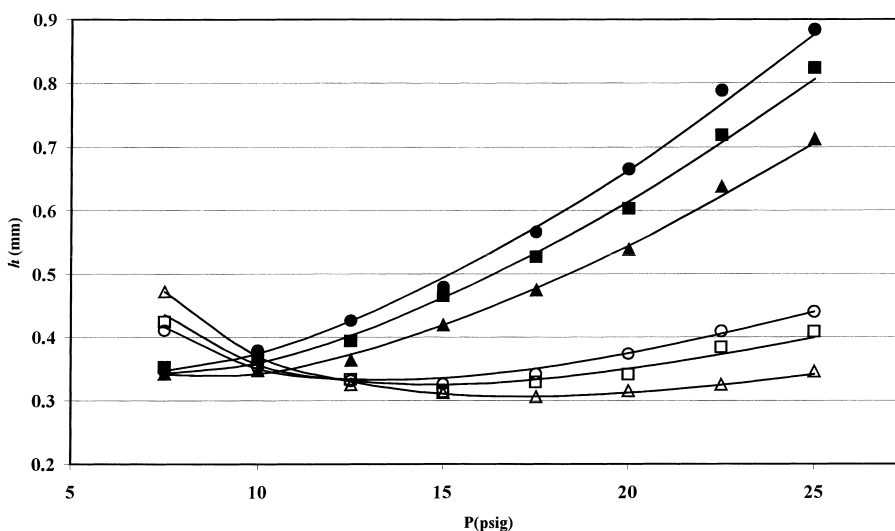


Fig. 7. Example of the behaviour of the plate height for *n*-alkanes as a function of inlet pressure. The data for three *n*-alkanes measured on the DB-1 column at the lowest and at the highest temperature used are shown. Black symbols, 100 °C; white symbols, 160 °C; triangles, C13; squares, C14; circles, C15. The full lines show the behaviour of the calculated values of plate height.

of the same order of magnitude owing to the comparable values of the retention and of the peak shape.

The comparison of the results of Tables 2 and 3 with those of Table 7 shows that two columns having the same length, diameter and stationary phase thickness (DB-1 and Supelcowax-10) may have different efficiency values. Notwithstanding this, and the fact that the elution times of alkanes and alcohols are quite different if measured on the polar or non-polar column, the errors between experimental and calculated values are small and of the same order of magnitude. The different efficiency, due to the characteristics and ageing of the two columns, does not influence the application of the calculation method and the accuracy of the results.

The $E\%$ values shown in Tables 2–7, i.e., the relative difference between h_{exp} and h_{cal} values, are influenced by temperature and inlet pressure, mainly for the compounds with a smaller number of carbon atoms, whose retention times and peak width at high temperatures and high flow-rates are very small. The error in the determination of these parameters does not depend on their small value only, because the Varian Star data system measures the retention time with a sufficient accuracy of ± 0.001 min, and the values of the peak width, measured by the same data

system with an approximation of 0.1 s, not accurate enough for the following calculations, were determined with a greater accuracy with the auxiliary calculation program described in Section 3. The main problem is related to the fact that the peaks of the early eluting compounds are climbing on the tail of the solvent's peak and are therefore distorted and sometimes out of scale. Fig. 6 shows the consequence of this phenomenon: the points shown on the left-hand side plot represent the experimental plate height values of *n*-octanol measured at 140 °C. It can be seen that these points scatter appreciably with respect to the calculated line showing the behaviour of the h_{cal} . On the contrary, the experimental values at 100 °C shown on the right-hand side fit perfectly with the calculated h_{cal} line, as they were obtained by starting from data measured on peaks not or less influenced by the solvent's peak tail. The vertical lines drawn on every experimental point show that the amount of the error in the measurement of the plate height value depends on the inlet pressure and on temperature. The length of these lines, different for each point, was calculated as follows.

If the measured experimental plate height could be expressed as:

$$h = h_o \pm \Delta h \quad (20)$$

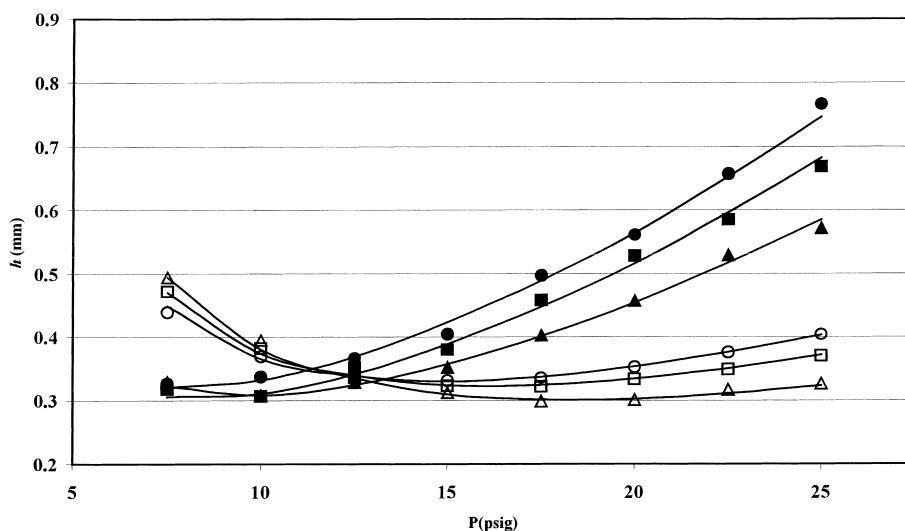


Fig. 8. Example of the behaviour of the plate height for 1-alcohols as a function of inlet pressure. The data for three alcohols measured on the DB-1 column at the lowest and at the highest temperature used are shown. Black symbols, 100 °C; white symbols, 160 °C; triangles, C10OH; squares, C11OH; circles, C12OH. The full lines show the behaviour of the calculated values of plate height.

where h_o is the height equivalent to the theoretical plate calculated with the formula:

$$h_o = \frac{L}{c} \cdot \left(\frac{b_{1/2}}{t_R} \right)^2 \quad (21)$$

then it possible to calculate the value of the indetermination of the h value, Δh , as:

$$\Delta h = \sqrt{\left(\frac{\partial h}{\partial b_{1/2}} \right)^2 \cdot \Delta b_{1/2}^2 + \left(\frac{\partial h}{\partial t_R} \right)^2 \cdot \Delta t_R^2} \quad (22)$$

where

$$\frac{\partial h}{\partial b_{1/2}} = 2 \cdot \frac{L}{c} \cdot \frac{b_{1/2}}{t_R^2} \quad (23)$$

and

$$\frac{\partial h}{\partial t} = -2 \cdot \frac{L}{c} \cdot \frac{b_{1/2}^2}{t_R^3} \quad (24)$$

therefore

$$\Delta h = 2 \frac{h_o}{b_{1/2}} \cdot \sqrt{\Delta b_{1/2}^2 + \frac{c}{L} \cdot h_o \Delta t_R^2} \quad (25)$$

if $\Delta b_{1/2} \cong 0.06$ s; $\Delta t_R \cong 0.06$ s; $c = 5.545$ and $L = 3000$ cm, then the indetermination Δh in the measurement can be approximated as:

$$\Delta h \cong 0.12 \cdot \frac{h_o}{b_{1/2}} \quad (26)$$

A comparison of the behaviour of n -alkanes and linear alcohols is shown in Figs. 7 and 8. Fig. 7 shows as an example the experimental plate height values (points) for three n -alkanes (C13, C14 and C15) measured on the DB-1 column at the lowest (100 °C) and at the highest (160 °C) temperatures used in the experiments. The lines represent the behaviour of the calculated plate height value. These data can be compared with those shown in Fig. 8 for three linear alcohols (C10OH, C11OH, C12OH).

6. Conclusions

The proposed calculation procedure allows the height equivalent to the theoretical plate and the retention time of all the peaks of chromatograms obtained in runs at any inlet pressure to be predicted with suitable accuracy, by starting from data obtained in two or three isobaric runs only. By repeating the procedure with changing temperature, the optimum analysis conditions and the pressure and temperature where the column exhibits the maximum efficiency can be selected without the need for time-

consuming true analyses carried out under different conditions. In this way, the resolution of closely eluting peaks can be easily checked. The pressure-programming rate to be used for keeping the column efficiency constant during temperature-programmed runs can also be calculated.

7. Nomenclature

a, b	constant values of Eq. (3) describing the dependence on temperature of dynamic viscosity η	P_a	atmospheric pressure (dyne cm^{-2})
A, B, C	constant values depending on the solute–solvent interaction at constant pressure (Eq. (6))	P_i	absolute pressure at the column inlet (dyne cm^{-2})
A', B'	coefficients depending on the solute–solvent interaction at constant temperature (Eq. (7))	P_j	pressure in the ΔL_j interval (dyne cm^{-2})
$b_{1/2}$	peak width at half height (s)	R	gas constant
c	constant for the experimental determination of the number of theoretical plates ($c = 5.545$)	r	internal radius of the column (cm)
d_f	thickness of the stationary phase layer (cm)	T	absolute temperature of the column (K)
D_g	diffusion coefficient of a given compound in the gas phase ($\text{cm}^2 \text{s}^{-1}$)	t_M	gas hold-up time (s)
D_s	diffusion coefficient of a given compound in the stationary phase ($\text{cm}^2 \text{s}^{-1}$)	t_R	gross retention time (s)
$E\%$	relative percent error between calculated h_{cal} and experimental h_{exp} plate height	t_{R_e}	experimental retention time used as input data for the calculation (s)
h	plate height	$u_{\text{cg},j}$	overall gas velocity along the column (cm s^{-1})
h_j	plate height in the ΔL_j tract	$u_{e,j}$	velocity of the compound in a column tract of length ΔL_j (cm s^{-1})
h_{exp}	plate height experimentally measured	x_{max}	maximum number of iterations in the program (see Fig. 1)
h_{cal}	calculated plate height	ΔG	free solution energy of a compound from the gas phase to the liquid phase (erg mol^{-1})
k'	mean capacity factor	Δh	error in the experimental determination of the height equivalent to one theoretical plate
L	column length (cm)	ΔH	solution enthalpy (erg mol^{-1})
L_j	length of column covered by the carrier gas starting from the column inlet (cm)	$\Delta L_{\text{cg},j}$	column tract covered by the carrier gas during the time interval Δt (cm)
N	overall number of theoretical plates of the column	ΔL_j	distance covered into the column by a given compound in the time interval Δt (cm)
N_j	number of theoretical plates in the ΔL_j tract	ΔS	solution entropy of the system (erg mol K^{-1})
P	absolute pressure at a generic point along the column (dyne cm^{-2})	Δt	a small time interval during the elution of a given compound (s)
P_o	absolute pressure at the column's outlet (dyne cm^{-2})	β	phase ratio of the column ratio between the volume of the gas and of the liquid phase
		η	dynamic viscosity of the carrier gas (poise)
		ε_o	maximum tolerated least-square error

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