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Prediction of retention times and efficiency in linear gradient programmed pressure analysis on capillary columns

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Abstract

A method for the prediction of the retention time and the resolution of chromatographic peaks in different experimental conditions by starting from few experimental data measured in isothermal and isobaric analyses was published previously. In this paper, the same mathematical model was implemented for calculating the retention times and the column efficiency in programmed pressure runs. Some models originated from the Golay equation and reported in the literature are compared, and a new modified equation for the calculation of the peak width at half height is proposed. The procedure for the prediction of the retention time and the peak width at half height at programmed pressure of the carrier gas and different column temperature and linear gradient by using retention data of different compounds obtained in few isobaric runs is described. The prediction of the retention time and the separation efficiency of compounds with different polarity gave good results for the programmed pressure runs with linear gradient. The effect of the variation of the initial parameters of the experimental analyses and of the mathematical model on the accuracy of the prediction has been evaluated.

Keywords: Capillary columns; Carrier gas; Inlet pressure; Pressure programming; Mathematical models; Plate height; Retention time; Peak width at half height

1. Introduction

The main advantages and disadvantages of pressure programming in capillary gas chromatography were summarised in previously published papers [1–4]. In one of these papers [3], a method for the automatic prediction of retention values in pressure programmed capillary gas chromatography by using as input data the retention times measured under only one isobaric analytical condition was described. 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 peaks closely eluting were narrow enough to permit complete or almost sufficient resolution.

In another paper, by calculation of the diffusion coefficients of the analysed compounds into the mobile and stationary phase [5,6] it was possible to evaluate the column efficiency and predict the retention time and the number of theoretical plates in isobaric run by using the retention times and the half-height widths of the peaks obtained in few isobaric runs.

In this paper, a method for the automatic prediction of programmed pressure retention values and theoretical plate numbers in capillary gas chromatography by using as input data the retention times and the peak width at half height measured under only few isobaric runs is proposed. The mathematical model employs for the calculation of the number of theoretical plates in programmed pressure with linear gradient a modification of the Golay equation [7,8]; the necessity

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of this modification is due to the fact that the simple equation of Golay cannot yield reliable values of the peak width at half height in programmed pressure, whereas it can perform this prediction in isobaric analysis. The suggested modification at the Golay equation does not decrease the accuracy of the prevision in isobaric conditions because the added term assumes in these conditions a value equal to unity leading back to the Golay equation.

The results obtained by applying the proposed mathematical model were moreover compared with those obtained using some equations found in literature. Berezkin et al. [9] compared two equations due to Van Deemter and Golay–Guiochon [10] with the Golay equation on different columns, carrier gas and temperature in isobaric conditions, showing that the Golay–Guiochon equation yields the best fitting with experimental results. In this paper the same equations were used in the mathematical model for the prediction of the efficiency in programmed pressure conditions and were compared with a new modified equation.

2. Theory

2.1. Prediction of the retention times

The gross retention time, t_{R}, of a compound in a capillary gas chromatographic column in isobaric and isothermal condition is:

$$t_{\mathrm{R}} = t_{\mathrm{M}}(1+k) \tag{1}$$

where k is the mean capacity factor and t_{M} is the gas hold-up time or dead time, which depends on the carrier gas, the column temperature and the head pressure as follows [3]:

$$t_{\mathrm{M}}(T, P) = \frac{32\eta(T)L^2}{3r^2} \cdot \frac{P_{\mathrm{i}}^3 - P_{\mathrm{o}}^3}{(P_{\mathrm{i}}^2 - P_{\mathrm{o}}^2)^2} \tag{2}$$

η being the dynamic viscosity of the carrier gas, L the column length, r its internal radius, P_{i} the absolute pressure at the column inlet and P_{o} the absolute pressure at the outlet. The dependence on temperature of η is given by:

$$\eta(T) = aT^b \tag{3}$$

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

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:

$$k(P) = \exp\,(A' \ln\ P + B') \tag{4}$$

where A' and B' are coefficients depending only on the solute–solvent interaction at a constant temperature.

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 them 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:

$$u_{e,j} = \frac{\Delta L_j}{\Delta t} \tag{5}$$

then:

$$L = \sum_{j=1}^{n} \Delta L_j = \sum_{j=1}^{n} u_{e,j}\,\Delta t \tag{6}$$

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

$$u_{e,j} = \frac{u_{\mathrm{cg},j}}{1+k(P_j)} \tag{7}$$

where $u_{\mathrm{cg},j}$ is the carrier gas linear velocity and P_j is the pressure in the ΔL_j interval. The $u_{\mathrm{cg},j}(P)$ can be calculated by using the following equation of the linear gas velocity [3]:

$$u_{\mathrm{cg}} = -\frac{4r^2}{32\eta} \cdot \frac{\mathrm{d}P}{\mathrm{d}L} \tag{8}$$

where $\mathrm{d}P/\mathrm{d}L$ is the change in gas pressure for a change of position $\mathrm{d}L$ along the column.

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

$$u_{\mathrm{cg},j} = \frac{\Delta L_{\mathrm{cg},j}}{\Delta t} \tag{9}$$

by solving Eq. (8) the explicit equation of $\Delta L_{\mathrm{cg},j}$ becomes (see Appendix A):

$$\Delta L_{\mathrm{cg},j} = L \cdot \frac{P_j^2 - \left(P_j^3 - \Delta t \cdot (3r^2(P_{\mathrm{i}}^2 - P_{\mathrm{o}}^2)^2/32L^2\eta)\right)^{2/3}}{P_{\mathrm{i}}^2 - P_{\mathrm{o}}^2} \tag{10}$$

with:

$$P_j = \sqrt{P_i^2 - \frac{L_j}{L}(P_{\mathrm{i}}^2 - P_{\mathrm{o}}^2)} \tag{11}$$

$\Delta L_{\mathrm{cg},j}$ is the column tract travelled by the carrier gas during the time interval Δt and L_j is the length covered by the compound starting from the column inlet. Eq. (6) becomes:

$$L = \sum_{j=1}^{n} \frac{\Delta L_{\mathrm{cg},j}}{1+k(P_j)} \tag{12}$$

From Eq. (12), one can obtain the value of n and therefore the t_{R} in isobaric condition by an iterative calculation procedure:

$$t_{\mathrm{R}} = n\,\Delta t \tag{13}$$

By taking into account the above listed definitions, it is possible to predict, in isothermal conditions, the retention time of a compound in programmed pressure by using the pressure gradient (g_p):

$$g_p = \frac{P_f - P_{in}}{n\,\Delta t} \tag{14}$$

where P_f is the pressure at the column inlet at time t_R and P_{in} is the starting pressure at column inlet. After i time intervals, the inlet pressure on column is:

$$P_i = P_{in} + g_p\,\Delta t\, i \tag{15}$$

When g_p is equal to zero and therefore in isobaric conditions the value of P_i is equal to P_{in}.

During the iterative calculation procedure, for every time interval Δt of Eq. (15) the new pressure P_i is calculated and its value is replaced in Eqs. (10) and (11). With this modification, the t_R in linear pressure programmed run is still obtained with Eq. (13).

2.2. Prediction of the plate height and peak width at half height

The number of theoretical plates of the column, N, is given by [11]:

$$N = 5.54\left(\frac{t_R}{b_{1/2}}\right)^2 \tag{16}$$

where t_R is the retention time and $b_{1/2}$ is the peak width at half height. The height equivalent to a theoretical plate as defined by the Golay equation [7,8] is constant not along the entire column by only in a small tract of length ΔL, and therefore N can be obtained by the sum of n terms, each of them referring to the tract ΔL:

$$N = \sum_{j=1}^{n} N_j = \sum_{j=1}^{n} \frac{\Delta L_j}{h_j} \tag{17}$$

N_j is the number of theoretical plates in the ΔL_j tract and h_j is the corresponding plate height, given by the equation described and discussed in a previous paper [12]:

$$h_j = \frac{2D_g}{u_{cg,j}} + \left[\frac{(1+6k(P_j)+11k(P_j)^2)r^2}{24D_g(1+k(P_j))^2} + \frac{2k(P_j)d_f^2}{3D_s(1+k(P_j))^2}\right] \cdot u_{cg,j} \tag{18}$$

where k is the capacity factor, r the internal radius of the column, P_j the pressure in the ΔL_j interval, $u_{cg,j}$ the carrier gas velocity in the ΔL_j interval, d_f the thickness of the stationary phase layer, D_g and D_s are the diffusion coefficients in the gas and stationary phases, respectively.

Eq. (17) can be applied in any pressure and temperature condition, it is therefore possible to calculate through an iterative calculation procedure [12,13] the number of theoretical plates for any pressure programmed run, and for sake of simplicity Eq. (18) can be summarised as:

$$h_j = \frac{A}{u_{cg,j}} + Bu_{cg,j} \tag{19}$$

Two other equations proposed in the literature have been applied. The first (Golay–Guiochon equation [9,10]) can be summarised as follows:

$$h_j = \frac{A}{u_{cg,j}} + Bu_{cg,j} + Cu_{cg,j}{}^2 \tag{20}$$

The terms A and B are the same of Eqs. (18) and (19) and C is:

$$C = \frac{\sigma_t^2}{(1+k(P))^2 L} \tag{21}$$

where σ_t is the dispersion describing the extra-column band broadening. The second (Van Deemter equation [9]) is:

$$h_j = \frac{A}{u_{cg,j}} + Bu_{cg,j} + E \tag{22}$$

where A and B are the same terms of Eqs. (18) and (19) and E is the eddy diffusion term.

A third equation, also derived as a modification of the Golay equation, has been used:

$$h_j = \left(\frac{A}{u_{cg,j}} + Bu_{cg,j}\right) \cdot \frac{u^o_{cg,j}}{u_{cg,j}} \tag{23}$$

where $u^o_{cg,j}$ is the velocity of the carrier gas in any point of the column if the analysis is carried in isobaric conditions at a pressure identical to the initial value of the gradient run. The same modification was therefore applied to Eqs. (20) and (22) and the equations of the proposed mathematical model, respectively becomes:

$$h_j = \left(\frac{A}{u_{cg,j}} + Bu_{cg,j} + Cu_{cg,j}\right) \cdot \frac{u^o_{cg,j}}{u_{cg,j}} \tag{24}$$

$$h_j = \left(\frac{A}{u_{cg,j}} + Bu_{cg,j} + E\right) \cdot \frac{u^o_{cg,j}}{u_{cg,j}} \tag{25}$$

The use in the model of Eqs. (19), (20), (22)–(25) permits to calculate the value of the height equivalent to the theoretical plate (h_j), the peak width at half height value is obtained by using Eqs. (16) and (17).

3. Experimental

The analyses were carried out on three capillary columns (Varian Associates, Palo Alto, CA, USA). Two non polar columns: a DB-1 (J&W) and a CP Sil 5CB filled with poly(dimethylsiloxane) stationary phase, and a polar column CP Wax 52CB (polyglycol). The length of the columns was 30 m and the phase thickness 0.25 μm. The nominal internal diameter was 0.320 mm, but the true value of this important parameter was measured by scanning electron microscopy (SEM) using a Stereoscan 440 SEM, LEO, Cambridge, UK, and found to be 0.327 mm for DB-1, 0.330 mm for CP Sil 5CB and 0.320 mm for CP WAX 52CB. The columns were installed in a Varian model 3800 gas chromatograph 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 inlet pressure of the column was measured both with the electronic hardware of the gas chromatogram with an accuracy of ±0.1 p.s.i. and with a mercury manometer directly connected to the injector septum by means of a thin needle; the accuracy of this measurements was ±1 mmHg (±133.3 Pa). In the calculation, the pressure values, reported in p.s.i. or p.s.i.g. units in the text and in the tables ($1\,\mathrm{Pa} = 1.45038 \times 10^{-4}$ p.s.i.) being the gas chromatograph's conditions input in this unit, were converted in cgs units (dynes/cm^2) and absolute values. The term p.s.i.g. (pounds per square inch gauge) is used in order to indicate pressure values above the atmospheric pressure. The conversion factor is taken with many decimal figures and the errors depend on the accuracy of the pressure transducer, as discussed at the end of the paper. In the tables and in the figures, we use the p.s.i. values given by the gas chromatograph, and in practice all the results are expressed as a function of the pressure drop along the column, taking into account the fact that the changes of atmospheric pressure have a small influence on the accuracy of the results, as shown below. The column temperature value, controlled and read by the gas chromatograph's software with an approximation of ±1 °C, was checked with an independent thermocouple with an accuracy of ±0.1 °C. The barometric pressure was measures with a good accuracy (0.1 mmHg = 13.3 Pa) with a precision mercury barometer and room temperature correction was applied.

Samples containing several terms of the homologous series of *n*-alkanes, of straight chain 1-alcohols and of some alkenes, chloroalkanes, ketones and others, were injected as pure compounds mixtures at the smaller amount permitted by the use of the microsyringe with the "needle tip" technique in order to obtain peaks of the smallest possible area, near to the detection limit of the used detector and as close as possible to the infinite dilution condition. The analyses were carried out at 80, 100 and 120 °C in the inlet pressure range 5–30 p.s.i.g. at 2.5 p.s.i. intervals for the preliminary isobaric runs and in the same range with different linear gradients in programmed pressure runs. The detector output signal value was sampled by the data system (Varian Star) at intervals of 0.1 s for all the runs, independent on the retention time and peak width.

The following parameters have to be known for the application of the calculation method in order to predict the retention time and peak width at half height values in programmed pressure: 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 and in the initial condition of programmed pressure runs. The Star Data System yields the values of the peak width with an approximation of 0.1 s, not enough accurate for the following calculations. Therefore, an auxiliary calculation program [12] which evaluates the raw data recorded by the data system and measures the horizontal distance between the front and the rear side of the peak at half height with an approximation of 0.06 s was used, increasing the accuracy of the calculated results. 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 retention time and of the plate height as a function of the inlet pressure.

4. Results and discussion

The retention times, t_{Rcalc} calculated as shown in Section 2.1 and the peak width at half height, $b_{1/2\mathrm{calc}}$, calculated with the method described in Section 2.2, were compared with the experimental values obtained on the three capillary columns in programmed pressure runs with linear gradient. The preliminary isobaric runs used for the prevision of all the programmed runs were three (at 5, 15 and 25 p.s.i.g.). Tables 1–3 show, respectively, on the DB-1, CP SIL 5CB and CP WAX 52CB columns the experimental retention times, t_{Rexp}, the calculated retention times, t_{Rcal}, the relative percent error with respect of the calculated values, $E_{\mathrm{rel}}\% = 100\,(t_{\mathrm{Rexp}} - t_{\mathrm{Rcalc}})/t_{\mathrm{Rexp}}$, the experimental peak width at half height, $b_{1/2\mathrm{exp}}$, the difference between experimental and calculated values of peak width at half height, $\Delta b_{1/2} = b_{1/2\mathrm{exp}} - b_{1/2\mathrm{calc}}$, and the absolute peak width difference $\Delta b_{1/2\mathrm{abs\ ave}}$ averaged on all the peaks listed in the table.

The experimental and predicted retention times fairly correspond, whereas different accuracy of the calculated peak width is obtained by the three methods. In the columns a–c of Tables 1–3 are shown the $\Delta b_{1/2\mathrm{calc}}$ values obtained by using in the mathematical model the Golay equation Eq. (19), the Golay–Guiochon equation Eq. (20), the Van Deemter equation applied to capillary columns Eq. (22). The $\Delta b_{1/2\mathrm{abs\ ave}}$ values show that these models are not completely satisfactory because only for small pressure gradients as those shown in Table 2 (0.5 p.s.i./min) the calculated values fit the experimental ones mainly when the Golay equation Eq. (19) is used. The three equations suggested yield accurate results in isobaric condition only, as shown previously [12]. In order to decrease the difference between experimental and calculated values in linearly pressure programmed runs the Golay equation was therefore modified. The added term $u^{\mathrm{o}}_{\mathrm{cg},j}/\mathrm{u}_{\mathrm{cg},j}$ of Eqs. (23)–(25) approaches unity when the pressure gradient decreases, in isobaric conditions the equations become identical to the original equations (Eqs. (19), (20) and (22)) and the results are similar to those obtained with the prediction method used for isobaric conditions analyses [12,13]. The column d of Tables 1–3 shows the results obtained with the modified Golay equation proposed in this work, Eq. (23). The modification introduced to the Golay equation permits

Table 1

Experimental retention time, t_{Rexp} (min); calculated retention time, t_{Rcal} (min); relative percent error, $E_{\mathrm{rel}}\%$; experimental peak width at half height, $b_{1/2\mathrm{exp}}$ (s); difference between experimental and calculated peak width at half height, $\Delta b_{1/2}$ (s), calculated by starting from Eqs. (19), (20), (22)–(25), respectively and the average absolute difference between experimental and calculated peak width at half height, $\Delta b_{1/2\mathrm{abs\ ave}}$ (s), obtained in a pressure programmed run: temperature, 78.1 °C; initial pressure, 5.08 p.s.i.g. and 1 p.s.i./min gradient (756.3 mmHg atmospheric pressure) on DB-1 column (30 m × 0.320 mm, 0.25 μm layer thickness)

Compound	t_{Rexp}	t_{Rcal}	$E_{\mathrm{rel}}\%$	$b_{1/2\mathrm{exp}}$	$\Delta b_{1/2}$					
					a	b	c	d	e	f
					Eq. Golay, Eq. (19)	Eq. Golay–Guiochon, Eq. (20)	Eq. Van Deemter, Eq. (22)	Eq. Golay mod., Eq. (23)	Eq. Golay–Guiochon mod, Eq. (24)	Eq. Van Deemter mod, Eq. (25)
1-Decene	5.787	5.783	0.063	1.779	−0.694	−0.724	−0.694	−0.046	−0.073	−0.046
Nitrobenzene	7.372	7.370	0.027	2.441	−1.016	−1.152	−1.014	0.070	−0.043	0.071
2-Nonanone	7.943	7.945	−0.025	2.425	−1.131	−1.223	−1.131	0.005	−0.075	0.005
Naphthalene	11.012	11.012	0.003	3.158	−1.971	−2.324	−1.867	0.016	−0.259	0.084
1-Nonanol	11.292	11.292	0.003	3.781	−2.279	−2.524	−2.279	0.038	−0.156	0.038
2-Decanone	11.919	11.922	−0.022	3.762	−2.295	−2.455	−2.285	0.058	−0.083	0.065
n-Dodecane	13.273	13.272	0.010	4.326	−2.848	−2.782	−2.848	0.077	0.083	0.077
$\Delta b_{1/2\mathrm{abs\ ave}}$					1.748	1.883	1.731	0.044	0.111	0.055

to predict with fair approximation the value of the peak width at half height in programmed pressure runs.

Columns e and f of Tables 1–3 show the $\Delta b_{1/2}$ values obtained by using the same modification applied on the equations of Golay–Guiochon, Eq. (24) and Van Deemter Eq. (25). The results obtained are similar but, notwithstanding the corrections introduced by the auxiliary terms (*C* and *E* terms) of Eqs. (24) and (25), do not offer an increased accuracy with respect of the modified Golay equation of Eq. (23). In fact, the influence of the added terms *C* and *E* on the Golay–Guiochon and Van Deemter equations is small and does not change appreciably the calculated values of $b_{1/2\mathrm{calc}}$. Moreover, the calculation carried out with the mathematical model by using the modified Golay equation requires a shorter time because the diffusion coefficients in this equation are two only whereas the two other equations require three parameters. The modified Eq. (23), suitable from the point of view of both accuracy and time required for the calculation, has been therefore used for the prediction of the results of analyses carried out at different temperature and initial pressure val-

Table 2

Experimental retention time, t_{Rexp} (min); calculated retention time, t_{Rcal} (min) relative percent error, $E_{\mathrm{rel}}\%$; experimental peak width at half height, $b_{1/2\mathrm{exp}}$ (s); difference between experimental and calculated peak width at half height, $\Delta b_{1/2}$ (s), calculated by starting from Eqs. (19), (20), (22)–(25), respectively and the mean absolute difference between experimental and calculated peak width at half height, $\Delta b_{1/2\mathrm{abs\ ave}}$ (s), obtained in a pressure programmed run: temperature, 118.5 °C; initial pressure, 10.09 p.s.i.g. and 0.5 p.s.i./min gradient (744.7 mmHg atmospheric pressure) on CP Sil 5CB column (30 m × 0.330 mm, 0.25 μm layer thickness)

Compound	t_{Rexp}	t_{Rcal}	$E_{\mathrm{rel}}\%$	$b_{l/2\mathrm{exp}}$	$\Delta b_{I/2}$					
					a	b	c	d	e	f
					Eq. Golay, Eq. (19)	Eq. Golay–Guiochon, Eq. (20)	Eq. Van Deemter, Eq. (22)	Eq. Golay mod., Eq. (23)	Eq. Golay–Guiochon mod, Eq. (24)	Eq. Van Deemter mod, Eq. (25)
n-Octane	1.797	1.793	0.204	0.737	0.108	0.034	0.088	0.062	0.055	0.040
1-Nonene	1.978	1.977	0.067	0.763	0.078	−0.001	0.054	0.032	0.025	0.007
1-Heptanol	2.182	2.182	0.015	0.861	0.075	−0.021	0.044	0.019	0.012	−0.013
2-Octanone	2.268	2.267	0.059	0.879	0.034	−0.020	0.000	0.023	0.015	−0.011
n-Decane	2.378	2.378	−0.014	0.887	0.022	0.002	−0.014	0.022	0.038	−0.014
1-Octanol	2.692	2.692	0.012	1.069	0.110	−0.012	0.064	0.047	0.037	−0.001
2-Nonanone	2.835	2.835	0.000	1.048	0.044	−0.073	−0.007	−0.009	−0.020	−0.062
1-Undecene	2.932	2.932	0.011	1.110	0.033	−0.001	−0.023	0.029	0.054	−0.027
1-Nonanol	3.570	3.570	0.000	1.406	0.058	−0.019	−0.027	0.058	0.066	−0.027
2-Decanone	3.805	3.803	0.044	1.470	0.071	−0.085	−0.024	0.027	0.012	−0.070
1-Dodecene	3.960	3.960	0.000	1.502	0.035	−0.137	−0.068	−0.016	−0.032	−0.122
n-Dodecane	4.108	4.107	0.032	1.578	0.033	−0.131	−0.079	−0.001	−0.017	−0.114
1-Decanol	5.050	5.050	0.000	1.992	0.060	−0.184	−0.111	0.012	−0.008	−0.163
2-Undecanone	5.427	5.427	0.006	2.095	0.002	−0.270	−0.197	−0.045	−0.067	−0.248
1-Tridecene	5.673	5.672	0.024	2.224	0.006	−0.279	−0.214	−0.034	−0.056	−0.256
n-Tetradecane	8.808	8.812	−0.042	3.541	−0.129	−0.670	−0.676	−0.129	−0.125	−0.676
$\Delta b_{1/2\mathrm{abs\ ave}}$					0.056	0.121	0.106	0.035	0.040	0.116

Table 3
Experimental retention time, t_{Rexp} (min); calculated retention time, t_{Rcal} (min); relative percent error, E_{rel}%; experimental peak width at half height, $b_{1/2\text{exp}}$ (s); difference between experimental and calculated peak width at half height, $\Delta b_{1/2}$ (s), calculated by starting from Eqs. (19), (20), (22)–(25), respectively and the mean absolute difference of between experimental and calculated peak width at half height, $\Delta b_{1/2\text{abs ave}}$ (s), obtained in a pressure programmed run: temperature, 98.2 °C; initial pressure, 10.11 p.s.i.g. and 1 p.s.i./min gradient (761.3 mmHg atmospheric pressure) on CP Wax 52CB column (30 m × 0.320 mm, 0.25 μm layer thickness)

Compound	t_{Rexp}	t_{Rcal}	E_{rel}%	$b_{l/2\text{exp}}$	$\Delta b_{1/2}$					
					a	b	c	d	e	*f*
					Eq. Golay, Eq. (19)	Eq. Golay–Guiochon, Eq. (20)	Eq. Van Deemter, Eq. (22)	Eq. Golay mod., Eq. (23)	Eq. Golay–Guiochon mod, Eq. (24)	Eq. Van Deemter mod, Eq. (25)
2-Heptanone	2.485	2.482	0.134	0.919	−0.150	0.012	−0.150	−0.025	0.087	−0.066
n-Tridecane	3.157	3.157	0.011	1.158	−0.171	−0.120	−0.171	−0.017	0.006	−0.042
1-Tridecene	3.587	3.587	0.009	1.292	−0.208	−0.195	−0.204	−0.033	−0.032	−0.040
2-Nonanone	4.177	4.177	0.008	1.490	−0.286	−0.267	−0.255	−0.030	−0.044	−0.034
1-Heptanol	5.062	5.062	0.007	1.877	−0.336	−0.336	−0.299	−0.013	−0.006	0.026
n-Pentadecane	5.948	5.953	−0.090	2.403	−0.538	−0.538	−0.497	−0.016	−0.056	−0.020
1-Pentadecene	7.017	7.022	−0.067	2.828	−0.733	−0.733	−0.687	0.028	−0.072	−0.032
2-Undecanone	8.462	8.462	0.004	3.169	−1.048	−1.049	−1.046	0.057	−0.143	−0.141
1-Hexadecene	10.190	10.192	−0.016	4.431	−1.470	−1.470	−1.422	0.036	−0.061	−0.022
1-Nonanol	10.694	10.692	0.022	3.924	−1.503	−1.504	−1.504	0.022	−0.133	−0.133
n-Heptadecane	12.501	12.500	0.008	5.551	−2.420	−2.420	−2.392	0.036	−0.268	−0.245
1-Decanol	15.636	15.618	0.113	6.174	−3.007	−3.009	−3.008	−0.085	−0.138	−0.137
$\Delta b_{1/2\text{abs ave}}$					0.989	0.971	0.970	0.033	0.087	0.078

ues with various linear pressure gradients. Table 4 shows the experimental and calculated retention times, the relative percent error and the $\Delta b_{1/2}$ values for two programmed runs on the poly(dimethylsiloxane) DB-1 column carried out at the same temperature and initial pressure but with different linear pressure gradients of 0.5 (PP1) and 2.0 (PP2) p.s.i./min, respectively. In both instances the errors of the retention time and the difference between calculated and experimental peak width are very small. Table 5 shows the results obtained by analysing a sample containing more compounds of different polarity on the poly(dimethylsiloxane) column CP SIL 5CB at the same temperature as in Table 4, but with different initial pressure and linear pressure gradients (PP3 and PP4). In this case too, the $\Delta b_{1/2\text{abs ave}}$ values are comparable. Table 6 shows the results of another programmed pressure (PP5) run carried out with the homologous series of *n*-alkanes and 1-alcohols on the same column with a greater gradient (2 p.s.i./min). The analysis on the CP WAX 52 CB column with linear gradient 2 p.s.i./min shown in Table 7 is another example of programmed pressure run (PP6) with a great pressure gradient and the accuracy of the results is fair also when a polar stationary phase is used.

The influence of the variation of the various parameters of the analysis on the calculated t_R and $b_{1/2}$ values has been evaluated by measuring the percent absolute error of the retention time and the $\Delta b_{1/2}$ values averaged on all the compounds analysed on the CP SIL 5CB column when the values of the parameters are changed of the amount that may be due to improper setting of the gas chromatograph or to mistakes or uncertainty in the input of the parameters to the

Table 4
Experimental retention time, t_{Rexp} (min); calculated retention time, t_{Rcal} (min); relative percent error, E_{rel}%; experimental peak width at half height, $b_{1/2\text{exp}}$ (s); difference between experimental and calculated peak width at half height, $\Delta b_{1/2}$ (s), calculated by starting from Eq. (23) and the mean absolute difference between experimental and calculated peak width at half height, $\Delta b_{1/2\text{abs ave}}$ (s), obtained in two pressure programmed run on DB-1 column (30 m × 0.327 mm, 0.25 μm layer thickness)

Compound	PP1					PP2				
	t_{Rexp}	t_{Rcal}	E_{rel}%	$b_{1/2\text{exp}}$	$\Delta b_{1/2}$	t_{Rexp}	t_{Rcal}	$E\%_{\text{rel}}$	$b_{l/2\text{exp}}$	$\Delta b_{1/2}$
1-Decene	4.897	4.893	0.075	1.731	−0.014	3.527	3.527	0.009	0.992	−0.018
Nitrobenzene	6.073	6.070	0.049	2.491	−0.068	4.235	4.235	0.000	1.318	0.054
2-Nonanone	6.280	6.278	0.027	2.298	0.000	4.355	4.357	−0.038	1.228	−0.010
Naphthalene	8.390	8.385	0.060	2.954	−0.072	5.573	5.578	−0.096	1.597	−0.038
1-Nonanol	8.657	8.652	0.062	3.120	0.068	5.728	5.727	0.023	1.629	0.063
2-Decanone	8.892	8.883	0.097	2.954	−0.080	5.860	5.857	0.057	1.663	0.062
n-Dodecane	9.769	9.755	0.143	3.143	−0.064	6.353	6.348	0.073	1.871	0.092
$\Delta b_{1/2\text{abs ave}}$					0.052					0.048

PP1: temperature, 98.2 °C; initial pressure, 5.07 p.s.i.g.; pressure gradient, 0.5 p.s.i./min; atmospheric pressure, 779.5 mmHg. PP2: temperature, 98.2 °C; initial pressure, 5.08 p.s.i.g.; pressure gradient, 2 p.s.i./min; atmospheric pressure, 750.05 mmHg.

Table 5
Experimental retention time, t_{Rexp} (min); calculated retention time, t_{Rcal} (min); relative percent error, E_{rel}%; experimental peak width at half height, $b_{1/2\text{exp}}$ (s); difference between experimental and calculated peak width at half height, $\Delta b_{1/2}$ (s), calculated by starting from Eq. (23) and the mean absolute difference between experimental and calculated peak width at half height, $\Delta b_{1/2\text{abs ave}}$ (s), obtained in two pressure programmed run on CP SIL 5CB column (30 m × 0.333 mm, 0.25 μm layer thickness)

Compound	PP3					PP4				
	t_{Rexp}	t_{Rcal}	E_{rel}%	$b_{l/2\text{exp}}$	$\Delta b_{1/2}$	t_{Rexp}	t_{Rcal}	$E\%_{\text{rel}}$	$b_{l/2\text{exp}}$	$\Delta b_{1/2}$
n-Octane	3.365	3.363	0.050	1.365	−0.022	1.843	1.842	0.072	0.687	0.042
1-Nonene	3.905	3.905	0.000	1.491	−0.083	2.158	2.157	0.062	0.743	−0.043
1-Heptanol	4.537	4.533	0.081	1.765	−0.091	2.530	2.528	0.066	0.910	−0.021
2-Octanone	4.773	4.772	0.028	1.809	−0.068	2.672	2.670	0.075	0.955	−0.012
n-Decane	5.117	5.117	0.007	1.819	−0.077	2.877	2.877	0.012	1.033	−0.005
1-Octanol	6.087	6.088	−0.022	2.241	−0.056	3.467	3.465	0.058	1.253	−0.041
2-Nonanone	6.477	6.480	−0.046	2.297	−0.072	3.705	3.707	−0.045	1.363	−0.018
1-Undecene	6.772	6.773	−0.020	2.332	−0.076	3.887	3.888	−0.034	1.425	−0.038
1-Nonanol	8.683	8.685	−0.023	2.969	−0.062	5.087	5.087	0.007	1.902	−0.072
2-Decanone	9.287	9.292	−0.050	3.103	−0.007	5.470	5.473	−0.061	2.059	−0.047
1-Dodecene	9.745	9.747	−0.017	3.170	−0.076	5.762	5.765	−0.052	2.247	−0.043
n-Dodecane	10.170	10.173	−0.033	3.344	−0.040	6.037	6.040	−0.050	2.333	−0.072
1-Decanol	12.809	12.812	−0.021	4.144	−0.105	7.762	7.760	0.026	3.090	−0.105
2-Undecanone	13.709	13.717	−0.056	4.388	−0.045	8.357	8.360	−0.036	3.290	−0.112
1-Tridecene	14.388	14.383	0.032	4.654	0.028	8.802	8.802	0.004	3.547	−0.107
n-Tetradecane	22.275	22.268	0.030	7.265	0.114	14.154	14.150	0.028	6.331	−0.014
$\Delta b_{1/2\text{abs ave}}$					0.064					0.049

PP3: temperature, 98.2 °C; initial pressure, 5.07 p.s.i.g.; pressure gradient, 0.5 p.s.i./min; atmospheric pressure, 744.7 mmHg. PP4: temperature, 98.2 °C; initial pressure, 10.07 p.s.i.g.; pressure gradient, 1 p.s.i./min; atmospheric pressure, 769.0 mmHg.

mathematical model. Three preliminary isobaric runs were carried out repeatedly with the following conditions: temperature 118.5 °C; inlet pressure values 5.07, 15.10, 25.09 p.s.i.g. and atmospheric pressure 744.7 mmHg; the parameters of the equation used for the calculation of the retention times (Eq. (13)) and of the h_j and then of the peak width (Eq. (23)) were determined by using the experimental data obtained in these analyses. Some programmed pressure runs with the following conditions were then carried out: temperature, 118.5 °C; atmospheric pressure, 744.7 mmHg; initial column pressure, 10.09 p.s.i.g., pressure gradient, 0.5 p.s.i./min, and the experimental values of t_R and $b_{1/2}$ were compared with those calculated starting from input values identical to the experimental ones. The results are shown in Table 2.

The parameters input to the program have been then modified as follows:

Table 6
Experimental retention time, t_{Rexp} (min); calculated retention time, t_{Rcal} (min); relative percent error, E_{rel}%; experimental peak width at half height, $b_{1/2\text{exp}}$ (s); difference between experimental and calculated peak width at half height, $\Delta b_{1/2}$ (s), calculated by starting from Eq. (23) and the mean absolute difference between experimental and calculated peak width at half height, $\Delta b_{1/2\text{abs ave}}$ (s), obtained in a programmed run (PP5) on CP Sil 5CB column (30 m × 0.330 mm, 0.25 μm layer thickness)

Compound	PP5				
	t_{Rexp}	t_{Rcal}	E_{rel}%	$b_{1/2\text{exp}}$	$\Delta b_{1/2}$
n-Octane	2.568	2.560	0.312	0.754	−0.057
1-Hexanol	2.752	2.750	0.073	0.865	−0.002
n-Nonane	2.968	2.965	0.101	0.856	−0.019
1-Heptanol	3.307	3.307	0.010	0.997	0.030
n-Decane	3.662	3.660	0.055	1.024	0.000
1-Octanol	4.242	4.245	−0.071	1.213	0.043
n-Undecane	4.798	4.800	−0.042	1.347	0.003
1-Nonanol	5.742	5.745	−0.052	1.654	0.056
n-Dodecane	6.578	6.577	0.020	1.990	0.105
$\Delta b_{1/2\text{abs ave}}$					0.035

Temperature, 98.2 °C; initial pressure, 5.07 p.s.i.g.; pressure gradient, 2 p.s.i./min; atmospheric pressure, 760.7 mmHg.

Table 7
Experimental retention time, t_{Rexp} (min); calculated retention time, t_{Rcal} (min); relative percent error, E_{rel}%; experimental peak width at half height, $b_{1/2\text{exp}}$ (s); difference between experimental and calculated peak width at half height, $\Delta b_{1/2}$ (s), calculated by starting from Eq. (23) and the mean absolute difference between experimental and calculated peak width at half height, $\Delta b_{1/2\text{abs ave}}$ (s), obtained in a programmed run (PP6) on CP Wax 52CB column (30 m × 0.3295 mm, 0.25 μm layer thickness)

Compound	PP6				
	t_{Rexp}	t_{Rcal}	E_{rel}%	$b_{l/2\text{exp}}$	$\Delta b_{1/2}$
2-Heptanone	2.917	2.920	−0.103	1.011	−0.025
n-Tridecane	3.253	3.257	−0.113	0.957	−0.017
1-Tridecene	3.477	3.483	−0.182	0.967	−0.033
2-Nonanone	3.805	3.808	−0.088	1.094	−0.030
1-Heptanol	4.168	4.172	−0.088	1.206	−0.013
n-Pentadecane	4.578	4.580	−0.044	1.228	−0.016
1-Pentadecene	5.070	5.075	−0.099	1.403	0.028
2-Undecanone	5.787	5.788	−0.023	1.565	0.057
1-Hexadecene	6.432	6.433	−0.021	1.815	0.036
1-Nonanol	6.618	6.618	−0.005	1.731	0.022
n-Heptadecane	7.353	7.352	0.018	2.117	0.036
1-Decanol	8.628	8.618	0.112	2.157	−0.085
$\Delta b_{1/2\text{abs ave}}$					0.033

Temperature, 118.5 °C; initial pressure, 5.07 p.s.i.g.; pressure gradient, 2 p.s.i./min; atmospheric pressure, 761.4 mmHg.

(1) Atmospheric pressure: ±20 mmHg; the barometric pressure was measured with a good accuracy (0.1 mmHg) but the daily or weekly average fluctuation observed was as high as 20 mmHg owing to weather changes. Therefore, if it is not available a precision barometer or the operator does not take into account the true atmospheric pressure (and this is the case of instrument software which takes the outlet column pressure as a constant and equal to 760 mmHg) differences between the true outlet pressure and the nominal one as high as ±20 mmHg can be observed. For this reason we used this value in for evaluating the importance of the accuracy of the parameters' setting and found (see below) that this fluctuations has a minor importance on the accuracy of the results as a variation of ±20 mmHg leads to a very low average error.

(2) Initial pressure: ±0.1 p.s.i., range corresponding to the uncertainty in the pressure input to the gas chromatograph's hardware; the differences between the true and the input initial pressure value of 0.1 p.s.i. was taken as equal to the error given by the instrument, notwithstanding the fact that better accuracy was obtained with the mercury manometer connected to the injector (1 mmHg equivalent to 133.3 Pa or 0.0193 p.s.i.).

(3) Pressure gradient: ±0.1 p.s.i./min; it was not possible to measure with independent technique the difference between preset and true pressure values during pressure programming, because the mercury manometer which give good accuracy when measuring the initial pressure, has a too long equilibration time and cannot follow correctly quick pressure changes. It was supposed that the error of the built-in electronic pressure transducer during programmed pressure runs is of the same order of magnitude of the measurement of isobaric pressure, i.e. 0.1 p.s.i.

(4) Column temperature: ±2 °C; this was the maximum difference observed in several runs between the values input to the gas chromatograph and these measured with the independent thermocouple.

(5) Internal diameter of the column: ±0.01 mm, corresponding to the average difference between the nominal i.d. value given by the producer and the values measured by SEM.

Fig. 1 shows the values of the absolute percent error averaged on the t_R values of all the 16 compounds listed in Table 2, analysed on the CP SIL 5CB column when the initial conditions are changed as shown above. The errors are very small when the changed parameters are the column temperature, the internal diameter and the atmospheric pressure because the coefficients A' and B' of the capacity factor (Eq. (4)) are modified both in the calculation of the preliminary isobaric analyses and of the pressure programmed runs, and this minimises the overall deviation of the results. On the contrary, the errors are much greater when the initial pressure and the pressure gradient are changed, because these parameters influence the results predicted in programmed pressure runs only. When the pressure programmed and the isobaric preliminary runs are evaluated by using the nominal parameters, i.e. the values input to the gas chromatograph during the experimental runs, the mathematical model predicts the retention times with errors of the same order of magnitude of the experimental fluctuations between different runs carried out in the same experimental conditions, because the errors are influenced in the same way by the capacity factor and by the diffusion coefficients.

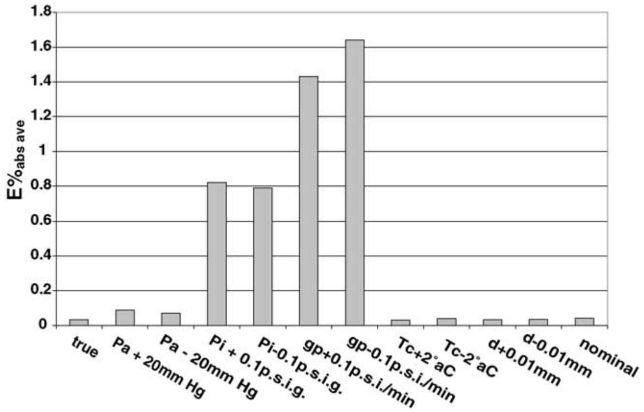

Fig. 1. Effect of changing the various analytical parameters on the accuracy of the retention time prediction on CP Sil 5CB column in a programmed run: temperature, 118.5 °C; initial pressure, 10.09 p.s.i.g. and 0.5 p.s.i./min gradient (atmospheric pressure 744.7 mmHg). The values of the absolute percent error averaged on the t_R values of all the 16 compounds listed in Table 2 are shown.

Fig. 2 shows the averaged difference between the experimental and calculated values of the width at half height obtained in the same conditions as above. The difference is almost constant ranging between 0.03 and 0.04% when all the parameters, except the pressure programming rate, are

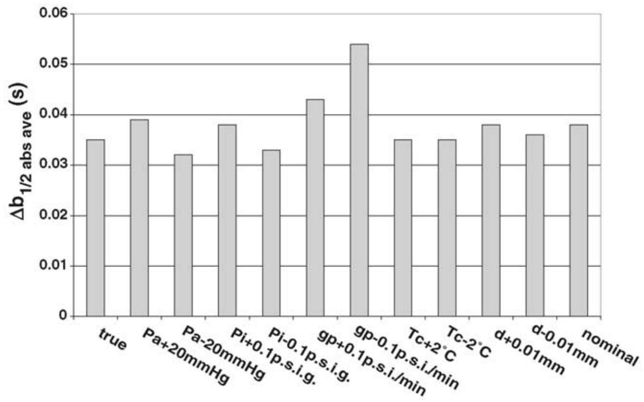

Fig. 2. Effect of changing the various analytical parameters on the accuracy of the peak width at half height prediction on CP Sil 5CB column in a programmed run: temperature, 118.5 °C; initial pressure, 10.09 p.s.i.g. and 0.5 p.s.i./min gradient (atmospheric pressure 744.7 mmHg). The values of the average absolute difference between experimental and calculated peak width at half height, $\Delta b_{1/2\text{abs ave}}$ (s) values of all the 16 compounds listed in Table 2 are shown.

changed as shown above, because the calculation method evaluates the number of theoretical plates in a constant interval Δt, corresponding to $\Delta L/h$ (Eq. (17)). The amount of the error is therefore distributed between the two terms (ΔL and h) and the mean plate number does not change. On the contrary, the retention time is evaluated in terms of ΔL values only and the error is not compensated. The effect of the pressure gradient is a little greater, according with the effect on the retention times shown in Fig. 1.

As the change of the initial pressure or programming gradient or the wrong input of these parameters to the mathematical model has an effect much greater than changing other parameters, the values of these parameters, given by the built-in pressure measuring devices of some instruments with an approximation of ±0.1 p.s.i., are not accurate enough to permit the correct application of the method. More accurate measurement of the true pressure, with an external mercury manometer or other device may be therefore necessary. In any case, in order to obtain good results with the proposed method, the correspondence of the instrument settings to the true values must be checked periodically.

5. Conclusions

The iterative calculation procedure suggested offers a fair accuracy for the prediction of the retention times both in isobaric and pressure programmed analyses. The Golay equation yields accurate results in the prediction of the peak width of gas chromatographic runs carried out at constant inlet pressure, but cannot predict the behaviour of the analyses in programmed pressure conditions and therefore other mathematical models have to be investigated. In order to check the possibility of a better approximation, the Golay equation has been replaced with the Golay-Guichon and Van Deemter equations reported in the literature but, as this solution did not improve the accuracy, the Golay equation was modified with a linear term proportional to the programming rate which becomes equal to unity in isobaric conditions, coming back to the unmodified Golay equation.

If the same procedure is applied to the Van Deemter and Golay–Guiochon equations, the model leads to acceptable differences between the experimental and calculated $b_{1/2}$ values, slightly greater than those obtained with the modified Golay equation, but the calculation time greatly increases. The proposed mathematical model permits therefore to predict with fair approximation the retention values and to evaluate the plate height, the peak width and the efficiency of capillary columns in any condition of programmed pressure linear gradient, by using as the input data only the experimental results of three analyses carried out in isobaric conditions selected within the pressure range of the programmed runs. The parameters whose variation mainly influences the accuracy of the results are the initial pressure value and the pressure programming gradient.

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Appendix A

The complete procedure followed in order to obtain Eq. (10) by starting from Eq. (8) is described below. Some equations were described and discussed previously [14,15]:

$$-\frac{\mathrm{d}P}{\mathrm{d}\ell} = \frac{32\eta}{4r^2}u \tag{A.1}$$

This equation is valid for the permanent isothermal motion of a gas; also the continuity equation for the conservation of the mass flow rate is considered:

$$Q_\mathrm{M} = \rho\Omega u = \cos\ t \tag{A.2}$$

where ρ is the gas density, Ω the area of the column section and Q_M is the mass flow rate; also the state equation for gases is taken into account:

$$\frac{P}{\rho} = \frac{R}{n}T \tag{A.3}$$

where R is the gas constant, T the absolute temperature and M is the mass of one kilomole of gas.

From Eqs. (A.2) and (A.3):

$$\{Pu\} = A = \cos\ t \tag{A.3$'$}$$

i.e. the product of the carrier gas velocity and of the pressure in a given point along the column is a constant value in isothermal conditions at a constant inlet pressure P_i, then Eq. (A.1) becomes:

$$-\frac{\mathrm{d}P}{\mathrm{d}\ell} = \frac{32\eta}{4r^2}\frac{A}{P} \tag{A.4}$$

and, by integration:

$$-\frac{1}{2}P^2 = \frac{32\eta}{4r^2}\cdot A\ell + K_1 \tag{A.5}$$

where ℓ is a given distance from the column inlet, P the pressure in the same point and K_1 is a constant. If for $\ell = 0$, the pressure value is P_i, then from Eq. (A.5):

$$K_1 = -\frac{1}{2}P_1^2 \tag{A.6}$$

Eq. (A.5) therefore becomes

$$-\frac{1}{2}P^2 = \frac{32\eta}{4r^2}A\ell - \frac{1}{2}P_1^2 \tag{A.7}$$

or, taking into account Eq. (A.3′):

$$-\frac{1}{2}P^2 = \frac{32\eta}{4r^2}\cdot\{Pu\}\ell - \frac{1}{2}\cdot P_1^2 \tag{A.8}$$

but, by definition $u = \mathrm{d}\ell/\mathrm{d}t$ and Eq. (A.8) becomes

$$\mathrm{d}t = \frac{16\eta}{r^2} \cdot \frac{P}{P_\mathrm{i}^2 - P^2} \cdot \ell\,\mathrm{d}\ell \tag{A.9}$$

If Eq. (A.4) is directly integrated between 0 and L and between P_i and P_o, Eq. (A.10) is obtained.

$$Pu = \frac{r^2(P_\mathrm{i}^2 - P_\mathrm{o}^2)}{16\eta L} \tag{A.10}$$

From Eqs. (A.10) and (A.8), the following equation is obtained:

$$P^2 = P_\mathrm{i}^2 - \frac{\ell}{L} \cdot (P_\mathrm{i}^2 - P_0^2) \tag{A.11}$$

then:

$$P_\mathrm{i}^2 - P^2 = \frac{\ell}{L}(P_\mathrm{i}^2 - P_0^2) \tag{A.12}$$

By replacing Eq. (A.12) into Eq. (A.9):

$$\mathrm{d}t = \frac{16\eta L}{r^2} \cdot \frac{P}{P_\mathrm{i}^2 - P_0^2} \cdot \mathrm{d}\ell \tag{A.13}$$

By obtaining P from Eq. (A.11), replacing it in Eq. (A.13) and integrating Eq. (A.13) between t_1 and t_2 and between ℓ_1 and ℓ_2 the following equation is obtained:

$$\Delta t = t_2 - t_1 = \frac{2}{3} \cdot \frac{16\eta L^2}{r^2(P_\mathrm{i}^2 - P_\mathrm{o}^2)^2} \cdot \left[\left(P_\mathrm{i}^2 - \ell_1 \cdot \frac{P_\mathrm{i}^2 - P_\mathrm{o}^2}{L}\right)^{3/2} - \left(P_\mathrm{i}^2 - \ell_2 \cdot \frac{P_\mathrm{i}^2 - P_\mathrm{o}^2}{L}\right)^{3/2}\right] \tag{A.14}$$

But:

$$P_\mathrm{i}^2 = P_1^2 + \frac{\ell_1}{L} \cdot (P_\mathrm{i}^2 - P_\mathrm{o}^2) \tag{A.15}$$

where P_1 is the pressure in the point ℓ_1. From Eqs. (A.14) and (A.15):

$$\Delta t = \frac{2}{3} \frac{16\eta L^2}{r^2(P_\mathrm{i}^2 - P_\mathrm{o}^2)} \cdot \left\{P_1^3 - \left[P_1^2 - \frac{\Delta\ell}{L} \cdot (P_\mathrm{i}^2 - P_0^2)\right]^{3/2}\right\} \tag{A.16}$$

where $\Delta\ell = \ell_1 - \ell_2$.

Obtaining $\Delta\ell$ from Eq. (A.16):

$$\Delta\ell = \frac{L}{P_\mathrm{i}^2 - P_\mathrm{o}^2} \cdot \left\{P_1^2 - \left[P_1^3 - \Delta t(P_\mathrm{i}^2 - P_\mathrm{o}^2) \cdot \frac{3}{2} \cdot \frac{r^2}{16\eta L^2}\right]\right\} \tag{A.17}$$

Eq. (A.17) is formally identical to Eq. (10) of the text, with the correspondence of the symbols

$$\Delta\ell = \Delta L_{\mathrm{cg},j} \quad \text{and} \quad P_1 = P_j.$$

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