

RETENTION IN MULTISTEP PROGRAMMED-TEMPERATURE GAS CHROMATOGRAPHY AND FLOW CONTROL. LINEAR HEAD PRESSURE PROGRAMS

RETENCION EN CROMATOGRAFIA GASEOSA CON TEMPERATURA PROGRAMADA EN ETAPAS MULTIPLES Y CONTROL DE FLUJO. PROGRAMAS CON GRADIENTE LINEAL DE PRESION DE ENTRADA

F. R. González¹, A. M. Nardillo²

SUMMARY

A comparative study of retention in different systems of flow control, that provide linear dependence with temperature of column's head pressure, is performed by numerical simulation considering multistep (or multiramp) PTGC as the most general situation. Calculation algorithms for each flow control mode are developed on the basis of general retention equation and the only additional hypothesis 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 the conversion of retention data from one chromatographic system to another with the same stationary phase.

Keywords: *temperature programming; head pressure; flow control systems.*

INTRODUCTION

The velocity of the carrier gas is a function of pressure drop along the column, and the way the later changes with temperature is conditioned by the employed flow control system, 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 associated a gas hold-up time function $t_M(T)$ biunivocally related by column's and carrier gas flow properties. Consequently, at the time of reporting PTGC retention data, also $P(T)$ ought to be informed, by itself or the associated $t_M(T)$.

For a few years ago the most widely applied devices for setting the carrier gas velocity (or the $P(T)$ function) were the mechanical flow controllers [1] consisting in a needle valve in

¹ División Química Analítica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata

² Miembro de la Carrera del Investigador del CONICET; Profesor Asociado, UNLP

serial array with a diaphragm operated valve. Although these were employed with the intention to keep a constant mass flow, their capacity to respond adequately to changing flow conditions along wide temperature intervals becomes rapidly overwhelmed [2]. In consequence, their behavior under actual temperature programming turns unpredictable from a practical standpoint. With the development of electronically driven mechanisms reliable mass flow control is 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 monotonously decreasing outlet volume flow rate with rising temperature [1,2], i. e. going in the opposite way to temperature programming in 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 a 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 different types of flow control are currently used, not existing a common standardization of $P(T)$. The nature of the retention equation in PTGC, in which the unknown variable (the retention time t_R) is an integration limit, does not permit to settle a priori a quantitative approach to the problem without making any explicit calculation.

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 of cylindrical coordinates that describes 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 , being L 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 [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 column's varying flow conditions, e. g. mechanical controllers and needle valve systems [2], 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]:

$$1 = \int_0^L (Q/L) dz = \sum_{\substack{\text{peak emerg.} \\ \text{all steps}}} \left[\underbrace{\frac{1}{(1+k)} \int_{t_i}^{t_f} \frac{dt}{t_M}}_{\text{isoth. steps}} + \underbrace{\int_{T_i}^{T_f} \frac{dT}{f'(T) t_M(T) [1+k(T)]}}_{\text{PT steps}} \right] \quad (6)$$

The sum is performed over all the steps of the global program involved from injection until 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, being T_0 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 it follows, all multistep retention expressions will be resumed in the same way. Although the retention time/temp. will not be indicated there, it will be assumed as 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 solution with temperature and pressure.

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

ΔH_s is the molar enthalpy of solution, a the entropic factor, β the phase ratio of the column and R the universal gas constant.

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

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

The “dead time constant” C_t 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 initial setting in a 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 isothermal-isobaric reference condition. Then, the constant is estimated by [2]:

$$C_t^{-1} = \frac{t_M^0 (P^{0^2} - 1)^2 p_o}{(P^{0^3} - 1) T_0^N} \quad (9)$$

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_t 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_t is [2]:

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

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:

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

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

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

Here we will estimate C_t , 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 eq. (6) can be written explicitly in terms of $P(T)$ or the head pressure function generated by the chromatograph:

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

Isoth. steps PT steps

Once C_t of the column is determined by one of the described possible procedures, and the head pressure program $p_i(T)$ is defined, the numerical estimation of retention from solute's thermodynamic parameters through eq. (13) is obtainable.

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). Only a 30 m long, 0.25 mm i. d. with 0.25 μm film width, AT-1, catalogue AllTech 13638 (Polydimethylsiloxane), capillary column was employed throughout this work, using nitrogen as the carrier gas. Detailed information about chromatograph's flow control configurations, main features of the electronic pressure control, as well as some aspects of 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, ranging 40-80 C around each solute's T_R from temperature program 1, Table 2. These runnings 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, being t'_R the adjusted retention time. Results are presented in Table 1 indicating the thermal interval where these were evaluated and the correlation coefficient. 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 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 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, data required for the numerical simulation.

Table 1
Entropic and enthalpic parameters of k .

Solute	$-\Delta H_i^0/k$ (K)	$(a/\beta) \times 10^6$	Temp. Interval C	Correl. coeff.
n-Octane	4175	5.533	50-120	0.99990
<i>p</i> -Xylene	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
n-Dodecane	5559	1.695	140-180	-
n-Tetradecane	5990	1.545	200-220	-
n-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 80C]→ →[I:0.5 min]→[PT: 10 C/min to 250]	CMF
3	same as 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 2	[PP: 51.715 Torr/min]
5	same as 2	CP

Initial temperature is $T_0 = 50$ C for every program, (p_o, 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-isoth. step, PT-lin. programmed temp. step, CMF-constant mass flow, CP-constant inlet pressure, PP-lin. progr. inlet pressure.

Table 3

Experimental and calculated retention times in different temperature-pressure programs

Solute	Retention Times (min)									
	Progr.1		Progr.2		Progr.3		Progr.4		Progr.5	
	CMF mode		CMF mode		PP mode		PP mode		CP mode	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
n-Octane	4.879	4.880	6.169	6.189	6.032	6.070	5.153	5.230	4.562	4.590
p-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
n-Dodecane	10.931	10.800	15.641	15.450	14.952	14.820	13.800	13.640	14.924	14.700
n-Tetradecane	13.585	13.350	18.570	18.500	17.720	17.440	16.672	16.330	18.246	17.870
n-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_o (Torr)	765		765		770		770		770	

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

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 ($f'(T) = r_T = const.$).

Being $p_i = p_i^0 = const.$, by using eq. (9), eq. (13) reduces to:

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

For the evaluation of retention through eq. (14) the only information to be entered into the calculation, besides 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 to the computer program. The mean error

of 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 reference [10]. Results are compared simultaneously with experimental and calculated data listed in table 11 in the paper of Snijders, Janssen and Cramers. Differences between the algorithms followed by the cited and present authors deserves a brief comment.

In reference [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 , as consequence that the carrier gas local velocity is evaluated for each coordinate and temperature increment. In reference [16] 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) and (12), i. e. calculating p_i 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 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 by eq. (9) and the procedure followed by Snijders et al. corresponds to the evaluation of C_i from eq. (12), which assumes valid Poiseuille's equation. The other aspect is that we approximated the temperature dependence of gas viscosity as a temperature power law. $N=0.646$ was entered for He as the carrier gas [18]. Small numerical differences between 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 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 Kovats retention index. This unique characteristic of parametrical dependence of retention on chromatograph's fluid dynamics is not accounted for systems where $p_i(T)$ is allowed to evolve during the temperature program, depending the retention 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.

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 hypothesis that are inherent to eq. (8), already mentioned in the section General (D'Arcy, ideal gas, thermal invariance of column's geometric parameters and gas viscosity factorization). Although it does not strictly defines 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 refence [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 $P(T)$ of a linear pressure programmable device, although restricted to a fixed compression rate and isobaric behavior 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 of program 5 or Table 4 (CP mode).

LINEAR PROGRAMMED INLET PRESSURE

Electronic pressure control adds the possibility of changing the rate of pressure increase at column's head, and also to vary 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 a 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 intermediat step replacing (T_0, p_i^0) by the correspondent initial temperature and pressure of the interval. Now the calculation algorithm requires the

introduction of eq. (16) in the isothermal cycle and (17) in the PT cycle. Furthermore, the computation program has to incorporate the necessary data input sentences for 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 isobaric condition for the isothermal steps and Program 4 includes variable pressure during the isothermal intervals. Again, the contrast with experimental data reveals a close accuracy in respect to programs described previously.

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 behavior 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 indistinguishable. Of course, equality (21) does not hold for multistep temperature programs, being valid, in this later case, only under some particular conditions.

Table 5 presents calculated values of the parameter for the eight solutes of this study, under the program defined by ramps: $r_T=15$ C/min and $r_p=15$ Torr/min, and 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 $k=0$ to the CP and PP computer programs, yielding t_M^{CP} and t_M^{PP} , respectively. At first glance it arises that 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 exceptional abnormal high value, respect to 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 shall intend to approach this problem in a forthcoming paper.

Table 5

Variations of eq.(21) parameter for different pairs of solutes (x,y)

$y \backslash x$	n-Octane	p-Xilene	1,3,5 TMBenzene	1-Undecene	Naphthalene	n-Dodecane	n-Tetradecane	n-Hexadecane
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
1,3,5TMBenzene				0.919	0.912	0.916	0.915	0.915
1-Undecene					0.900	0.912	0.913	0.914
Naphthalene						<u>0.951</u>	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, $r_T=15$ C/min, $T_0=50$ 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 $\sigma=0.0083$.

Table 6 is an arrangement of characteristic data from four different tables of the same type of Table 5. The later is designated as "A" in Table 6. The data has been ordered by increasing r_p ramps. E is a multiramp program. Reported \bar{X} value is the average retention time parameter of eq. (21). Variations, accounted by the standard deviation σ of 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 $(t_M^{PP} / t_M^{CP})^2$, 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 a mere empirism. In 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:

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

Table 6

Behavior of eq.(21) parameter under different T-P programs

Designation	Temp.Progr. r_T (C/min)	Press.Progr. r_P (Torr/min)	\bar{X}	σ	n- Oct/Unret.	$(t_M^{PP}/t_M^{P^2})$
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	—

In consequence, for a gross estimation of the effect on retention by 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 $k=0$ to the respective computer programs. Equation (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 cannot be obtained, being necessary the complete numerical simulation.

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 behavior, even for homologues substances, is very complex, leaving no other way than the estimation through numerical simulation from thermodynamic parameters. In 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 along the development of this work seeking for some general correlation of retention under different pressure single ramps, leading to discouraging results.

ACKNOWLEDGEMENT

This work was sponsored by the Consejo Nacional de Investigaciones Científicas y Técnicas and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires. The authors are very grateful to Prof. Dr. L.F.R. Cafferata, who provided the chromatographic facilities.

REFERENCES

- [1] Hinshaw, J.V.- *LC-GC*, **13**, 792 (1995).
- [2] Gonzalez, F.R.; Nardillo, A.M.- *J. Chromatogr. A* , **757**, 109 (1997) .
- [3] Wicar, S.- *J. Chromatogr.*, **295**, 395 (1984).
- [4] Hermann, B.W.; Freed, L.M.; Thompson, M.Q.; Phillips, R. J.; Klein, K.J.; Snyder, W.D.- *J. High Res. Chromatogr., Instrum.*, **13**, 361 (1990).
- [5] Akporhonor, E.F.; Le Vent, S.; Taylor, D.R.- *J. Chromatogr.*, **405**, 67 (1987).
- [6] Dose, E.V.- *Anal. Chem.*, **59**, 2414 (1987).
- [7] Bautz, D.E.; Dolan, J.W.; Snyder, L.R.- *J. Chromatogr.*, **541**, 1 (1991).
- [8] Gerbino, T.C.; Castello, G.; Pettinati, U.- *J. Chromatogr.*, **634**, 338 (1993); **635**, 338 (1993).
- [9] Gerbino, T.C.; Petit Bon, P.- *Ann. Chimica*, **84**, 305 (1994).
- [10] Snijders, H.; Janssen, H.G.; Cramers, C.- *J. Chromatogr. A*, **718**, 339 (1995).
- [11] Curvers, J.; Rijks, J.; Cramers, C.; Knauss, K.; Larson, P.- *J. High. Res. Chromatogr., Chromatogr. Commun*, **8**, 607, 611 (1985).
- [12] Guan, Y.; Kiraly, J.; Rijks, J.A.- *J. Chromatogr*, **472**, 129 (1989).
- [13] Fernández-Sánchez, E.; García-Domínguez, J.A.; Menéndez, V.; Santiuste, J.M.- *J. Chromatogr.*, **498**, 1 (1990).
- [14] Said, A.S.; Jarallah, A.M.; Al-Ameeri, R.S.- *J. High Res. Chromatogr., Chromatogr. Commun*, **9**, 1 (1986).
- [15] Messadi, D.; Ali-Mukhnache, S.- *Chromatographia*, **37**, 64 (1993).
- [16] Gonzalez, F.R.; Nardillo, A.M.- *J. Chromatogr. A*, **766**, 147 (1997).
- [17] Al-Thamir, W.K.; Purnell, J.H.; Wellington, C.A.; Laub, R.J.- *J. Chromatogr*, **173** , 388 (1979).
- [18] Ettre, L.S.- *Chromatographia*, **18**, 15 (1984).