

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

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Abstract

The simultaneous temperature and inlet pressure programming (TPP) in gas chromatographic analysis decreases the retention time and the maximum value of temperature required for the elution of high boiling substances. Therefore, compounds sensitive to thermal degradation can be better analysed and column ageing is reduced. However, the empirical choice of proper analysis conditions requires many preliminary runs; this paper describes a procedure for the theoretical prediction of retention times in TPP using few preliminary runs carried out in isobaric and isothermal conditions. The used program permits the prediction of the retention times of the compounds analysed with any different TPP run carried out within the temperature and pressure ranges investigated with the preliminary runs. The influence of various analytical parameters on the accuracy of the prediction values was investigated. The proposed model also predicts the relative position in the chromatogram of closely eluting peaks and the possible coincidence of retention times or inversion of the elution order with changing temperature. It is also possible to foresee the analytical conditions, which offer a baseline separation of all of the peaks of the sample.

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1. Introduction

Although inlet pressure increase was suggested at the beginning of gas chromatography as a mean to increase analysis speed, and a survey on the advancement of this technique was reported in the book published by Purnell in 1962 [1], temperature programming was preferred due to the availability of suitable temperature programmers and high temperature stationary phases. The possibility of automatically modifying inlet pressure at a controlled and reproducible rate was available in 1964–1965, with the first mechanical pressure programming units. However, the difficulty of monitoring exactly the change of the flow-rate during pressure programming made studies on this subject partly abandoned. Many gas chromatographic instruments are now equipped with suitable inlet pressure programmers and electronic pressure and

flow-rate measuring units and this technique can be now easily applied. Even though the great improving possibilities offered by simultaneous temperature and pressure programming, there are relatively few papers published on this subject [2–7] and the proposed models often are very complex [6].

The main advantages of simultaneous temperature and pressure programming (TPP) can be summarised as follows:

- (1) As a lower temperature is reached during the run, the number of liquid phases applicable to a given problem is increased.
- (2) Low temperature reduces the possibility of decomposition of thermally unstable samples.
- (3) As the height of a peak is related to the flow-rate, broad peaks will be sharpened allowing for better detection of small concentration samples.
- (4) Although in pressure programming the flow rates are usually higher than the optimum value corresponding to the minimum of the Golay curve, the simultaneous temper-

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ature programming moves the minimum to higher flow rate values leading to better conditions.

However, as four independent variables have to be set (initial temperature and pressure values, temperature and pressure programming rate) the empirical choice of the conditions for the best separation requires a large number of preliminary runs. Therefore, the simulation of retention times in TPP analysis by using as input values the data of few isothermal and isobaric runs can decrease the time required for the optimisation of the analytical parameters. In this paper, a mathematical model is described, which simulates the retention times in TPP runs by using the retention times, measured with few preliminary runs and permits to obtain the best analytical conditions in a short time. It also evaluates the relative position of the peaks and predicts any retention time inversion due to temperature program. In the instance of peak coincidence or inversion an auxiliary program permits to predict the best TPP run which offers a required value of resolution between all the interfering compounds.

2. Theory

The retention time, in a capillary column under isothermal and isobaric conditions, is described as follows:

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

where $k = t'_R/t_M$ the mean retention (or capacity) factor and t_M , the gas hold-up time, depend on temperature and pressure [7–10]. The k value is influenced by thermodynamic parameters through the following equation [11]:

$$k(T, P) = \frac{1}{\beta} e^{(-\Delta G(T, P)/RT)} \quad (2)$$

where β is the phase ratio of the column, $\Delta G = \Delta H - T\Delta S$ is the free energy of solution or partition of a given compound, R the universal gas constant and T is the absolute temperature.

In a previously published paper [12] it has been found that the k value slightly depends on the pressure, but in this instance the dependence of k on pressure was not taken into account because it is small and of the same order of magnitude of the experimental error. For practical purposes it can be considered as a constant; the computation time is reduced and the increase of the error is negligible. When the temperature interval is small, the dependence of ΔH and ΔS on T could be taken as linear, so the k becomes [13,14]:

$$k(T) = e^{((A/T)+B+CT)} \quad (3)$$

where A , B and C are parameters depending only on the solute–solvent interactions. They must be known in order to predict the retention time values in TPP runs. By calculating the gas hold-up time and by using experimental retention times for each compound eluted in all of the isothermal and isobaric conditions of the preliminary runs, through Eqs. (1)

and (3) one obtains:

$$\ln \left(\frac{t_R}{t_M} - 1 \right) = \ln k = \frac{A}{T} + B + CT \quad (4)$$

then using Eq. (4) by interpolation, with the least square method on $\ln k$, it is possible to obtain the coefficients A , B , C of each compound eluted in the range covered by the preliminary runs (in this instance 60–160 °C and 5–30 psig). These coefficients are valid within the whole temperature and pressure range.

The next step of the model describes a method to calculate the retention times in TPP runs using the equation introduced above. The retention time can be considered as the sum of n time intervals of equal length Δt . During any TPP run the temperature gradient could be written as:

$$g_T = \frac{T_j - T_0}{t} \quad (5)$$

where t is the time from the beginning of the run, T_j the temperature in the column at time t and T_0 is the starting temperature of the analysis. In the same way it is possible to write the pressure gradient as:

$$g_P = \frac{P_{in,j} - P_{in,0}}{t} \quad (6)$$

where t is the time from the beginning of the run, $P_{in,j}$ the pressure at the column inlet at time t , $P_{in,0}$ is the starting pressure at column inlet. After j time intervals, the temperature and inlet pressure in the column are:

$$T_j = T_0 + jg_T \Delta t \quad (7)$$

$$P_{in,j} = P_{in,0} + jg_P \Delta t \quad (8)$$

During a generic j th time interval the compound will move inside the column of a ΔL_j , length changing along the column as a function of the carrier gas flow rate and temperature; if in this tract the compound speed $u_{e,j}$ is considered as a constant, then:

$$u_{e,j} = \frac{\Delta L_j}{\Delta t} \quad (9)$$

and

$$L = \sum_{j=1}^n \Delta L_j = \sum_{j=1}^n u_{e,j} \Delta t \quad (10)$$

the moving speed of the peak of a compound in ΔL_j is:

$$u_{e,j} = \frac{u_{cg,j}(T_j, P_j)}{1 + k(T_j)} \quad (11)$$

where $u_{cg,j}$ is the carrier gas velocity in the ΔL_j interval, P_j the pressure in the ΔL_j interval and T_j is the temperature in the column after j time intervals of length Δt .

The u_{cg} as a function of pressure is defined, using the D'Arcy law [7,13,15]:

$$u_{cg} = -\frac{4r^2}{32\eta} \frac{dP}{dL} \quad (12)$$

where dP/dL is the pressure change of the carrier gas along the column. By solving Eq. (12) as described in a previous paper [12], the following equation is obtained:

$$\Delta L_{cg,j}(T_j, P_j) = L \frac{P_j^2 - (P_j^3 - \Delta t(3r^2/32L^2\eta(T_j))(P_{in,j-1}^2 - P_o^2)^{2/3})}{P_{in,j-1}^2 - P_o^2} \quad (13)$$

With

$$P_j = \sqrt{P_{in,j-1}^2 - \frac{L_j}{L}(P_{in,j-1}^2 - P_o^2)} \quad (14)$$

where $\Delta L_{cg,j}$ is the column length which the carrier gas travels during the small Δt interval and L_j is the total length from the injector travelled by the compound after j intervals Δt because:

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

By starting from Eq. (15) and using an iterative computation procedure it is possible to obtain the value of the number n of column intervals travelled by the eluted compound. The value of ΔL depends on temperature and pressure conditions and on the compound analysed. The following example can explain the correlation: if a compound X elutes with a retention time of 5 min and Δt has a known constant value of 0.1 s, then the value of n is 3000. In this instance the ΔL value is about 1 cm. This calculation can be carried out for every compound when temperature, pressure and k values are known.

The retention time of a compound eluted in any TPP condition will be given by:

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

The flow diagram of the program used for the prediction of the retention times on the basis of the described theory is shown in Fig. 1.

3. Experimental

A Varian mod. 3800 gas chromatograph was used (Varian Associates, Palo Alto, CA, USA) equipped with a split-splitless capillary injector (split ratio 1/20) and a flame ionisation detector. Three capillary column having a length of 30 m and 0.25 μm phase thickness were used: two non polar poly(dimethylsiloxane) columns: DB-1 (J&W Scientific, Folsom, CA, USA) and CP SIL 5CB (Varian Associates) and a polar poly(ethylenglycol) column: CP WAX 52CB (Varian Associates). All the used columns had a nominal internal diameter of 0.320 mm. The true value of this important parameter was measured by scanning electron microscope using a Stereoscan 440 SEM, LEO, Cambridge, UK, and was found to be 0.327 mm for DB-1, 0.330 mm for CP SIL 5CB and

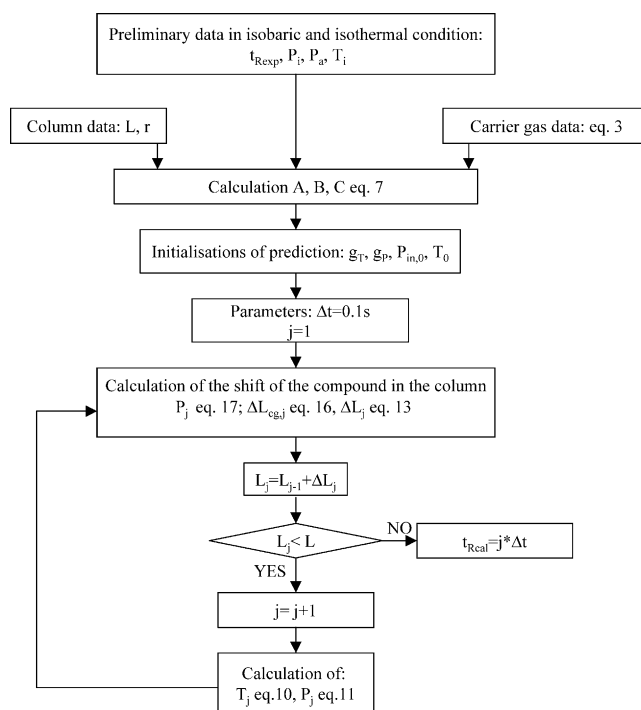


Fig. 1. Flow diagram of the program used to predict the retention time in programmed pressure and temperature analysis. The meaning of the used symbols is described in Section 2.

0.320 mm for CP WAX 52CB. The analysis was carried out in the temperature range from 60 to 160 °C and in the pressure range from 5 to 30 psig. The term psig (pounds per square inch gauge) is used in order to indicate the values above the atmospheric pressure given by the gas chromatograph software and therefore is referred to the constant pressure of the isobaric runs and to the initial value of the programmed pressure runs. The pressure gradient is indicated as psi values (1 psi = 6894.76 Pa). Samples containing several terms of the homologous series of n -alkanes, of straight chain 1-alcohols and of some alkenes, chloroalkanes, ketones and others compounds selected in order to investigate the effect of polarity, were injected without solvent at the smaller amount permitted by the use of the microsyringe with the “needle tip” technique in order to avoid interference due to the tail of the solvent peak in the analyses carried out at the highest values of inlet pressure and temperature. The chromatograms were integrated and the retention times measured with an accuracy of ± 0.001 min by using a “Star” data system (Varian Associates).

The temperature of the column was monitored by using an auxiliary thermocouple inserted into the coils of the capillary column, with a precision of ± 0.1 °C, greater than the gas chromatograph’s measurement of the average oven temperature (± 1 °C). The linearity and the exact value of the inlet pressure were monitored by connecting to the injector a mercury manometer with a precision of ± 1 mmHg (133.3 Pa or 0.0193 psi), greater than that offered by the built-in hardware

Table 1

Experimental retention times, t_{Rexp} (min); relative percent error, $E\%_{\text{rel a}}$, of the prediction of the retention times by using the data of nine preliminary runs ($T=78.3, 98.2$ and 118.5°C ; $P=5.08, 15.10$ and 25.10 psig); relative percent error, $E\%_{\text{rel b}}$, of the prediction with three preliminary runs ($T=78.3, 98.2$ and 118.5°C ; $P=15.10$ psig); average absolute percent error $E\%_{\text{abs ave}}$ for two TPP runs obtained on CP SIL 5CB capillary column ($30\text{ m} \times 0.330\text{ mm}$, $0.25\ \mu\text{m}$ layer thickness)

Compound	TPP 1			TPP 2		
	t_{Rexp}	$E\%_{\text{rel a}}$	$E\%_{\text{rel b}}$	t_{Rexp}	$E\%_{\text{rel a}}$	$E\%_{\text{rel b}}$
<i>n</i> -Octane	3.707	0.054	0.189	2.970	0.056	0.056
1-Nonene	4.568	0.029	0.066	3.358	0.040	-0.060
1-Heptanol	5.553	-0.066	-0.066	3.787	-0.035	-0.079
2-Octanone	5.867	-0.023	-0.051	3.947	-0.034	-0.118
<i>n</i> -Decane	6.352	0.005	-0.021	4.170	0.000	-0.080
1-Octanol	7.650	-0.065	-0.087	4.767	-0.098	-0.133
2-Nonanone	8.090	-0.041	-0.062	5.007	-0.027	-0.093
1-Undecene	8.438	-0.004	-0.043	5.178	-0.039	-0.103
1-Nonanol	10.502	-0.029	-0.076	6.220	-0.054	-0.107
2-Decanone	11.052	-0.027	-0.072	6.545	-0.051	-0.102
1-Dodecene	11.474	0.020	-0.023	6.775	0.000	-0.074
<i>n</i> -Dodecane	11.856	0.022	-0.006	6.983	-0.029	-0.076
1-Decanol	13.979	-0.019	-0.067	8.192	-0.016	-0.077
$E\%_{\text{abs ave}}$		0.031	0.064		0.037	0.089

TPP 1: initial temperature 78.3°C , temperature gradient $2^\circ\text{C}/\text{min}$, initial pressure 5.08 psig, pressure gradient 0.5 psi/min, atmospheric pressure 744.7 mmHg;

TPP 2: initial temperature 98.5°C , temperature gradient $2^\circ\text{C}/\text{min}$, initial pressure 5.08 psig, pressure gradient 1 psi/min, atmospheric pressure 760.7 mmHg.

Table 2

Experimental retention times, t_{Rexp} (min), relative percent error, $E\%_{\text{rel a}}$, of the prediction of the retention times by using the data of nine preliminary runs ($T=78.3, 98.2$ and 118.5°C ; $P=5.08, 15.10$ and 25.10 psig); relative percent error, $E\%_{\text{rel b}}$, of the prediction with three preliminary runs ($T=78.3, 98.2$ and 118.5°C ; $P=15.10$ psig); average absolute percent error $E\%_{\text{abs ave}}$ for two TPP runs obtained on CP WAX 52CB capillary column ($30\text{ m} \times 0.320\text{ mm}$, $0.25\ \mu\text{m}$ layer thickness)

Compound	TPP 3			TPP 4		
	t_{Rexp}	$E\%_{\text{rel a}}$	$E\%_{\text{rel b}}$	t_{Rexp}	$E\%_{\text{rel a}}$	$E\%_{\text{rel b}}$
2-Heptanone	5.219	-0.083	-0.179	2.969	-0.034	-0.146
<i>n</i> -Tridecane	6.883	-0.005	-0.029	4.031	-0.058	-0.058
1-Tridecene	7.779	0.009	0.009	4.616	-0.014	-0.014
2-Nonanone	8.848	0.015	0.034	5.319	-0.050	-0.019
1-Heptanol	10.432	0.051	0.019	6.394	-0.016	-0.016
<i>n</i> -Pentadecane	11.732	0.045	0.003	7.282	0.027	-0.018
1-Pentadecene	13.107	0.028	-0.036	8.226	0.032	-0.028
2-Undecanone	14.725	0.000	-0.079	9.336	-0.007	-0.079
1-Hexadecene	16.415	-0.010	-0.091	10.522	0.051	-0.044
1-Nonanol	16.856	-0.024	-0.113	10.830	0.015	-0.077
<i>n</i> -Heptadecane	18.318	-0.038	-0.138	11.851	0.051	-0.062
1-Decanol	20.484	-0.086	-0.168	13.357	-0.010	-0.085
$E\%_{\text{abs ave}}$		0.033	0.075		0.030	0.054

TPP 3: initial temperature 78.4°C , temperature gradient $2^\circ\text{C}/\text{min}$, initial pressure 5.08 psig, pressure gradient 0.5 psi/min, atmospheric pressure 760.7 mmHg;

TPP 4: initial temperature 78.4°C , temperature gradient $3^\circ\text{C}/\text{min}$, initial pressure 10.10 psig, pressure gradient 1 psi/min, atmospheric pressure 760.7 mmHg.

of gas chromatograph (± 0.1 psi), because these parameters influence strongly the results of the t_{R} prediction. The atmospheric pressure was measured with a mercury barometer with a precision of 0.1 mmHg.

4. Results and discussion

Tables 1–3 show the results obtained with different linear TPP runs on CP SIL 5CB, CP WAX 5CB and DB-1 capillary columns. The true values of initial temperature and pressure and of the corresponding gradients, measured as described

in Section 3, are reported in the legends of the tables. The experimental retention times, t_{Rexp} , the relative percent error, $E\%_{\text{rel a}}$ obtained by using three isobaric run and three isothermal run as preliminary analyses and the relative percent error, $E\%_{\text{rel b}}$, obtained by using one isobaric run and three isothermal run as preliminary analyses, are shown. The relative percent errors are calculated as:

$$E\%_{\text{rel}} = 100 \times \frac{t_{\text{Rexp}} - t_{\text{Rcal}}}{t_{\text{Rexp}}} \quad (17)$$

where t_{Rcal} is the calculated retention times, obtained with the equations shown in Section 2. For every compound, the

Table 3

Experimental retention times, t_{Rexp} (min); relative percent error, $E\%_{\text{rel a}}$, of the prediction of the retention times by using the data of nine preliminary runs ($T=58.4^\circ\text{C}$, 88.3°C and 118.5°C , $P=5.08$, 15.10 and 25.10 psig); relative percent error, $E\%_{\text{rel b}}$, of the prediction with three preliminary runs ($T=58.4^\circ\text{C}$, 88.3°C and 118.5°C , $P=15.10$ psig); average absolute percent error $E\%_{\text{abs ave}}$ for four TPP runs obtained on DB-1 capillary column ($30\text{ m} \times 0.327\text{ mm}$, $0.25\ \mu\text{m}$ layer thickness)

Compound	TPP 5			TPP 6			TPP 7		TPP 8	
	t_{Rexp}	$E\%_{\text{rel a}}$	$E\%_{\text{rel b}}$	t_{Rexp}	$E\%_{\text{rel a}}$	$E\%_{\text{rel b}}$	t_{Rexp}	$E\%_{\text{rel b}}$	t_{Rexp}	$E\%_{\text{rel b}}$
1-Decene	8.603	-0.178	-0.275	7.657	0.004	0.061	5.317	-0.150	4.843	-0.024
Nitrobenzene	10.685	0.109	-0.031	9.511	-0.025	0.130	6.620	-0.038	6.165	0.000
2-Nonanone	11.483	-0.003	-0.090	10.336	-0.039	0.119	7.142	-0.089	6.773	-0.116
1-Nonanol	14.638	0.043	0.225	13.315	0.100	-0.250	9.720	0.060	9.340	-0.107
Naphthalene	14.944	-0.007	0.004	13.796	-0.029	0.005	9.415	0.097	8.943	0.024
2-Decanone	15.489	0.047	0.015	14.313	0.021	0.014	10.139	0.056	9.714	-0.088
<i>n</i> -Dodecane	16.576	-0.064	-0.095	15.474	0.112	-0.090	11.067	0.056	10.585	0.024
$E\%_{\text{abs ave}}$		0.065	0.105		0.047	0.096		0.078		0.055

TPP 5: initial temperature 58.1°C , temperature gradient $2^\circ\text{C}/\text{min}$, initial pressure 5.08 psig, pressure gradient 0.5 psi/min, atmospheric pressure 756.3 mmHg; TPP 6: initial temperature 58.4°C , temperature gradient $1.5^\circ\text{C}/\text{min}$, initial pressure 5.08 psig, pressure gradient 1 psi/min, atmospheric pressure 756.3 mmHg; TPP 7: initial temperature 68.6°C , temperature gradient $1^\circ\text{C}/\text{min}$, initial pressure 5.08 psig, pressure gradient 2 psi/min, atmospheric pressure 760 mmHg; TPP 8: initial temperature 58.5°C , temperature gradient $2^\circ\text{C}/\text{min}$, initial pressure 10.10 psig, pressure gradient 2 psi/min, atmospheric pressure 760 mmHg.

absolute average percent error $E\%_{\text{abs ave}}$, obtained by averaging the absolute values of the errors for all the compounds, is reported. The errors are random and no clear dependence on the analysed compound can be observed. The use of only three preliminary analyses does not decrease appreciably the relative percent error for any TPP condition on the three columns.

The influence of the variation of the parameters of the analysis on the calculated t_{R} values has been evaluated by measuring the percent relative error of the retention time for all the compounds. The relative percent error values, $E\%_{\text{rel}}$, on the CP SIL 5CB column when the analytical parameters are changed of the amount that may be due to improper

setting of the gas chromatograph or to mistakes or uncertainty in the input of the parameters to the mathematical model are shown in Table 4. The values were obtained as follows: nine preliminary runs were carried out by combination of the following true values of the parameters: temperature 78.3 , 98.2 and 118.5°C ; pressure 5.08 , 15.10 and 25.10 psig. A TPP run with the following true conditions was then carried out: temperature 78.3°C , atmospheric pressure 744.7 mmHg, initial column pressure 5.08 psig, pressure gradient 0.5 psi/min and temperature gradient $2^\circ\text{C}/\text{min}$. When the evaluation of the calculated t_{R} is done by using the true values of the parameters, very accurate results are found (see third column of Table 4). When the TPP runs and the iso-

Table 4

Effect of changing the analytical parameters on the accuracy of the retention time prediction on CP SIL 5CB column in a programmed run: initial temperature 78.3°C , temperature gradient $2^\circ\text{C}/\text{min}$, initial pressure 5.08 psig, pressure gradient 0.5 psi/min, atmospheric pressure 744.7 mmHg. The values of the experimental retention times, t_{Rexp} (min), the relative percent error, $E\%_{\text{rel}}$, of the prediction with nine preliminary run ($T=78.3$, 98.2 and 118.5°C ; $P=5.08$, 15.10 and 25.10 psig); and average absolute percent error $E\%_{\text{abs ave}}$ are shown

Compound	t_{Rexp}	$E\%_{\text{rel}}$											
		True parameters	Nominal parameters	$P_a + 20$ mmHg	$P_a - 20$ mmHg	$T_1 + 2^\circ\text{C}$	$T_1 - 2^\circ\text{C}$	$P_1 + 1$ psig	$P_1 - 1$ psig	$gT + 0.1^\circ\text{C}/\text{min}$	$gT - 0.1^\circ\text{C}/\text{min}$	$gP + 0.1$ psi/min	$gP - 0.1$ psi/min
<i>n</i> -Octane	3.707	0.054	-0.800	0.054	0.009	1.493	-1.520	1.403	-1.340	0.189	-0.081	2.572	-2.734
1-Nonene	4.568	0.029	-0.919	0.029	-0.007	2.328	-2.452	1.233	-1.211	0.285	-0.263	2.875	-3.145
1-Heptanol	5.553	-0.066	-1.056	-0.036	-0.096	2.935	-3.247	1.044	-1.177	0.384	-0.516	3.055	-3.608
2-Octanone	5.867	-0.023	-1.017	0.006	-0.051	3.045	-3.290	1.028	-1.102	0.460	-0.534	3.187	-3.659
<i>n</i> -Decane	6.352	0.005	-0.992	0.031	-0.021	3.233	-3.432	1.002	-1.018	0.582	-0.572	3.311	-3.773
1-Octanol	7.650	-0.065	-1.068	-0.044	-0.087	3.529	-3.834	0.828	-0.959	0.719	-0.850	3.464	-4.118
2-Nonanone	8.090	-0.041	-1.030	-0.021	-0.062	3.523	-3.791	0.803	-0.906	0.783	-0.886	3.543	-4.203
1-Undecene	8.438	-0.004	-1.011	0.016	-0.043	3.591	-3.796	0.806	-0.834	0.845	-0.893	3.611	-4.211
1-Nonanol	10.502	-0.029	-0.965	0.003	-0.060	3.685	-3.901	0.638	-0.711	1.114	-1.219	3.748	-4.456
2-Decanone	11.052	-0.027	-0.947	0.003	-0.057	3.637	-3.827	0.606	-0.661	1.164	-1.264	3.788	-4.506
1-Dodecene	11.474	0.020	-0.880	0.049	-0.009	3.666	-3.756	0.630	-0.590	1.255	-1.272	3.855	-4.483
<i>n</i> -Dodecane	11.856	0.022	-0.863	0.051	-0.006	3.663	-3.731	0.613	-0.568	1.316	-1.313	3.874	-1.504
1-Decanol	13.979	-0.019	-0.830	0.005	-0.055	3.534	-3.679	0.470	-0.508	1.507	-1.617	3.832	-4.585
$E\%_{\text{abs ave}}$		0.031	0.952	0.027	0.043	3.220	3.404	0.854	0.891	0.816	0.868	3.440	3.999

T(°C)	Compounds				
	t_R (min)				
60	Nitrobenzene 26.124	2-Nonanone 31.943	Naphthalene 53.368	1-Nonanol 63.336	2-Decanone 67.779
80	Nitrobenzene 12.959	2-Nonanone 14.435	Naphthalene 23.396	1-Nonanol 24.303	2-Decanone 26.409
90	Nitrobenzene 9.924	2-Nonanone 10.652	Naphthalene + 1-Nonanol 16.645		2-Decanone 17.994
100	Nitrobenzene 6.135	2-Nonanone 7.983	1-Nonanol 12.046	Naphthalene 12.531	2-Decanone 12.983
110	Nitrobenzene 6.694	2-Nonanone 6.825	1-Nonanol 9.223	Naphthalene + 2-Decanone 9.854	
120	Nitrobenzene + 2-Nonanone 5.853		1-Nonanol 7.454	2-Decanone 7.898	Naphthalene 8.030

Fig. 2. Change of the retention time and inversion of the elution order for five compounds (nitrobenzene, 2-nonanone, naphthalene, 1-nonanol and 2-decanone) analysed on DB-1 capillary column in isobaric run (5 psig) at different temperatures.

baric preliminary runs are evaluated by using the nominal parameters (80, 100 and 120 °C and 5, 15 and 25 psig, respectively), i.e. the values input to the gas chromatograph during the setting of the runs, the mathematical model predicts the retention times with tolerable error of the order of 1% (see fourth column of Table 4). In this instance all the experimental t_R value are smaller than those calculated. As the true pressure values were greater than the nominal ones and the true temperatures were smaller than the nominal, it seems that with the observed differences between true and nominal input values the effect of the pressure variation predominates and counterbalances that of the difference of temperature.

The influence of the various analytical parameters on the final accuracy of the prediction is different, as can be seen in the other columns of Table 4. The variation of the atmospheric pressure with respect of the true value, P_a , has a negligible effect on the results, as a variation of ± 20 mmHg leads to a very low average error. The high value of the possible fluctuation of the atmospheric pressure was selected notwithstanding the fact that its value was measured with a good accuracy (0.1 mmHg with precision mercury barometer and temperature correction), but the daily or weekly average fluctuation observed was as high as 20 mmHg owing to weather changes. Therefore, if a precision barometer is not available or the operator does not take into account the true atmospheric pressure differences between the true outlet pressure and the nominal one as high as ± 20 mmHg can be observed.

On the contrary, a difference of ± 2 °C in the setting of the initial temperature, T_i , which can be observed during routine

work, causes a very high average error because temperature influences the determination of the dead time and therefore the calculation of A , B and C parameters of Eq. (4). The differences between the true and the input initial pressure values have an effect smaller than that of temperature. The temperature gradient has been checked with the independent thermocouple and, when temperature increases rapidly, a difference between preset and actual values of the order of 0.1 °C was observed. It was not possible to measure with independent technique the difference between preset and true pressure values during pressure programming, because the mercury manometer connected to the injector which give good accuracy when measuring the initial pressure, has a too long equilibration time and cannot follow correctly quick pressure changes. It was supposed that the error of the built in electronic pressure transducer during programmed pressure runs is of the same order of magnitude of the measurement of isobaric pressure, i.e. 0.1 psi. In this instance the influence on the calculation is great, as shown in the last column of Table 4. As the true analytical parameters may be different from the values set with the control panel of the gas chromatograph, it is important to check the accuracy of the calibration of the instrument.

The data shown in Table 3 (non-polar DB-1 column) for the programmed runs TPP 5 and TPP 6 do not show any inversion of the elution order because these programmed runs were carried out in a temperature range where all the peaks are eluted in the same order. On the contrary, the runs TPP 7 and TPP 8 show that some compounds are eluted in a different sequence. Fig. 2 shows the inversion of the elution order of the compounds analysed on the DB-1 column at

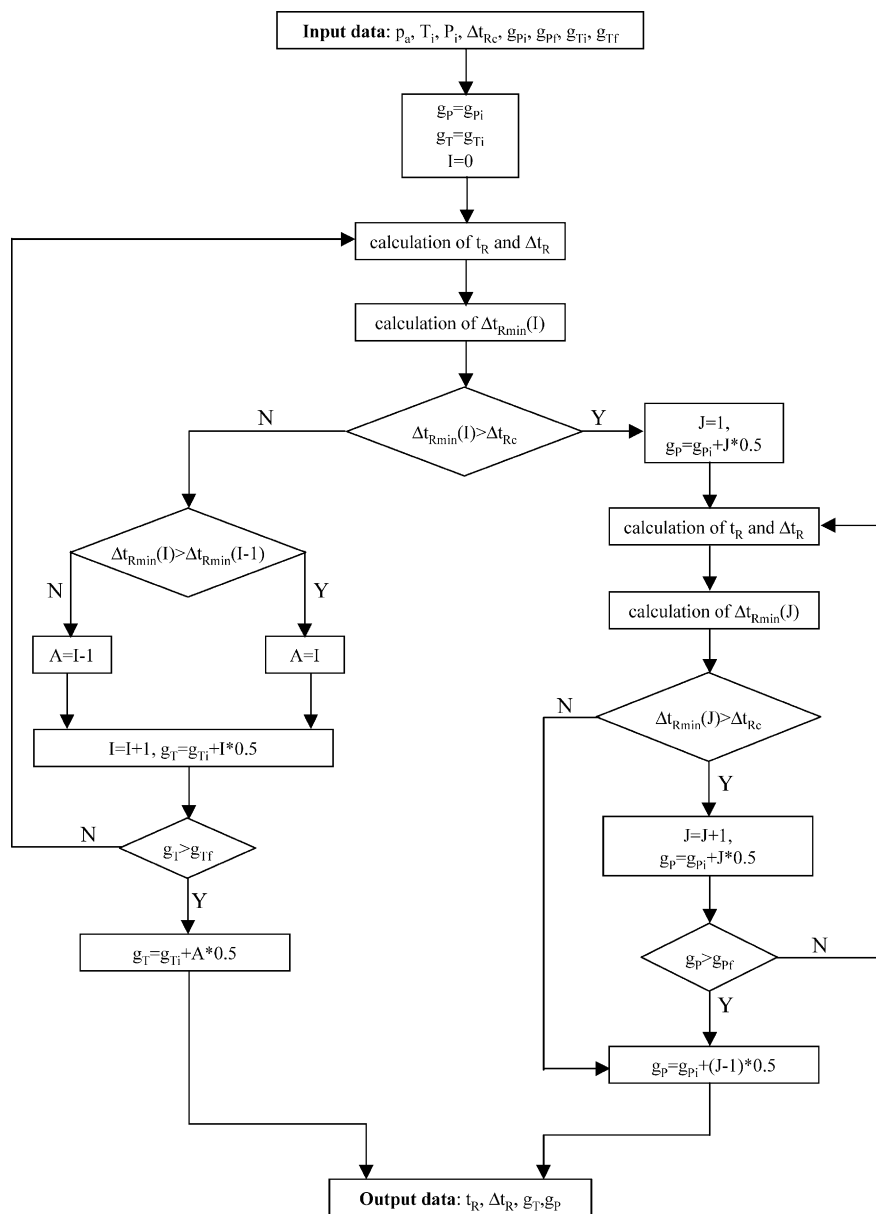


Fig. 3. Flow diagram of the auxiliary program used to predict the conditions of interfering peak. Symbols for input data: P_i is the inlet pressure, T_i the initial temperature, Δt_{Rc} is a minimum difference in retention time for the baseline resolution, g_{pi} the initial pressure gradient, g_{pf} the final pressure gradient, g_{Ti} the initial temperature gradient and g_{Tf} is the final temperature gradient.

the constant inlet pressure of 5 psig when the temperature is changed from 60 to 120 °C. The calculation program can predict the inversion of the elution order and permits the identification of the compounds when the starting data are obtained in isobaric condition at three temperatures covering the full range used in the further prediction. However, quantitative analysis requires a good separation of the peaks in order to decrease the reciprocal contribution of the two adjacent areas. The condition necessary for the baseline separation of all of the interfering peaks was obtained with an auxiliary program (flow diagram shown in Fig. 3) which predicts the analytical conditions yielding the required differ-

ence between the retention times. This value can be deduced by observing the separation achieved in the three preliminary runs. In the case shown, the chromatograms of the preliminary analyses described in the example of Fig. 2 have shown that a minimum difference of about 20 s between the retention times of adjacent peaks was necessary in order to obtain a baseline separation of all the compounds. This value, Δt_{Rc} , is input to the program shown in Fig. 3 and the chromatogram of Fig. 4, corresponding to the run TPP 7 of Table 3, is obtained. The true minimum difference of retention times necessary to obtain baseline resolution was found to be 18.5 s.

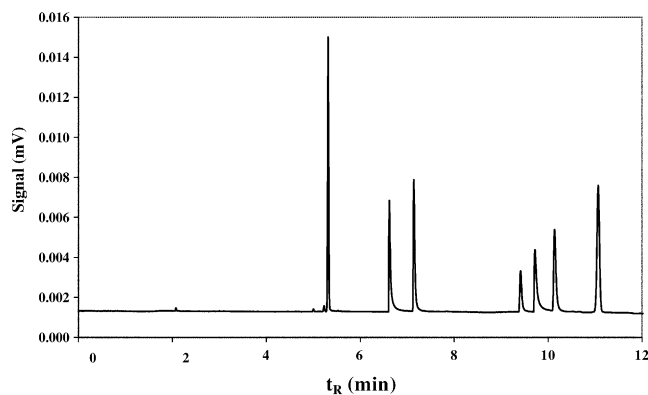


Fig. 4. Chromatogram obtained on DB-1 capillary column with the conditions shown in Table 3 for the programmed pressure and temperature run TPP 7.

5. Conclusions

The simulation of retention times described in this paper is very accurate and can be carried out using the retention data measured in few preliminary runs. It was also investigated which parameters have to be known with the best accuracy (the most important parameters are the starting conditions of temperature and pressure, then the gradients of temperature and pressure) and which ones have negligible influence on the accuracy of the simulations, as the atmospheric pressure.

With the auxiliary program described above, the mathematical model can predict both the retention times in TPP analysis and the inversions of the peak sequence and permits to select the better analytical conditions which offer a baseline resolution of adjacent peaks.

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