Automatic prediction of retention times in programmed-pressure isothermal gas chromatography

S. Vezzani, D. Pierani, P. Moretti, G. Castello*

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

Abstract

A method for the prediction of the retention times of the compounds analysed during programmed-pressure gas chromatography with capillary columns is described. The method can be applied to analyses carried out with different pressure profiles: constant linear programming rate, initial and final isobaric tract. Only one preliminary isobaric run is necessary in order to find the input data which permit to obtain accurate results. The effects of the various parameters of the analysis on the accuracy of the predicted values were investigated. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The techniques of programming the column temperature during gas chromatographic analysis are well established and permit to reduce the analysis time and increase the boiling point range of the sample. In many cases, almost the same effects can also be achieved by programming the flow-rate of the carrier gas increasing the inlet pressure of the column stepwise or continuously. During this operation, the temperature of the column may either be kept constant or the two methods can be combined and both the temperature and the flow-rate programmed during the analysis. The first application of this method, which provides a fairly large flexibility in the solution of separation problems [1], was proposed in 1959 when Lipsky et al. [2] and at the same time Wolff and Wolff [3,4] applied a step

programming of the carrier gas inlet pressure to reduce separation time in the analysis of fatty acid esters. Two years later, Valussi and Cofleri [5,6] demonstrated the advantage of increasing the carrier gas inlet pressure during the analysis of natural fatty acid samples, emphasized that the accuracy of the analysis remained the same as observed in isorheic analysis and reported results obtained by using linearly programmed carrier gas flow-rate. Morgantini [7] who, for the first time used the term ''programmed flow gas chromatography'', described a device which permitted the linear programming of the carrier gas flow-rate and discussed some theoretical aspects of the technique.

An important contribution to the advancement of the technique can be found in the book published by Purnell in 1962 [8]. As stated by him ''this approach 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 HETP vs. *u* were employed, flow

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*Corresponding author. Fax: +39-10-3536-199.
E-mail address: castello@chimica.unige.it (G. Castello)

changes of up to an order of magnitude might be employed in a single run without much loss of efficiency'' (HETP=height equivalent to a theoretical plate). All the early workers employed pressure or flow programming to speed up the analysis. Another approach which also led to the suggestion of flow programming was taken by Scott [9]. His conclusion was that if the carrier gas flow-rate were increased during analysis, peak symmetry could be improved. In a later paper [10] Scott described a unit constructed for flow programming. Another treatment of the theoretical aspects of the utilization of stepwise programming was published by Vergnaud [11]. Costa Neto et al. [12,13] published some detailed investigations on the influence of changes in the carrier gas flow-rate on various parameters and demonstrated the potentialities of this technique. Other authors reported various theoretical and practical aspects of the technique [14–20]. Although the published papers clearly defined the technique of programmed flow gas chromatography and even considered the theoretical and instrumental aspects, a general view on the evolution of this method was not easily available. The reason for this is probably that the papers dealt primarily with applications of gas chromatography to different kinds of samples, and the application of the technique was not evident from the title or summary; except for the paper of Lipsky et al. [2]. In the book ''Advances in Gas Chromatography'' [1] a review of the papers available up to the year 1968 can be found.

In 1964–1965 the first commercial pressure programming units became available, but the development of gas chromatographs equipped for pressure programming was partly abandoned because of the impossibility of monitoring exactly the flow-rate change during pressure programming. Today, instead, some instruments equipped with electronic pressure controller are able to follow with precision the stepwise change of pressure in the column during the analyses.

The main advantages of pressure programming can be summarized as follows [1,21]:

1. It shortens the analysis time for wide molecular mass range mixtures while permitting the operations of the column at a lower temperature.
2. Since the analysis is at lower temperature, the bleeding of the liquid phase is significantly less. It should be kept in mind that column bleeding increases exponentially with temperature while only linearly with flow-rate.
3. Because of the lower temperature, the number of liquid phases applicable to a given problem is increased.
4. Lower column temperature reduces the possibility of decomposition of thermally unstable samples.
5. Since the height of a peak is related to the flow-rate, broad peaks which would emerge later will be much sharper allowing for better detection of small concentration.
6. Since the pressure of the gas in the column can be changed instantaneously and equilibrium can be reached in a very short time, resetting of the original starting conditions after a programmed run can be accomplished instantaneously, and no lengthy cooling-off period is necessary.
7. In practical analysis the flow-rates are almost always higher than the optimum value corresponding to the minimum of the Van Deemter curve. On the other hand, if pressure programming is used, the conditions can be adjusted so that the flow-rate at the critical separations (usually in the earlier part of the chromatogram) is low, close to the optimum, but it is increased successively and thus the overall analysis time will still be equal to or shorter than that of the run with constant flow-rate.

Like any method, pressure programming also has some disadvantages: (1) pressure programming decreases column efficiency for the later eluting peaks. Fortunately, however, the critical separations are usually in the earlier part of the chromatogram, where the flow-rate is still close to the optimum; in fact, as mentioned above, it might be closer than it would be in a practical constant flow run. Besides this, where the Van Deemter plot (HETP vs. u) is fairly flat, the reduction in efficiency is not too significant. (2) Another disadvantage concerns the instrumentation, since in the past the pressure was controlled by an external instrument and the dead volume of the connecting tubes may retard the action of the programmer. Only in the last years, many chromatographs are equipped with electronic pressure controller which permit to obtain good reproducibility.

In this paper, a method for the automatic prediction of programmed pressure (PP) retention values in capillary gas chromatography (GC) by using as input

data retention times measured under only one iso-baric analytical condition is proposed. To predict the retention of the components of a sample in all possible programmed runs permits one to select the best conditions for the separation of closely eluting compounds. In previous papers [22] the prediction of retention values during temperature programming was described, however, some difficulties arise if high temperature must be reached when the compound to be analyzed are thermally unstable. Further, as the polarity of some columns changes with changing temperature [23–26], pressure programming in isothermal conditions decreases the possibility of inversion of the elution order of some compounds.

One of the advantages of the calculation method for the prediction of retention data during isothermal pressure programming is that it only depends on the exact knowledge of the inlet, outlet and atmospheric pressure and on the constancy of temperature, whereas the prediction of the retention during temperature programming is influenced not only by the inlet and outlet pressure, but also by the change of carrier gas viscosity with temperature. Moreover, for the prediction in programmed temperature analysis, the effective carrier gas hold-up time $t_M(T)$ must be calculated with precision because it changes with temperature, whereas in isothermal pressure programming this evaluation is not necessary.

2. Theory

The general equations used for the prediction of t_R values in a programmed run are [22,27–30]:

$$g = \int_{P_i}^{P_f} \frac{dP}{t_R(P)} \tag{1}$$

and

$$g = \frac{P_f - P_i}{t_R(\pi)} \tag{1a}$$

where $P_i \leq \pi \leq P_f$; g is the pressure gradient; P_i and P_f are the initial and final inlet pressure of the linear tract of pressure program and $t_R(P)$ is the function which represents the dependence of the retention time of a given compound on the pressure change:

$$t_R(P) = t_M(P) \cdot (1 + k) \tag{2}$$

where $t_M(P)$ is the function of the change of gas hold-up time depending on pressure and k is the capacity factor, independent on pressure and only dependent on the phase–compound interaction and on temperature. It is most important that both the reference isobaric runs used to establish the input data for the prediction program and the various pressure programmed runs are done at the same temperature because the capacity factor depends on the absolute column temperature, T, according to the following equation:

$$k(T) = \exp\left(\frac{A}{T} + B + CT\right) \tag{3}$$

where A, B and C are constants linked to thermodynamic parameters. Therefore incorrect knowledge of temperature would result in a large error. The relationship of $t_M(P)$ can be calculated by using the following equation of the linear gas velocity [22,29–33]:

$$u = -\frac{4r^2}{32\eta} \cdot \frac{dp}{dl} \tag{4}$$

where: r is the internal column radius (cm); u is the linear gas velocity (cm/s); η is the dynamic viscosity of the carrier gas (poise) and dp/dl is the change in gas pressure for a change of position dl along the column.

Solving Eq. (4) as shown in Refs. [22,29–33], the explicit equation of t_M becoms:

$$t_M(P_{il}) = \frac{z}{(P_{iL}^2 - P_o^2)^2}$$
$$\cdot \left\{ P_{il}^3 - \left[P_{il}^2 - \frac{l}{L} \cdot (P_{iL}^2 - P_o^2) \right]^{3/2} \right\} \tag{5}$$

with:

$$P_{il}^2 = P_{iL}^2 - \frac{l_x}{L} \cdot (P_{iL}^2 - P_o^2) \tag{6}$$

where L, is the column length (cm); P_{iL} is the column inlet pressure, absolute (p.s.i.g.); P_o is the column outlet pressure, absolute (p.s.i.g.); l_x is the tract of the column, starting from its head, covered by a compound at a given time (cm); P_{il} is the absolute pressure in the column at l_x position (p.s.i.g.); $l \leq L - l_x$, is the tract of the column, starting

from the point l_x covered by the carrier gas in a given time (cm).

The term z of Eq. (5) is given by:

$$z = \frac{2}{3} \cdot \frac{16\eta L^2}{r^2} \tag{7}$$

The dynamic viscosity, η, of the carrier gas changes with temperature [34–36] but at values below 70 p.s.i.g. its dependence on pressure is negligible; η can be predicted by using the following relationship:

$$\eta(T) = \alpha T^{\beta} \tag{8}$$

where T is the temperature in K, α and β are constants dependent on the carrier gas used, respectively 5.024 and 0.648 for helium.

In the program and in the following discussion all the pressure values of the carrier gas are expressed in p.s.i.g. because the softwares of the available gas chromatographs show the pressure values in this unit, whereas the atmospheric pressure P_a is given, as generally used, in millimeters of mercury or Torr (1 p.s.i. = 51.7149 mmHg = 6894.76 Pa). The pressure profiles of the types of PP analyses that were taken into account in order to evaluate the accuracy and precision of the prediction method are shown in Fig. 1, where the flow-chart of the different calculation methods used depending on pressure profile is also reported. The total PPt_R is the sum of the retention times of the compound during the initial isobaric tract, in the programmed pressure tracts with one pressure gradient and in the final upper isobaric tract. In this instance, in order to predict the PPt_R of every compound it is necessary to calculate its position in the column and the pressure existing at that point when the programming mode changes, e.g., when the initial isobaric tract ends and the linear pressure gradient starts, when the gradient changes and when the upper isobaric tract takes place. A general equation of the PPt_R is:

$$PPt_R = t_1 + t_2 + t_3 \tag{9}$$

where t_1 is the retention time of the substance during the initial isobaric tract of the programmed run; $t_2 = (P_f - P_i)/g$ is the retention time during the linear program at the rate g between the initial, P_i, and final, P_f, pressures; t_3 is the retention time at the end of the isobaric tract at pressure P_f.

3. Layout of the program

Fig. 1 shows the flow chart of the different options of the program.

In order to predict the retention times in programmed pressure analysis, the program has to calculate the z term of Eq. (7) and for each compound the term $(1+k)$ from Eq. (2).

It is therefore necessary to input the parameters of the column: length, L, internal column radius, r, type of carrier gas used (the coefficients α and β of Eq. (8) for helium, hydrogen and nitrogen are standard values of the base program). The program requires the following parameters of the experimental isobaric run whose results are necessary for the calculation of the term $(1+k)$: temperature of analysis, T, (it must be the same for the test runs carried out in isobaric conditions, and for any setting of programmed pressure analysis to be predicted); retention times of each compound, $t_R(P_{iL})$; value of isobaric pressure used, P_{iL}; atmospheric pressure, P_a; pressure value at the column outlet, P_o. During the calculation, the program also needs the value of: the pressure steps, ΔP, which are used as integration steps for the trapezoid method used for solving the integral of Eq. (1) [27,28]; approximate position along the column, Δl, of a compound during the change of pressure gradient. The standard values suggested for this parameters which offer a good compromise between the calculation time and the precision of the results are: ΔP between 0.001 and 0.01 p.s.i.g.; Δl between $L/256$ and $L/1024$ cm. It must be taken into account that in the various programming runs described below, the generic pressure terms of Eq. (1) are replaced by the initial pressure at the column head, P_{iL}, and by its changes, dP_{iL}. In the following paragraphs, some details are given in order to enable the reader to reproduce and operate the program.

Different types of programmed runs were taken into account.

3.1. Type A: linear pressure gradient, with $PPt_R = t_2$

In this case it is necessary to input the following data: atmospheric pressure, P_a, the value of the pressure gradient, g, the initial column inlet pressure, P_{iL}, pressure value at the column outlet, P_o. For each compound, the program finds the value of the
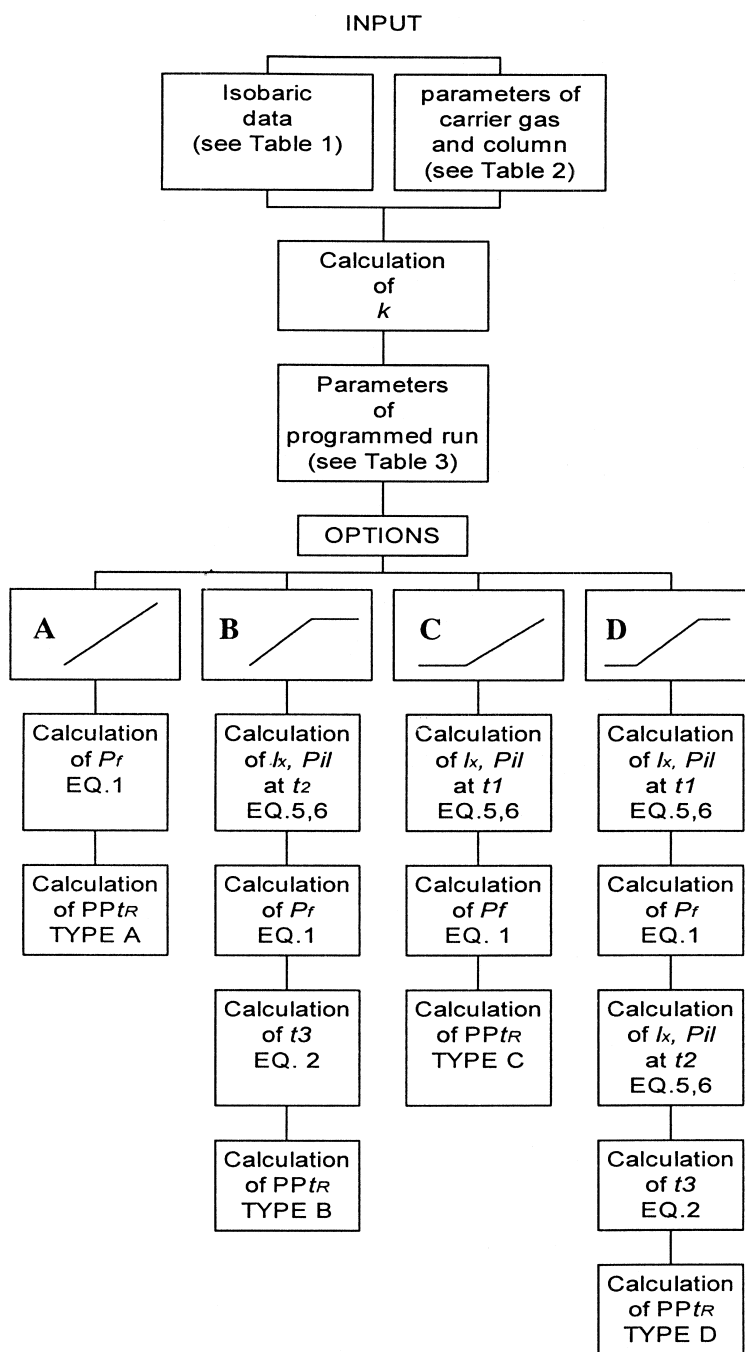
INPUT

Fig. 1. Flow-chart of the different calculation used to predict the PPt_R with various types of programmed-pressure analysis (see text).

integral of the Eq. (1) such as to equal the value of g. Setting $l=L$, $l_x=0$ therefore, from Eq. (6), $P_{il}=P_{iL}$; replacing such values in Eq. (5) and setting $P_i=P_{iL}$

in Eq. (1), the program begins to calculate the integral of Eq. (1), with the trapezoid method, starting from the value $P_f=P_{iL}+\Delta P$ and increasing

at each step P_f of an amount ΔP until the value of the integral is equal to the g value. From Eq. (1a) the value t_2 is: $t_2 = (P_f - P_{iL})/g$

3.2. Type B: linear pressure gradient followed by an upper isobaric tract with $PPt_R = t_2 + t_3$

In this case it is necessary to input the following data: atmospheric pressure, P_a, the value of the pressure gradient, g; the initial column inlet pressure, P_{iL}, the column inlet pressure at the end of the pressure gradient, P_{fL}; pressure value at the column outlet, P_o. At first, the program calculates through Eq. (1a) the time required to reach the end pressure P_{fL} by starting from P_{iL} with the gradient g, $t_g = (P_{fL} - P_{iL})/g$. For each compound, the value P_f of the integral of Eq. (1) is found as in the type A run. The value t_2 is calculated from Eq. (1a), like in the type A run: if $t_2 \leq t_g$ the compound is eluted at $PPt_R = t_2$.

If $t_2 > t_g$, the compound is still in the column at time t_g, so the program calculates its position.

Setting $P_i = P_{iL}$ and $P_f = P_{fL}$ in Eq. (1) and $P_{il} = P_{iL}$ in Eq. (5), there exists a value of l in Eq. (5) such as to satisfy Eq. (1). The dicotomic method is used to calculate l: starting from a value $l = L/2$ the program calculates the integral from Eq. (1) with the trapezoid method. If the integral value is greater or less than g, the value of l must also be greater or smaller than $L/2$: the new value of l, l_{new}, is $l_{new} = l \pm l/2$ and the program calculates again the integral value from Eq. (1) and so on. The loop will stop when the increase or the decrease of l_{new} is less than Δl. With this last value, setting $l_x = l$ and $P_{iL} = P_{fL}$ in Eq. (6), the program calculates the value of P_{il}. Replacing this value in Eq. (5) and setting $l = L - l_x$ (final column tract) and $P_{iL} = P_{fL}$ it calculates, from Eq. (5), the time, t_M, spent by the carrier gas to cover the column tract l. From Eq. (2) one obtains $t_3 = t_M(1 + k)$; the total retention time of the compound is therefore: $PPt_R = t_g + t_3$.

3.3. Type C: initial isobaric tract and linear pressure gradient with $PPt_R = t_1 + t_2$

In this case it is necessary to input the following data: atmospheric pressure, P_a; the value of the pressure gradient, g; the initial column inlet pres-

sure, P_{iL}; the initial isobaric run time, t_0; pressure value at the column outlet, P_o.

For each compound, the program calculates if the retention time is smaller or equal to t_0: setting $l = L$, $l_x = 0$ and therefore from Eq. (6) $P_{il} = P_{iL}$; replacing these values in Eq. (5) the program obtains the t_M value which is replaced in Eq. (2) to obtain t_1; if $t_1 \leq t_0$ then $PPt_R = t_1$, otherwise the compound, at the time t_0, is still in column. In this instance the program calculates the position, l_x, of this compound in the column. By setting $t_R = t_0$ in Eq. (2), the time, t_M, required by a molecule of carrier gas to reach the point l_x is calculated. By setting $P_{il} = P_{iL}$, $l = l_x$ and $t_M(P_{il}) = t_M$ in Eq. (5) it is possible to calculate the l_x value which is placed in Eq. (6). Then P_{il} is replaced in Eq. (5). Like in type A run, the program calculates the pressure P_f from the integral of Eq. (1), by setting $P_i = P_{iL}$ and $l = L - l_x$ in the modified Eq. (5). When the value of the integral of Eq. (1) becomes equal to the value of g, like in the type A run, from Eq. (1a) one obtains: $t_2 = (P_f - P_{il})/g$; finally the total retention time is: $PPt_R = t_0 + t_2$.

3.4. Type D: initial isobaric, linear gradient, final isobaric tract with $PPt_R = t_1 + t_2 + t_3$

This case is only a combination of the programmed runs type C and type B.

4. Experimental

A Varian gas chromatograph Model 3600 (Varian, Palo Alto, CA, USA) equipped with a split–splitless capillary injector and a flame ionization detector using helium as carrier gas, connected to an electronic pressure controller EPC 1000 (Alltech, Deerfield, IL, USA) was used for isobaric and programmed pressure analysis. A bonded-phase slightly polar poly(95% dimethyl, 5% phenyl)siloxane DB-5 capillary column (J&W Scientific, Folsom, CA, USA) having a length of 30 m and a nominal I.D. of 0.32 mm was used. The true internal diameter of the column was checked by scanning electron microscopy (SEM) (Stereoscan 440, Leica Cambridge, Cambridge, UK) and found to be 291.7 µm. The analyses were carried out in the range 10 to 30

Table 1
Compounds analysed, symbols used in the tables and the figures, experimental retention times, $t_{R,exp}$, under isobaric conditions of: $P_i = 15.15$ p.s.i.g. (for analytical parameters see Table 2)

Compound	Symbol	$t_{R, exp}$ (min)
Toluene	tol	1.668
Chlorobenzene	clbz	2.050
n-Heptanol	c7oh	3.143
n-Decane	c10p	3.632
n-Octanol	c8oh	5.240
Nitrobenzene	nitro	5.735
1,3,5-Trichlorobenzene	135tcb	7.398
1,2,4-Trichlorobenzene	124tcb	9.552
Naphtalene	napht	9.885
n-Dodecane	c12p	11.347
1,2,3-Trichlorobenzene	123tcb	11.715

p.s.i.g. at a temperature of 80°C, by using a sample containing all the compounds listed in Table 1. Aromatic compounds were selected as probes; n-alcohols and n-alkanes were also added in order to measure the polarity with the ΔC [23,26] method. The chromatograms were integrated and the retention times measured with an accuracy of ±0.001 min by using a ''Star'' (Varian) data system.

The temperature of the column was monitored by using a thermocouple, with a precision of ±0.1°C, greater than that offered by the built-in hardware of gas chromatograph (±0.5°C). It may be different from the value set with the control panel of the gas chromatograph, depending on the accuracy of the calibration of the instrument. As discussed previously [22,37] the uncertainty of the exact column temperature may be the source of valuable error in the prediction of retention times; therefore the sensing tip of the thermocouple was stuck to the column's coil in order to allow a measurement as accurate as possible and reduce the effect of thermal gradient within the oven. The linearity and the exact value of the inlet pressure were monitored by connecting to the injector a mercury manometer with a precision of 0.5 mmHg, greater than that offered by the built-in hardware of gas chromatograph (±0.3 p.s.i.g.), because these parameters influence strongly the results of the t_R prediction. The atmospheric pressure is measured with a mercury barometer with a precision of 0.1 mmHg.

5. Results and discussion

Table 1 lists the compounds, the abbreviated symbols used in the other tables and figures and their experimental retention times, $t_{R,exp}$, for isobaric conditions ($P_i = 15.15$ p.s.i.g.). Table 2 lists the parameters of the isobaric run, relative to the column, to the carrier gas and to the analysis conditions used for the prediction. Both the values of retention time of Table 1 and the parameters relative to the column, to the carrier gas and other conditions shown in Table 2 are used as input data in the first part of the program. When the code 1 is set for the carrier gas, the program uses Eq. (8) with the parameters for helium in order to obtain the viscosity at the given temperature. Other parameters are used for nitrogen (code 2) and hydrogen (code 3). In Table 3 the different options relative to the programmed run are described.

The retention times, $t_{R,calc}$, calculated with the different methods shown in Fig. 1 and the conditions listed in Tables 2 and 3, were compared with the experimental values obtained with the analysis on a DB-5 column under the same conditions. Table 4 shows the experimental retention times, $t_{R,exp}$, and the relative percent error with respect of the calculated values, $E\%$, obtained with the equation:

$$E_{rel}\% = 100 \, (t_{R,calc} - t_{R,exp})/t_{R,exp} \tag{10}$$

The overall percentage error $E\%_{ave}$, obtained by averaging the values for all the compounds with their sign, and the absolute percentage error, $E\%_{abs}$, obtained by averaging the absolute values, are also shown. The correspondence of calculated with ex-

Table 2
Parameters used for starting the program

Isobaric run	Symbol	Value
Column length	L	3000 cm
Column diameter	$2r$	0.2917 mm
Column temperature		83°C
Atmospheric pressure	P_a	759.6 mmHg
Outlet pressure	P_o	0 p.s.i.g.
Inlet pressure	P_i	15.15 p.s.i.g.
Carrier gas type	1	Helium
Pressure gradient	g	0 p.s.i.g./min

Table 3
Different types of programmed run and their analysis parameters

Option	inlet pressure (P_i) (p.s.i.g.)	Initial isobaric tract (min)	Gradient (p.s.i.g./min)	Final pressure (P_f) (p.s.i.g.)
A	15.15	–	1	(a)
B	15.15	–	2	25
C	15.15	3	0.5	(a)
D	15.15	3.5	1	20
A1	10.10	–	2	(a)

[a] P_f is automatically set by the program as a function of the retention time of the last eluting compound.

perimental values is about the same, independent on the complexity of the pressure program, showing that the used formulas allow one to calculate the retention time during any pressure programmed run, PPt_R, by using only one isobaric reference run as the source of the starting data. The tenth and eleventh columns of Table 4 show that if the initial pressure (10.10 p.s.i.g.) of the programmed run is different from the initial pressure of isobaric run (15.15 p.s.i.g.) the relative percent errors are comparable with those obtained by using as the starting pressure of the programmed run the same used for the isobaric analysis. The exact knowledge of the pressure value is therefore more important than its correspondence with that of the reference run.

The effects of the variation of the analytical parameters are shown in Table 5. By using the true values (initial pressure 15.15 p.s.i.g., gradient 1 p.s.i.g./min and atmospheric pressure 759.6 mmHg) an $E\%_{ave}$ of 0.049 was obtained with type A program (see Table 4). When the pressure parameters indicated in the fourth column are set in the pressure program instead of the true values, much greater errors are obtained. This confirms that the effect of wrong initial pressure or programming gradient or atmospheric pressure is much greater than that of changing other parameters. For this reason the informations given by the built-in measuring devices of some instruments, with an approximation of ± 0.3 p.s.i.g., are not accurate enough to permit the best application of the method. More accurate measurement of the true pressure, with an external mercury

Table 4
Experimental retention time, $t_{R,exp}$, relative percent error, $E\%$, relative percent, $E\%_{ave}$ and absolute averaged, $E\%_{abs}$, errors between calculated and experimental PPt_R obtained under the different types of programmed runs listed in Table 3 (for symbols of compounds refer to Table 1)

Compound	Type									
	A		B		C		D		A1	
	$t_{R,exp}$ (min)	$E\%$	$t_{R,exp}$ (min)	$E\%$	$t_{R,exp}$ (min)	$E\%$	$t_{R,exp}$ (min)	$E\%$	$t_{R,exp}$ (min)	$E\%$
tol	1.606	−0.374	1.531	−0.066	1.670	0.193	1.671	0.133	2.065	−0.001
clbz	1.936	0.206	1.841	0.217	2.060	−0.174	2.059	−0.125	2.456	0.366
c7oh	2.907	−0.241	2.709	−0.148	3.140	0.636	3.135	0.569	3.506	−0.172
c10p	3.314	−0.121	3.075	−0.326	3.615	0.691	3.620	0.828	3.922	0.203
c8oh	4.581	0.414	4.156	0.577	5.145	0.680	5.122	0.741	5.237	−0.421
nitro	5.011	−0.420	4.516	−0.244	5.671	−0.547	5.627	−0.480	5.589	−0.162
135tcb	6.220	0.160	5.515	−0.049	7.124	0.224	6.990	0.286	6.747	−0.178
124tcb	7.715	0.324	6.874	−0.556	8.964	0.401	8.726	−0.627	8.068	0.272
napht	7.972	−0.151	7.007	0.525	9.303	−0.248	8.863	0.605	8.240	0.546
c12p	8.891	0.438	7.892	0.735	10.461	0.181	9.958	0.675	9.065	0.661
123tcb	9.142	0.306	8.172	0.150	10.827	−0.435	10.299	0.092	9.280	0.538
$E\%_{ave}$		0.049		0.074		0.146		0.245		0.150
$E\%_{abs}$		0.286		0.326		0.401		0.469		0.320

Table 5
Effect of changing some parameters of the isobaric and programmed run on the accuracy of the prediction of PPt_R

Parameters	Symbols	Nominal value	Actual value	$E\%_{ave}$	$E\%$
Isobaric run					
Inlet pressure	P_i (p.s.i.g.)	15.15	15.50	1.722	
			14.90	−1.591	
Programmed run					
Atmospheric pressure	P_a (mmHg)	759.6	780		−0.086
			740		0.159
Inlet pressure	P_i (p.s.i.g.)	15.15	15.50		−1.551
			14.90		1.550
Gradient	g (p.s.i.g./min)	1	1.1		−1.106
			0.9		1.280

manometer or other accurate 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.

As seen previously [37], when methods for the prediction of retention times in temperature programmed analysis are used, the geometrical parameters of the column (diameter, length) and the viscosity of carrier gas have the greatest effect on the accuracy. For programmed pressure analysis the dead time value, calculated by the program, is obtained directly from the t_R values of the isobaric analysis and therefore the geometrical parameters and the viscosity of carrier gas do not influence the accuracy of the results.

6. Conclusions

The comparison of the experimental data with those predicted with the calculation method have shown that, by using only one isobaric run as the source of the input data and simple computer programming, satisfactory accuracy in the prediction of programmed pressure analyses with various linear speed and with or without an isobaric initial tract can be obtained. Depending on the experience of the programmer and on the language available (BASIC, Visual BASIC for Excel and any other compiler) the program can be modified in order to fit to the necessities of the GC system operator. It is important to remember that the accuracy of the results obtained during programmed analyses with complex pressure

profiles depends on the exact knowledge of the atmospheric pressure and on accurate measurement of the initial and gradient inlet pressure of the column.

An executable version for MS-DOS of the program of prediction in programmed pressure is available on request.

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