

# Retention in multistep programmed-temperature gas chromatography and flow control

## Linear head pressure programs

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### Abstract

A comparative study of retention in different systems of flow control that provide linear dependence with the temperature of the column's head pressure is performed by numerical simulation considering multistep (or multiramp) PTGC (programmed-temperature gas chromatography) as the most general situation. Calculation algorithms for each flow control mode are developed on the basis of a general retention equation and the only additional hypothesis is that certain geometric parameters of the column remain practically constant along the program. Procedures are individually contrasted with experiment, prior to application. The comparative view indicates that simple correlations cannot be obtained between retention times and temperatures in two different pressure controls or pressure programs. It seems that numerical procedures are unavoidable when it is required to convert the retention data from one chromatographic system to another with the same stationary phase.

**Keywords:** Temperature programming; Head pressure; Flow control systems

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### 1. Introduction

The velocity of the carrier gas is a function of pressure drop along the column, and the way the latter changes with temperature is determined by the flow control system used; thus, retention is primarily affected by the function  $P(T)$  generated by the chromatograph ( $T$  is the absolute temperature and  $P$  is the inlet/outlet absolute pressure ratio in the column:  $P=p_i/p_o$ ). Each  $P(T)$  function has an associated gas hold-up time function  $t_M(T)$  biunivocally related by the column's and carrier gas flow properties. Consequently, when the PTGC retention data

is generated, the  $P(T)$  should also be recorded, by itself or using the associated  $t_M(T)$ .

For a number of years the most widely applied devices for setting the carrier gas velocity (or the  $P(T)$  function) were the mechanical flow controllers [1] consisting of a needle valve in a serial array with a diaphragm-operated valve. Although these were employed with the intention of keeping a constant mass flow, their capacity to respond adequately to changing flow conditions across wide temperature intervals becomes rapidly compromised [2]. In consequence, their behaviour under actual temperature programming becomes unpredictable from a practical standpoint. With the development of electronically driven mechanisms reliable mass flow control is

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possible for PTGC [1,3,4]. On the other hand, the constant inlet pressure condition is easily accomplished, even with mechanical devices, but presents a monotonically decreasing outlet volume flow-rate with rising temperature [1,2], i.e. going in the opposite way to temperature programming with respect to the analysis time. With the advent of computer-controlled head pressure numerous possibilities [1] are opened to pressure programming in PTGC.

Much attention has been given in recent years to the estimation of retention in programmed temperature from thermodynamic parameters, involving not only single-step temperature programming, but also including the choice of different heating rates steps, or isothermal steps [5–10]. Simultaneously, effort has been devoted to searching some sort of correlation of PTGC retention data for different columns using the same stationary phase through a programmed temperature retention index [9,11–15]. Less attention was dedicated to the study of the interrelations between programmed temperature retention resulting from different  $P(T)$  functions. We believe these relations are important, as there are different types of flow control in current use — there is no common standardization of  $P(T)$ . The nature of the retention equation in PTGC, in which the unknown parameter (the retention time  $t_R$ ) is an integration limit, does not permit one to settle a priori on a quantitative approach to the problem without making any explicit calculation.

## 2. General

The statement of the applied algorithms of calculation in this paper is based on two related works where the fundamental theory can be found [2,16].

The differential equation of peak motion in isothermal chromatography is:

$$\frac{dz}{dt} = \frac{u(z)}{(1+k)} \quad (1)$$

where  $z$  is the axial variable (cylindrical coordinates) that describes the peak position in the column at time  $t$ ,  $u(z)$  is the local carrier gas velocity,  $k$  column's capacity factor and  $dz/dt$  is the migration rate of the peak at  $z$  position. The local gas velocity  $u(z)$  may be

substituted by:  $u(z) = \bar{u}/Q(z)$ , where  $\bar{u}$  is the average linear velocity along the column, which can be replaced in turn by  $L/t_M$ , where  $L$  is the length of the column and  $Q(z) = \bar{u}/u(z)$  is the local velocity factor. For example, if D'Arcy's equation and the ideal gas equation of state are used for describing the motion of the gas,  $Q$  is given by [2]:

$$Q(z) = (3/2) \frac{(P^2 - 1)}{(P^3 - 1)} [P^2 - (z/L)(P^2 - 1)]^{1/2} \quad (2)$$

From Eq. (1), the movement of the band along the column during any isothermal step of a given global temperature program would be given by:

$$\int_{z_i}^{z_f} Q(z) dz = \frac{L}{(1+k)} \int_{t_i}^{t_f} \frac{dt}{t_M} \quad (3)$$

Where ( $z_i$ ,  $z_f$ ) are the initial and the final positions of peak along the step, and ( $t_i$ ,  $t_f$ ) are the corresponding times.  $Q$  and  $t_M$  are functions of  $P$ . In the case of chromatographs where the flow control system responds to the column's varying flow conditions, e.g. when mechanical controllers and needle valve systems [2] are used,  $P$  remains constant during isothermal steps. The same holds for the constant mass-flow control.  $P$  would only change during an isothermal interval when it is programmed to do so, being in this case a function of time. For this reason  $t_M$  was included inside the integral in Eq. (3), as the most general condition.

The differential equation of peak motion in programmed temperature (PT) can be written as [2]:

$$\frac{dz}{dT} = \frac{L}{f'(T) Q(z,T) t_M(T) [1+k(T)]} \quad (4)$$

$T=f(t)$  is the function that relates time and temperature representing the chosen temperature program ( $f' = dT/dt$ ). Now  $t_M$  is a function of  $P(T)$ . Hence, for any PT step of the general program, we can write:

$$\int_{z_i}^{z_f} Q(z, T) dz = L \int_{T_i}^{T_f} \frac{dT}{f'(T) t_M(T) [1+k(T)]} \quad (5)$$

and for the part of the global program that covers the complete elution of the band [16]:

$$1 = \int_0^L (Q/L) dz$$

$$= \sum_{\text{all stages}}^{\text{peak emerg.}} \left[ \frac{1}{(1+k)} \int_{t_i}^{t_f} \frac{dt}{t_M} \right. \\ \left. + \int_{T_i}^{T_f} \frac{dT}{f'(T) t_M(T) [1+k(T)]} \right] \quad (6)$$

isoth.steps  
PT steps

The sum is performed over all the steps of the global program involved from injection until the solute's peak emerges at the end of the column. In the first step  $t_i=0$ , if it is isothermal; otherwise  $T_i=T_0$  if it is a PT one, where  $T_0$  is the initial temperature of the program. In the final step involved in peak elution:  $t_f=t_R$ , or  $T_f=T_R$ , depending on the case. The initial and final steps with their particular limits are not indicated explicitly in Eq. (6) with the intention of keeping the expression as brief as admissible, considering that there are four possibilities in placing the limits. As shown in the following, all multistep retention expressions will be resumed in the same way. Although the retention time/temperature will not be indicated, it will be assumed that it is implicitly present in the last step.

Currently, the capacity factor, given by Eq. (7), is evaluated neglecting the variation of the enthalpy and entropy of the solution with temperature and pressure.

$$k = \frac{a}{\beta} e^{-\Delta H_S/RT} \quad (7)$$

where  $\Delta H_S$  is the molar enthalpy of solution,  $a$  is the entropic factor,  $\beta$  is the phase ratio of the column and  $R$  is the universal gas constant.

The dependence of  $t_M$  with  $P$ , for packed or capillary columns [2], is given by:

$$t_M = (C_i T^{-N} p_o)^{-1} \frac{(P^3 - 1)}{(P^2 - 1)^2} \quad (8)$$

The 'dead time constant'  $C_i$  is a flow property of the column/carrier gas couple that may be estimated by several methods:

*From a single point (from initial conditions):* An operation position of the flow control system is selected, to be used during the PTGC running, e.g. setting a fixed number of knob turns of a mechanical flow controller, or by an initial setting in an electronic pressure control. At the initial temperature  $T_0$  and head pressure  $p_i^0$ , the initial gas hold-up time  $t_M^0$  is measured in such a isothermal-isobaric reference condition. Then, the constant is estimated by [2]:

$$C_i^{-1} = \frac{t_M^0 (P^{0.2} - 1)^2 p_o}{(P^{0.3} - 1) T_0^N} \quad (9)$$

*From  $t_M$  measured as a function of  $P$ :* Setting different inlet pressures to the column at a fixed temperature and outlet pressure,  $t_M(p_i)$  is measured. Plotting the dead time as a function of the adimensional variable  $(P^3 - 1)/(P^2 - 1)^2$ ,  $C_i$  can be estimated from the resultant slope (Eq. (8)).

*From volumetric flow-rate measurements:* The relationship between 'column's flow-rate constant'  $C_c$  and  $C_i$  is [2]:

$$C_i = \frac{3}{2} \frac{C_c}{V_d} \quad (10)$$

The dead volume of the column  $V_d$  is usually estimated from the isothermal elution volumes of two or more  $n$ -alkanes [17].  $C_c$  can be estimated from volume flow-rate measurements performed at constant temperature and outlet pressure [2].

*From column's geometric parameters and gas constant:* According to Eq. (10), the physical meaning of the 'dead time constant' is interpreted by the following equation:

$$C_i = \frac{3}{4} \frac{B}{L^2 \epsilon_u C_G} \quad (11)$$

$C_G$  is a constant of the carrier gas and  $\epsilon_u$  is the interparticle porosity. For capillary columns  $\epsilon_u=1$ . In the evaluation of the permeability  $B$  an additional hypothesis is used. If the gas flow in the capillary is approximated using Hagen-Poiseuille's equation, which is valid only for incompressible fluids,  $B=d_c^2/32$ ; thus:

$$C_i = \frac{3}{128 C_G} \left( \frac{d_c}{L} \right)^2 \quad (12)$$

Here we will estimate  $C_i$ , for all retention expressions, from Eq. (9) exclusively, defining  $T_0$ ,  $p_i^0$  and  $t_M^0$  as the initial values of the program measured before starting the PTGC running.

Finally, making use of Eq. (8), retention equation Eq. (6) can be written explicitly in terms of  $P(T)$  or the head pressure function generated by the chromatograph:

$$C_i^{-1} = \sum_{\text{all steps}}^{\text{peak emerg.}} \left[ \frac{1}{(1+k)T^N} \int_{t_i}^{t_i'} \frac{(p_i^2 - p_o^2)^2 dt}{(p_i^3 - p_o^3)} \right]_{\text{isoth. steps}} + \left[ \int_{t_i}^{t_i'} \frac{(p_i^2 - p_o^2)^2 dT}{f'(T)(p_i^3 - p_o^3)(1+k)T^N} \right]_{\text{PT steps}} \quad (13)$$

Once  $C_i$  of the column is determined by one of the described possible procedures, and the head pressure program  $p_i(T)$  is defined, we can make a numerical estimation of the retention from the solute's thermodynamic parameters using Eq. (13).

### 3. Experimental

A Hewlett-Packard 5890 Series II Plus chromatograph, connected to a HP 3395 integrator, was used in three selectable operation modes: constant head pressure (CP), constant mass flow (CMF) and linear pressure programming (PP). The capillary column used had the following features: 30 m long, 0.25 mm I.D. with 0.25  $\mu\text{m}$  film width, AT-1, catalogue AllTech 13638 (polydimethylsiloxane) and nitrogen was used as the carrier gas. Detailed information about the chromatograph's flow control configura-

tions, the main features of the electronic pressure control, as well as some aspects of the response performance can be obtained from the paper by Hermann et al. [4]. Injection was carried out with a split ratio ranging from 30:1 to 70:1, depending on the case, with FID detection. Methane was used as the unretained solute for  $t_M^0$  estimation. Eight hydrocarbons were employed individually and as solutions to undertake two tasks. First, for thermodynamic parameter determination, solutions of two or three solutes with similar boiling points were used, running isothermal chromatograms at temperature intervals of 20°C in the range 40–80°C around each solute's  $T_R$  from temperature program 1, Table 2. These tests were made in the constant mass flow mode of pressure control. The entropic and enthalpic terms of  $k$  were estimated from mean square linear regression of  $\ln(t_R'/t_M) - 1/T$  data, where  $t_R'$  is the adjusted retention time. The results are presented in Table 1; the thermal intervals where these were evaluated and the correlation coefficients are indicated. The temperature–head pressure programs defined in Table 2 were ran injecting a mixture of the eight substances. Chloroform was the solvent for naphthalene. In those cases where the initial isothermal-isobaric dead time  $t_M^0$  was not determinable from the same chromatogram (programs 1 and 4), it was evaluated previously by two or three methane injections at the program's initial conditions ( $T_0$ ,  $p_i^0$ ). In program 1  $t_M^0$  is longer than the isothermal-isobaric initial step, and in program 4 the pressure varies from the beginning. Experimental retention times from temperature–pressure programs are presented in Table 3 under 'exp' headings, indicating the corresponding initial conditions and data required for the numerical simulation.

Table 1  
Entropic and enthalpic parameters of  $k$

Solute	$-\Delta H_s/R$ (K)	$(\alpha\beta) \times 10^6$	Temperature interval (°C)	Correlation coefficient
<i>n</i> -Octane	4175	5.533	50–120	0.99990
<i>p</i> -Xilene	4262	6.924	50–120	0.99979
1,3,5-Trimethylbenzene	4661	4.417	70–120	0.99998
1-Undecene	5313	1.729	100–160	0.99978
Naphthalene	5107	4.623	120–180	0.99986
<i>n</i> -Dodecane	5559	1.695	140–180	–
<i>n</i> -Tetradecane	5990	1.545	200–220	–
<i>n</i> -Hexadecane	6760	0.635	160–220	1.00000

Table 2  
Description of applied  $T$ - $P$  programs

Designation	Temperature program	Pressure program
1	[I: 1 min]→[PT: 10°C/min to 200°C]	CMF
2	[I: 2.5 min]→[PT: 5°C/min to 80°C]→ →[I: 0.5 min]→[PT: 10°C/min to 250°C]	CMF
3	Same as for designation 2	[CP:2.5 min]→[PP: 21.7 Torr/min to 1412 Torr]→ [CP: 0.5 min]→[PP: 43.4 Torr/min]
4	Same as for designation 2	[PP: 51.715 Torr/min]
5	Same as for designation 2	CP

Initial temperature is  $T_0 = 50^\circ\text{C}$  for every program, ( $p_0, p_i^0$ ) are: (765, 1277) Torr in 1 and 2, (770, 1282) Torr in 3 and 4, (770, 1546) Torr in 5.

Symbols: I, isothermal step; PT, linear programmed temperature step; CMF, constant mass flow; CP, constant inlet pressure; PP, linear programmed inlet pressure.

#### 4. The constant head pressure mode

We will assume this mode as a special case of a linear head pressure programming with zero compression rate and we shall employ it as a reference. The ramps are restricted to linear temperature programs with heating rates  $r_T$  °C/min ( $f'(T) = r_T = \text{const.}$ ).

With  $p_i = p_i^0 = \text{const.}$ , by using Eq. (9), Eq. (13) reduces to:

$$\frac{t_M^0}{T_0^N} = \sum_{\text{all steps}}^{\text{peak emerg.}} \left[ \frac{1}{(1+k) T^N} \int_{t_i}^{t_f} dt \right]_{\text{isoth. steps}} + \left[ \frac{1}{r_T} \int_{T_i}^{T_f} \frac{dT}{(1+k) T^N} \right]_{\text{PT steps}} \quad (14)$$

Table 3  
Experimental and calculated retention times in different temperature–pressure programs

Solute	Retention times (min)									
	Progr. 1 CMF mode		Progr. 2 CMF mode		Progr. 3 PP mode		Progr. 4 PP mode		Progr. 5 CP mode	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
<i>n</i> -Octane	4.879	4.880	6.169	6.189	6.032	6.070	5.153	5.230	4.562	4.590
<i>p</i> -Xilene	5.777	5.778	7.685	7.769	7.450	7.559	6.359	6.490	5.974	6.030
1,3,5-Trimethylbenzene	7.296	7.270	10.539	10.560	10.154	10.200	8.710	8.790	8.865	8.850
1-Undecene	9.285	9.260	13.644	13.580	13.081	13.070	11.831	11.830	12.601	12.540
Naphthalene	10.445	10.360	14.990	14.860	14.317	14.250	13.066	12.990	14.094	13.950
<i>n</i> -Dodecane	10.931	10.800	15.641	15.450	14.952	14.820	13.800	13.640	14.924	14.700
<i>n</i> -Tetradecane	13.585	13.350	18.570	18.500	17.720	17.440	16.672	16.330	18.246	17.870
<i>n</i> -Hexadecane	15.975	15.830	20.983	20.800	20.025	19.890	19.050	18.860	20.962	20.770
Mean error (%)	0.66		0.68		0.76		1.15		1.01	
$t_M^0$ (min)	2.224		2.224		2.215		2.214		1.489	
$p_i^0$ (Torr)	1277		1277		1282		1282		1546	
$p_0$ (Torr)	765		765		770		770		770	

Programs from Table 2. Mean error % defined as:  $[(t_R^{\text{exp}} - t_R^{\text{calc}}) / t_R^{\text{calc}}] \times 100$  (same definition as in Table 4 and Ref. [10]).

For the evaluation of retention using Eq. (14) the only data to be entered into the calculation, apart from the selected program's parameters, are the initial isothermal dead time and the initial temperature, the thermodynamic parameters for  $k(T)$  and the constant  $N$  of the carrier gas. Applying Eq. (14) to a single ramp reduces to the expression derived by Messadi [15].

In Table 3, program 5, the experimental retention data belonging to the eight hydrocarbons, measured in the isobaric condition (CP) indicated in the lower lines, are listed under the heading 'exp.'. In the same table the results, rendered by the numerical solution of Eq. (14) through a Basic computer program, are shown under the 'calc.' heading. Measured values of the initial temperature and dead time, the parameters of  $k$  given in Table 1 and the constant  $N$  for nitrogen (0.725, [18]) were entered into the computer program. The mean error of the predicted retention is in the order of 1%, as indicated in the table. The applied time and temperature increments in the computer program were 0.01 min and 0.1 K, respectively.

In the same way, Table 4 shows calculated retention times using the reported thermodynamic parameters and the isobaric multistep temperature

programs indicated in [10]. Results are compared simultaneously with experimental and calculated data listed in Table 11 in the paper of Snijders et al. [10]. Differences between the algorithms followed by the cited and present authors deserves a brief comment.

In Ref. [10] the geometric parameters of the column  $L$  and  $d_c$  are introduced with two purposes. First,  $L$  is the integration limit of variable  $z$  (the carrier gas local velocity is evaluated for each coordinate and temperature increment). In Ref. [16] it is shown that procedures including the explicit calculation of the local velocity at each temperature are equivalent to that used here, where  $L$  becomes irrelevant. Second, the length and diameter of the column were necessary in Ref. [10] for determining the head pressure through an expression equivalent to the combination of Eqs. (8,12), i.e. calculating  $p_1$  from the measured value of  $t_M^0$ . The head pressure is present in the estimation of the local velocity. In spite of the number of operations included in the algorithms, with additional input of parameters, that from Ref. [10] and the present procedure are formally equivalent [16], involving the same basic chromatographic hypothesis. Only two minor differences are to be considered. In the present work  $C_i$  is evaluated using Eq. (9) and the procedure followed

Table 4  
Comparison of calculated and experimental retention times for the constant inlet pressure mode

Solute	Retention times (min)											
	Temp. progr. E			Temp. progr. F			Temp. progr. G			Temp. progr. H		
	a	b	c	a	b	c	a	b	c	a	b	c
<i>p</i> -Chlorotoluene	6.097	6.064	6.049	5.045	5.027	4.999	6.100	6.057	6.048	5.051	5.021	4.999
sec.-Butylbenzene	7.270	7.203	7.217	6.080	6.014	6.022	7.270	7.195	7.217	6.080	6.008	6.022
Diphenyl ether	12.680	12.794	12.626	12.280	12.375	12.233	12.680	12.749	12.626	12.280	12.371	12.233
1-Hexadecene	14.380	14.353	14.339	15.320	15.275	15.293	14.660	14.616	14.636	15.320	15.273	15.293
1-Chlorotetradecane	14.580	14.877	14.541	15.560	16.217	15.532	14.960	15.459	14.932	15.620	16.262	15.532
Myristic acid, methylester	14.920	15.122	14.881	16.250	16.661	16.234	15.540	15.899	15.528	16.300	16.781	16.285
Hexachlorobenzene	15.030	15.215	14.996	16.280	16.715	16.262	15.680	15.979	15.664	16.325	16.858	16.314
Anthracene	15.519	15.665	15.483	17.160	17.480	17.143	16.510	16.763	16.503	17.400	17.849	17.409
Palmitic acid, methylester	16.205	16.313	16.175	18.730	18.978	18.724	17.970	18.167	17.969	19.300	19.547	19.291
Oleic acid, methylester	17.165	17.256	17.149	20.570	20.767	20.584	19.880	20.040	19.892	20.895	21.071	20.888
Pyrene	17.430	17.530	17.418	20.780	20.951	20.791	20.130	20.260	20.136	21.055	21.201	21.041
Mean error (%)	0.93		0.93	1.53		1.52	1.29		1.23	1.77		1.68

(a) Calculated retention times from Eq. (14). Values of input parameters:  $T_0 = 50^\circ\text{C}$ ,  $t_M^0 = 1.081$  min, thermodynamic and temp. program parameters from Ref. [10],  $N = 0.646$  (He).

(b) Experimental retention times from Ref. [10].

(c) Calculated retention from Ref. [10].

All temperature programs have an initial isothermal step from  $t = 0$  to  $t = 1.081$  min. Mean error defined as in Table 3.

by Snijders et al. corresponds to the evaluation of  $C_1$  from Eq. (12), which assumes that Poiseuille's equation is valid. The other aspect is that we approximated the temperature dependence of the gas viscosity as a temperature power law.  $N=0.646$  was entered for He as the carrier gas [18]. Small numerical differences between the calculated retention times in Table 4 arise, principally, from: (a) machine roundup associated with the number of operations performed by the computer, (b) the values given to the increments in the summation, and (c) the intrinsic error of the  $L$  input [16].

The outstanding characteristic of the constant pressure mode in multistep PTGC, that becomes even more evident from Eq. (14), is that retention is parametrically dependent on the head pressure or the chromatograph's gas control design (implicitly through  $t_M^0$ ). This is just what occurs in isothermal chromatography, where the influence of the flow conditions can be eliminated reporting the retention data in a standardized way relative to the retention framework of  $n$ -alkanes, by means of the Kovats retention index. This unique characteristic of parametrical dependence of retention on the chromatograph's fluid dynamics is not accounted for in systems where  $p_i(T)$  is allowed to evolve during the temperature program, where the retention depends on this function (Eq. (13)). The simplicity of the retention expression, more precisely the missing influence of  $p_i(T)$ , makes the constant pressure mode an appropriate reference for the comparison of retention measured under different flow control systems.

## 5. The constant mass-flow mode

During a temperature program running, with constant mass flow of the carrier gas, the evolution of  $P(T)$  can be described by [2]:

$$P(T) = \left[ 1 + (P^{0^2} - 1) \left( \frac{T}{T_0} \right)^{1+N} \right]^{1/2}$$

or

$$p_i(T) = \left[ p_o^2 + (p_i^{0^2} - p_o^2) \left( \frac{T}{T_0} \right)^{1+N} \right]^{1/2} \quad (15)$$

This equation presumes valid the same hypotheses that are inherent in Eq. (8), already mentioned in Section 2, i.e. D'Arcy's equation, ideal gas, thermal invariance of the column's geometric parameters and gas viscosity factorization. Although it does not strictly define a linear pressure increase with rising temperature, in practical chromatographic conditions it behaves like a linear head pressure program (see, for example, Fig. 4 from Ref. [1] and Fig. 5 from Ref. [2]). If the initial value of  $P$  is  $P^0=2$ , and  $T_0=323$  K, deviations from linearity would become significant beyond 600 K. The number of comparisons to undertake in this study are simplified due to the property that this flow control mode presents, having the same  $P(T)$  as a linear pressure programmable device, although restricted to a fixed compression rate and isobaric behaviour at isothermal steps.

Now, the calculation of the retention time of a solute will require the numerical solution of Eq. (13) with  $p_i(T)$  given by Eq. (15). In addition to the input information necessary in the CP mode, the initial inlet and the outlet pressures of the column ( $p_i^0$ ,  $p_o$ ) must be entered. A computer program solving the system of equations, applying the same time and temperature increments reported previously, was employed for retention estimation. In Table 3, programs 1 and 2, experimental and calculated retentions, are compared for the solutes under constant mass flow (CMF). Errors are in the same order as for program 5 or Table 4 (CP mode).

## 6. Linear programmed inlet pressure

Electronic pressure control adds the possibility of changing the rate of pressure increase at the column's head, and also of varying  $p_i$  along isothermal steps. In this later specific situation, considering linear programming:

$$p_i(t) = p_i^0 + r_p t \quad (16)$$

where  $r_p$  is the compression rate (e.g. Torr/min).

We may also write for an initial PT ramp [2]:

$$p_i(T) = p_i^0 + \frac{r_p}{r_T} (T - T_0) \quad (17)$$

The same holds for any intermediate step replacing

$(T_0, p_i^0)$  by the corresponding initial temperature and pressure of the interval. Now the calculation algorithm requires the introduction of Eq. (16) in the isothermal cycle and Eq. (17) in the PT cycle. Furthermore, the computation program has to incorporate the necessary data input sentences for the pressure program's parameters.

Table 3, programs 3 and 4, presents the calculated retentions for two multistep pressure–temperature programs. Program 3 is an example of an isobaric condition for the isothermal steps and program 4 includes variable pressure during the isothermal intervals. Again, a contrast with experimental data reveals a close accuracy in respect to programs described previously.

## 7. Comparison of retention under different pressure programs

With the intention of avoiding redundant examinations we must recall two aspects commented previously. First, comparisons can be conducted using the CP mode as a reference, as it can be assumed to be a special case of linear pressure programming with  $r_p=0$ . Second, the CMF mode might be considered a particular linear PP with a fixed  $r_p$ , having the restriction of invariable pressure isothermal intervals, thus representing only another example of the linear PP mode with these two characteristics.

The first duty to face is to select some appropriate combination of parameters that would allow a wide overview of retention behaviour with temperature–pressure programming. We will start considering the

simplest choice, consisting of  $T$  and  $p_i$  single ramps, excluding isothermal intervals. The relationship between retention time and temperature is:

$$t_R = \frac{T_R - T_0}{r_T} \quad (18)$$

Then, we may write for any pair of eluted substances  $x$  and  $y$ :

$$\frac{(t_{R_x} - t_{R_y})^{PP}}{(T_{R_x} - T_{R_y})^{PP}} = \frac{1}{r_T} \quad (19)$$

And, by analogy, in the isobaric mode having the same heating rate:

$$\frac{(t_{R_x} - t_{R_y})^{CP}}{(T_{R_x} - T_{R_y})^{CP}} = \frac{1}{r_T} \quad (20)$$

Taking the difference between the last two expressions and rearranging:

$$\frac{(t_{R_x} - t_{R_y})^{PP}}{(t_{R_x} - t_{R_y})^{CP}} = \frac{(T_{R_x} - T_{R_y})^{PP}}{(T_{R_x} - T_{R_y})^{CP}} \quad (21)$$

So, when comparing retention differences of pairs between the PP and CP modes, or between different PP, with the parameter defined by Eq. (21), the use of retention times or temperatures results are indistinguishable. Of course, Eq. (21) does not hold for multistep temperature programs, which is valid, in this latter case, only under some particular conditions.

Table 5 presents calculated values of the parameter for the eight solutes of this study, under the

Table 5  
Variations of Eq. (21) parameter for different pairs of solutes ( $x, y$ )

	$x$	$n$ -Octane	$p$ -Xilene	1,3,5-TMBenzene	1-Undecene	Naphthalene	$n$ -Dodecane	$n$ -Tetradecane	$n$ -Hexadecane
$y$									
Unretained		0.934	0.932	0.930	0.927	0.923	0.924	0.922	0.921
$n$ -Octane			0.930	0.928	0.924	0.918	0.920	0.918	0.918
$p$ -Xilene				0.926	0.922	0.916	0.919	0.917	0.917
1,3,5-TMBenzene					0.919	0.912	0.916	0.915	0.915
1-Undecene						0.900	0.912	0.913	0.914
Naphthalene							0.951	0.918	0.917
$n$ -Dodecane								0.914	0.915
$n$ -Tetradecane									0.916

The  $T$ – $P$  program is defined by:  $r_p = 15$  Torr/min,  $r_T = 15^\circ\text{C}/\text{min}$ ,  $T_0 = 50^\circ\text{C}$ ,  $p_i^0 = 1282$  Torr,  $p_o = 770$  Torr and  $t_M^0 = 2.224$  min. The mean value of the Eq. (21) parameter is:  $\bar{X} = 0.920$  and the standard deviation is  $\sigma = 0.0083$ .



program defined by ramps:  $r_T = 15^\circ\text{C}/\text{min}$  and  $r_P = 15 \text{ Torr}/\text{min}$ , and the specified initial temperature  $T_0$ , initial head pressure  $p_i^0$ , isothermal-isobaric initial gas hold-up time  $t_M^0$ , and outlet pressure  $p_o$ . Residence times of the unretained solute were calculated entering  $k=0$  into the CP and PP computer programs, yielding  $t_M^{\text{CP}}$  and  $t_M^{\text{PP}}$ , respectively. At first glance it is seen that the Eq. (21) parameter has a very low variation along the table, roughly decreasing from left to right and from top to bottom. There is an exceptionally abnormal high value, with respect to the surrounding values, for the naphthalene/*n*-dodecane pair. This exception was also observed in the other three  $T$ - $P$  ramps reported in Table 6, and it is related to the fact that the elution of this pair has an isothermal retention cross-over in the temperature interval of the program. We intend to approach this problem in a forthcoming paper.

Table 6 is an arrangement of characteristic data from four different tables of the same type as Table 5. The latter is designated as 'A' in Table 6. The data has been ordered by increasing  $r_P$  ramps. E is a multiramp program. The reported  $\bar{X}$  value is the average retention time parameter of Eq. (21). Variations, accounted for by the standard deviation  $\sigma$  of the Eq. (21) parameter, are amplified by increasing the compression rate  $r_P$ , expanding under multiramp programs. In the sixth column the parameters for the least-retained pair (*n*-octane/unretained) are tabulated. This pair provides a near limiting value of the parameter in the table (not considering the crossing couple). The next column presents the value of  $(t_M^{\text{PP}}/t_M^{\text{CP}})^2$ , which is found to be very close to the limiting value of the least-retained couple. However, the nature of this apparent correlation is not justified, being merely an experimental observation. In the case of corroboration, a simple thumb rule could be

settled for non-crossing solutes, or solutes of similar structure, under single  $T$ - $P$  ramps with discrete compression rates:

$$\frac{(t_{R_x} - t_{R_y})^{\text{PP}}}{(t_{R_x} - t_{R_y})^{\text{CP}}} = \frac{(T_{R_x} - T_{R_y})^{\text{PP}}}{(T_{R_x} - T_{R_y})^{\text{CP}}} \approx \text{const.} \approx \left( \frac{t_M^{\text{PP}}}{t_M^{\text{CP}}} \right)^2 \quad (22)$$

In consequence, for a gross estimation of the effect on retention of changing the pressure control mode (in a given temperature program), the unavailability of thermodynamic parameters would not be crucial. The dead times are readily acquainted by entering  $k=0$  into the respective computer programs. Eq. (22) could also be applied to two PP with different  $r_P$ .

In the case of multiramp programs this approximation does not fit, and, in this way, useful information that is necessary for complete numerical simulation cannot be obtained.

## 8. Conclusions

All three applied calculation algorithms for the CP, CMF and linear PP modes are supported on the same basic chromatographic hypothesis [16], so the fact that all yield close accuracy of prediction (Table 3) was expected a priori. The order of the mean error of calculated retentions is lower than the retention differences between studied  $T$ - $P$  programs, so the reliability of the procedure applied in the comparative study is assured.

Multistep  $T$ - $P$  programs are actually globally non-linear programs, and retention behaviour, even for homologue substances, is very complex, leaving

Table 6  
Behavior of Eq. (21) parameter under different  $T$ - $P$  programs

Designation	Temperature program $r_T$ ( $^\circ\text{C}/\text{min}$ )	Pressure program $r_P$ (Torr/min)	$\bar{X}$	$\sigma$	<i>n</i> -Octane/unretained	$(t_M^{\text{PP}}/t_M^{\text{CP}})^2$
A	15	15	0.920	0.0083	0.934	0.938
B	10	CMF (equiv. to 22.5 Torr/min)	0.881	0.0103	0.910	0.906
C	10	51.715	0.805	0.0185	0.820	0.817
D	5	60	0.810	0.0196	0.873	0.897
E	Progr. 3, Table 2	Progr. 3, Table 2	0.860	0.0300	0.941	—

no alternative to estimation through numerical simulation from thermodynamic parameters. The only case where changing the pressure program has a uniform effect on the whole chromatogram is that of single  $T$ - $P$  ramps applied to solutes of similar nature (Eq. (22)). For example, rising  $r_p$  means that the chromatogram is going to be uniformly compressed.

Other empirical combinations of retention parameters were used during the development of this work; we were seeking some general correlation of retention under different pressure single ramps, but we had discouraging results.

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