

Automatic prediction of retention times in multi-linear programmed temperature analyses

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

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

Received 24 September 1996; revised 13 November 1996; accepted 19 November 1996

Abstract

A method for the prediction of retention times of compounds analysed during programmed-temperature gas chromatography with capillary columns is described, which employs an explicit equation for the calculation of the gas hold-up time. The method can be applied to analyses carried out with different temperature profiles: constant linear programming rate, initial and final isothermal tract, different temperature gradients in the same analysis. The effect of the various parameters of the analysis on the accuracy of the predicted values was investigated.

Keywords: Retention times; Programmed-temperature gas chromatography

1. Introduction

In a previous paper [1] a method for the automatic prediction of programmed temperature (PT) retention values in capillary gas chromatography by using as input data retention times measured under isothermal analytical conditions was proposed. To predict the retention of the component of a sample in all the possible programmed runs permits one to select the conditions for the separation of closely eluting compounds when their different polarity changes the relative retention values as a function of temperature. When highly polar columns are used, mainly if their polarity changes with temperature [2–4], a suitable prediction method reduces the number of preliminary runs that have to be carried out in order to select the best programming rate. The conditions yielding the best compromise between resolution and analysis time can also be found.

Several prediction methods have been published previously [5–23]. In all of them the knowledge of the carrier gas hold up time or dead time, t_M , necessary in order to calculate the values of the retention time, t_R , of the different compounds, is obtained through the direct measurement or the calculation of the average carrier gas velocity, u . These methods are therefore suitable for the prediction of t_R values in linear programmed runs, when the temperature increases with a steady rate throughout the entire analysis time. When the overall programmed run includes tracts with different temperature gradient (multi-linear programming) or an initial and final isothermal tract, the use of the average gas velocity does not allow the correct prediction of PT retention time (PTt_R) values. In this instance, it would be necessary to know the position of every compound in the column at the beginning and at the end of the isothermal tracts and when the temperature gradient changes, and calculate the carrier gas pressure existing in that position of the column. A

*Corresponding author.

similar approach was recently followed by Snijders et al. [21], which suggests a procedure based on extracting thermodynamic values from Kovats retention indices and using these values to calculate retention times and peak widths on capillary columns either in isothermal single- or multi-ramp temperature programmed mode. In short, the procedure proposed in Ref. [21] divides the chromatographic process in short segments corresponding to very small time intervals within which both the retention factor and the carrier gas velocity can be assumed constant. By using experimentally measured t_M values to calculate u and taking into account the change of viscosity and compressibility of the carrier gas with temperature, the method calculates the total distance a solute travels by summation of the distances travelled in the individual small time segments. On the basis of previously published experiments that permitted the theoretical calculation of t_M and the study of the influence of column parameters and analysis conditions on the dead time values [24] and the prediction of retention times in linearly PT runs [1], we used a different procedure, described here, in order to calculate retention times in PT runs with both initial and final isothermal tracts and different gradients of the programmed portion (multi-linear programming). At first, the carrier gas hold time was calculated by means of an explicit equation yielding the time spent by a molecule of the carrier gas within the column, as a sum of the contributes due to the different tracts of finite length of the programmed run (initial isotherm, different gradients, final isotherm) and taking into account the change of viscosity with temperature. The effective carrier gas hold-up time $t_M(T)$ calculated with this method is therefore a function of the temperature programming, while the t_M measured with an inert, not retained, gas or with the methane retention is a constant values characteristic of the initial condition of the analysis. The gross retention time of a given substance, $t_R(T)$, is therefore obtained by the sum of the effective carrier gas hold-up contribute and of the solute–solvent interaction expressed by the capacity factor, k .

The precision of the results depends strongly on the exact knowledge and on the constancy of the various parameters of the analysis. In a previous paper [24], the influence of the column length and

diameter, carrier gas viscosity, inlet and outlet column pressure, on the accuracy and precision of the calculated t_M was evaluated. It has been found that the greatest error is due to the uncertainty in the knowledge of the internal diameter of the column. In PT analysis the influence of temperature is much greater than that of the other parameters listed above. Initial temperature, linearity of temperature gradient, end temperature of the programmed run and temperature of the upper isothermal tract must be exactly known in order to permit the prediction of the PTt_R .

Experiments were therefore carried out by monitoring with precision thermometers and thermocouples, the true temperature of the column during various PT analyses. It was therefore determined in a quantitative approach the incidence of the discrepancy between the true change of column temperature with time, *real* $T(t)$, and values set and monitored by temperature programmer of the instrument, *assumed* $T(t)$. The comparison of experimental PTt_R values with those predicted by starting from isothermal t_R data allowed us to evaluate the accuracy of the prediction method and the influence of the various analytical parameters on the precision of the results.

2. Theory

The general equation used for the prediction of t_R values in a programmed run was the same as used previously [1,25,26]

$$g = \int_{T_i}^{T_f} \frac{dT}{t_R(T)} \quad (1)$$

where g is the temperature gradient, T_i and T_f are the initial and final temperature of the linear tract of temperature program and $t_R(T)$ is the function which represents the dependence of the retention time of a given compound on the change in temperature.

The function $t_R(T)$ is:

$$t_R(T) = t_M(T) \cdot (1 + k(T)) \quad (2)$$

where $t_M(T)$ is the effective gas hold-up time and $k(T)$ is the capacity factor k , expressed by:

Table 1

Compounds analysed, symbols used in the tables and figures, their boiling points, T_b , and molecular mass, M_r , retention times calculated, experimental values and relative percent error, $E\%_{rel}$, in a linear programmed run on a SPB-octyl column

| Compounds | Symbols | T_b | M_r | t_{Rcalc} | t_{Rexp} | $E\%_{rel}$ |
|------------------------|---------|-------|--------|-------------|------------|-------------|
| Chlorobenzene | clbz | 132 | 112.56 | 2.039 | 2.039 | -0.018 |
| Bromobenzene | brbz | 156 | 157.02 | 3.156 | 3.155 | 0.027 |
| 1,4-Dichlorobenzene | 14dcb | 174 | 147.01 | 4.647 | 4.643 | 0.088 |
| 1,3-Dichlorobenzene | 13dcb | 173 | 147.01 | 4.647 | 4.643 | 0.088 |
| 1,2-Dichlorobenzene | 12dcb | 180.5 | 147.01 | 5.081 | 5.077 | 0.079 |
| Nitrobenzene | nitro | 210.8 | 123.11 | 5.333 | 5.330 | 0.054 |
| 1,2-Chloroaniline | 12cla | 208.8 | 127.57 | 6.562 | 6.562 | 0.005 |
| 1,3-Chloroaniline | 13cla | 229.9 | 127.57 | 8.054 | 8.055 | -0.018 |
| 1,4-Chloroaniline | 14cla | 232 | 127.57 | 8.076 | 8.077 | -0.012 |
| 1,3,5-Trichlorobenzene | 135tcb | 208 | 181.45 | 8.717 | 8.703 | 0.160 |
| 1,3-Chloronitrobenzene | 13cnb | 235–6 | 157.56 | 9.395 | 9.392 | 0.034 |
| 1,2,4-Trichlorobenzene | 124tcb | 213.5 | 181.45 | 9.480 | 9.462 | 0.190 |
| Naphtalene | napht | 218 | 128.19 | 9.560 | 9.550 | 0.103 |
| 1,4-Chloronitrobenzene | 14cnb | 242 | 157.56 | 9.652 | 9.641 | 0.115 |
| 1,2-Chloronitrobenzene | 12cnb | 246 | 157.56 | 9.812 | 9.805 | 0.068 |
| 1,2,3-Trichlorobenzene | 123tcb | 218–9 | 181.45 | 10.263 | 10.253 | 0.098 |
| $E\%_{ave}$ | | | | | | 0.066 |
| $E\%_{abs}$ | | | | | | 0.072 |

Initial temperature 60.5°C, gradient 4.01°C/min.

evaluate accuracy and precision of the prediction method are shown in Fig. 1, where the flow-chart of the different types of calculation methods used depending on temperature profile is also reported.

The total PTt_R is the sum of the retention times of the compound during the initial isothermal tract, in the programmed temperature tract at one or more temperature gradients and in the final upper isothermal tract. In this instance, in order to predict the PTt_R of every compound, it is necessary to calculate its position in the column and the pressure existing at that point when the programming mode changes, e.g., when the initial isothermal ends and the linear temperature gradient starts, when the gradient changes and when the upper isothermal tract takes place. A general equation of the PTt_R is:

$$PTt_R = t_1 + t_2 + t_3 + t_4 + t_5 \quad (9)$$

where t_1 is the retention time of the substance during the initial isothermal tract of the programmed run; $t_2 = (T_f - T_i)/g$ is the retention time during the linear program at the rate g between the initial, T_i , and final, T_f , temperatures; $t_3 = (T_c - T_i)/g_1$ and $t_4 = (T_f - T_c)/g_2$ are the retention times due to temperature programmed tracts at different rates, g_1 and g_2 ,

between T_i , an intermediate temperature, T_c , and the final T_f ; t_5 is the retention due to the final isothermal tract at T_f .

Different types of programmed runs were taken into account:

Type A: linear temperature gradient, with $PTt_R = t_2$.

Type B: linear temperature gradient followed by an upper isothermal tract with $PTt_R = t_2 + t_5$.

Type C: initial isothermal tract and linear temperature gradient with $PTt_R = t_1 + t_2$.

Type D: initial isothermal, linear gradient, final isothermal tract with $PTt_R = t_1 + t_2 + t_5$.

Type E: linear gradient g_1 and linear gradient g_2 (multilinear programmed run) with $PTt_R = t_3 + t_4$.

Type F: initial isothermal, linear gradient g_1 , linear gradient g_2 and final isothermal tract with $PTt_R = t_1 + t_3 + t_4 + t_5$.

When a sample contains many compounds having a wide range of boiling points and different polarities, some of them are eluted early when the column is still at the initial isothermal temperature, and their t_R values correspond obviously to those measured in one of the isothermal runs used for

calibration, if its temperature corresponds to that of the initial isotherm, or can be calculated by interpolation using the values of the calibration isothermal runs. Heavy compounds, on the other hand, may remain into the column after the end of the temperature programming and, if the final temperature is not high enough, show heading peaks with actual retention values greater than those of symmetrical peaks. For this reason when possible, the final isothermal tract is only used to ensure that no residual component remains in the column before cool-down; however, when using stationary phases with a low thermal stability that do not allow the reaching of high temperatures during the linear programmed run, the use of the upper isotherm is mandatory for the complete elution of the sample and, therefore, the prediction of the retention times in this segment of the run is necessary.

3. Experimental

A Model 3600 gas chromatograph (Varian, Palo Alto, CA, USA) equipped with a split-splitless injector and a flame ionization detector, was used for isothermal and programmed temperature analysis. Fused silica capillary columns, 30 m×0.32 mm I.D. were used (Supelco, Bellefonte, PA, USA). The stationary phases of the columns were: polydimethylsiloxane (SPB-I) and poly(50% *n*-octyl/50% methylsiloxane) (SPB-octyl).

The analyses were carried out on the columns in the range 60 to 200°C (140° for the octyl column), at 20°C intervals, by using samples containing all the compounds listed in Table 1. They were selected in order to represent the different polarity classes [32], containing both electron donor atoms and active hydrogen (chloroanilines) donor atoms but not active hydrogen (nitro- and chloronitrobenzenes), *p*-electrons of the aromatic ring (naphthalene) more or less influenced by the inductive effect of halogens in different position (chlorobenzenes). Linear alkanes (C₇ to C₂₂) and alcohols (C₅ to C₁₃) were also analysed in order to measure the polarity of the columns with the ΔC method [2,33]. PT analyses were made with different initial and final temperatures, length of the initial and final isothermal tracts, and programming temperature rates.

The built-in flow control of the instrument was designed in order to maintain the inlet pressure to the column as constant, during both isothermal and programmed temperature analysis. The prediction of the PTt_R was carried out by BASIC programming on personal computers (Pentium 120 processor) with the calculation methods previously described [1] and with Eqs. (2–5). The method which gave the best approximation of that predicted for experimental PTt_R was an interpolation method indicated in Ref. [1] as the quadratic or “Q” method. With this method three isothermal retention time values only were used for calculation.

The temperature of the column was monitored by using a chromel–alumel thermocouple, with a precision of $\pm 0.05^\circ\text{C}$, greater than that offered by the built-in hardware of gas chromatograph ($\pm 0.5^\circ\text{C}$). The used thermocouple was previously calibrated, in the whole temperature range used for the experiments, by comparison with a certified mercury thermometer ($\pm 0.01^\circ\text{C}$). The linearity and the exact value of the programming rate were monitored throughout the analyses by connecting the thermocouple to the input of a potentiometric strip-chart recorder. This procedure was followed in order to know exactly the true temperatures of the isothermal tracts and the value of the gradient (with a precision of $0.01^\circ\text{C}/\text{min}$) because these parameters influence strongly the results of the t_R prediction.

4. Results and discussion

Table 1 lists the compounds used following the elution order on SPB-octyl column, the abbreviated symbols used in the following tables and figures, the boiling points and the molecular masses. The retention times calculated with the type A method (see Fig. 1), $t_{R\text{calc}}$, are compared with the experimental values obtained with an analysis on a SPB-octyl column with simple linear temperature gradient at a rate of $4.01^\circ\text{C}/\text{min}$ starting from 60.5°C . The true temperature and gradient values, measured as described in Section 3, are reported in this and in the following tables. They may be different from the values set with the control panel of the gas chromatograph, depending on the accuracy of the calibration of the instrument. The knowledge of the

exact temperature values is very important for the correct application of the calculation methods. The last column of Table 1 shows the relative percentage error

$$E_{\text{rel}} \% = 100(t_{\text{Rcalc}} - t_{\text{Rexp}})/t_{\text{Rexp}} \quad (10)$$

for every compound, the overall percentage error $E\%_{\text{ave}}$, obtained by averaging the values for all the compounds with their sign, and the absolute value of $E\%_{\text{rel}}$.

Table 2 shows the percentage error values, calculated as above, for different types of programmed temperature runs on the SPB-octyl column. The type A linear programmed run of Table 1 is also shown for comparison purposes. The correspondence of calculated with experimental values is about the same, independent on the complexity of the temperature program, showing that the used formulas allow one to calculate the PT of any type of programming,

by using a few isothermal reference runs as the source of the starting data. Table 3 shows similar data measured on the SPB-1 column. In both columns and in all of the program types, the errors are random and no clear dependence on a compound can be observed.

The importance of the exact knowledge of the initial temperature and of the gradient is shown in Fig. 2, where the experimental PTt_{R} for all the compounds (plotted in order of increasing retention time) are compared with the values calculated by using different initial temperatures and gradients. The difference between the PTt_{Rcalc} and the PTt_{Rexp} are shown, the line at ordinate zero representing the PTt_{Rexp} . The best fit (symbol X) is obtained by using the true temperature and gradient values (60.5°C and 4.01°C/min, respectively) corresponding to the simple linear programmed analysis shown in Table 1. The other values show the difference of PTt_{Rcalc} ,

Table 2

Relative percent, $E\%$, averaged, $E\%_{\text{ave}}$, and absolute averaged, $E\%_{\text{abs}}$, errors between calculated or experimental PTt_{R} in different types of programmed runs (see text)

| Type | A | B | C | D | E | F |
|--------------------|--------|--------|--------|--------|--------|--------|
| T_i (°C) | 60.5 | 60.2 | 60.2 | 60.6 | 60.45 | 60.38 |
| t_i (min) | 0 | 2 | 2 | 0 | 0 | 2 |
| g_1 (°C/min) | 4.01 | 2.03 | 2.03 | 5.02 | 4.02 | 4.02 |
| T_c (°C) | | | | | 80.3 | 70.3 |
| g_2 (°C/min) | | | | | 2.02 | 2.02 |
| T_f (°C) | | | 80.1 | 80.1 | | 80.2 |
| Compounds | $E\%$ | $E\%$ | $E\%$ | $E\%$ | $E\%$ | $E\%$ |
| clbz | -0.018 | -0.099 | -0.143 | -0.050 | -0.022 | -0.065 |
| brbz | 0.027 | -0.051 | -0.105 | -0.005 | -0.081 | 0.012 |
| 14dcb | 0.088 | 0.093 | 0.043 | 0.002 | -0.054 | -0.008 |
| 13dcb | 0.088 | 0.093 | 0.043 | 0.002 | -0.054 | -0.008 |
| 12dcb | 0.079 | 0.103 | -0.007 | 0.064 | 0.129 | 0.147 |
| nitro | 0.054 | 0.021 | -0.078 | 0.096 | -0.047 | -0.049 |
| 12cla | 0.005 | 0.033 | -0.055 | 0.065 | -0.026 | -0.117 |
| 13cla | -0.018 | -0.048 | -0.108 | -0.101 | -0.117 | 0.016 |
| 14cla | -0.012 | -0.046 | -0.089 | 0.053 | 0.020 | 0.094 |
| 135tcb | 0.160 | 0.068 | 0.009 | 0.107 | -0.090 | 0.153 |
| 13cnb | 0.034 | -0.082 | -0.041 | 0.035 | 0.095 | 0.008 |
| 124tcb | 0.190 | 0.075 | 0.119 | 0.046 | 0.210 | 0.092 |
| napht | 0.103 | 0.002 | -0.044 | -0.110 | 0.053 | -0.074 |
| 14cnb | 0.115 | -0.016 | -0.065 | 0.121 | 0.014 | 0.117 |
| 12cnb | 0.068 | -0.031 | -0.064 | -0.048 | -0.150 | 0.003 |
| 123tcb | 0.098 | -0.007 | 0.066 | -0.066 | -0.123 | -0.105 |
| $E\%_{\text{ave}}$ | 0.066 | 0.007 | -0.032 | 0.013 | -0.015 | 0.014 |
| $E\%_{\text{abs}}$ | 0.072 | 0.055 | 0.067 | 0.060 | 0.080 | 0.067 |

Column: SPB-octyl. The heating rates of linear, g , and multi-linear runs, g_1 , and g_2 , are shown.

Table 3
Relative percentage, $E\%$, averaged, $E\%_{ave}$, and absolute averaged, $E\%_{abs}$, errors between calculated and experimental PTt_R in different types of programmed runs (see text)

| Type | A | B | C | D | E |
|----------------|--------|--------|--------|--------|--------|
| T_i (°C) | 60.25 | 60.3 | 60.1 | 60.3 | 60.25 |
| t_1 (min) | 2 | 0 | 2 | 0 | 2 |
| g_1 (°C/min) | 2.01 | 5.04 | 2.015 | 4.01 | 4.02 |
| T_c (°C) | | | | 80.1 | 70.1 |
| g_2 (°C/min) | | | | 2.01 | 2.01 |
| T_f (°C) | | 80.1 | 80.1 | | 80.1 |
| Compounds | $E\%$ | $E\%$ | $E\%$ | $E\%$ | $E\%$ |
| clbz | 0.046 | 0.356 | -0.633 | 0.534 | -0.060 |
| 14dcb | 0.106 | 0.138 | -0.170 | 0.221 | 0.059 |
| 13dcb | -0.072 | 0.089 | -0.392 | 0.082 | -0.050 |
| 12dcb | 0.107 | 0.173 | -0.125 | 0.193 | -0.067 |
| nitro | 0.145 | 0.081 | -0.008 | 0.157 | 0.004 |
| 12cla | -0.006 | 0.140 | -0.048 | -0.050 | -0.023 |
| 13cla | -0.037 | 0.002 | -0.055 | -0.047 | -0.079 |
| 14cla | -0.042 | 0.050 | -0.007 | -0.054 | 0.025 |
| 135tcb | -0.041 | 0.041 | 0.040 | 0.058 | -0.041 |
| 13cnb | -0.031 | -0.113 | -0.022 | -0.052 | -0.036 |
| 124tcb | 0.021 | 0.004 | 0.084 | -0.038 | 0.034 |
| napht | -0.010 | -0.107 | 0.061 | 0.052 | -0.036 |
| 14cnb | -0.001 | 0.034 | 0.038 | -0.109 | -0.118 |
| 12cnb | -0.008 | -0.150 | 0.006 | 0.014 | -0.081 |
| 123tcb | -0.012 | -0.004 | -0.032 | -0.045 | -0.070 |
| $E\%_{ave}$ | 0.011 | 0.049 | -0.084 | 0.061 | -0.036 |
| $E\%_{abs}$ | 0.045 | 0.099 | 0.114 | 0.113 | 0.051 |

Column: SPB-1. The heating rates of linear, g , and multi-linear runs, g_1 and g_2 , are shown.

from the experimental value obtained by using an initial temperature of 59°C (symbol □) or of 61°C (symbol ■) and the true gradient 4.01°C/min or, respectively, a gradient of 3.8°C/min (symbol ○) or 4.2°C/min (symbol ●) and the true initial temperature, 60.5°C. The absolute differences change with the compounds and the elution times, but it was found that an error of about 0.01°C in the determination of the initial temperature has the same effect as an error of 0.1°C/min in the determination of the programming gradient.

The importance of temperature on the accuracy of the calculation is shown in Table 4, where the effects of the change of the various analytical parameters are shown. By using the true values (initial temperature 60.2°C, gradient 2.03°C/min and final temperature 80.1°C) an $E\%_{ave}$ of -0.032 was obtained. The table shows the values of $E\%_{ave}$ when the various

parameters are changed as indicated in the third column, and confirms that the effect of wrong initial temperature or programming gradient is much greater than that of changing other parameters as the column length, the initial and final pressure, and the parameters α and β used to calculate the gas viscosity. As seen previously [24], the geometrical parameter which has the greatest effect on the accuracy is the column diameter, but its influence is one order of magnitude smaller than that of temperature. The importance of the exact knowledge of temperature for the correct prediction of PTt_R emphasizes the fact that the temperatures readout and control of the gas chromatograph must be carefully calibrated. In many instruments, both the isothermal temperatures and the programming rate are set with the approximation of one degree, that may produce errors as great as 1–2% in the predicted PTt_R . Therefore, in order to obtain good results with the proposed method, the correspondence of the instrument settings to the true values must be checked previously. Conversely, a separate and more accurate temperature sensor, capable of measuring the initial temperature and the gradient with an approximation of 0.1°C, should be installed just on the column coil, in order to avoid the effect of temperature gradients into the column oven. The continuous recording of the oven and column temperature has shown another reason of possible error in the prediction. Fig. 3 shows, in arbitrary units, the behaviour of the oven temperature during a programmed run. When heating starts at T_i , the initial rise of temperature, real $T(t)$, is more or less greater than that required by the program, assumed $T(t)$, and only after a short interval the actual temperature trend (points) becomes coincident with the nominal value (line). This effect may be counterbalanced by the thermal mass of the column, whose temperature follows with some delay that of the oven (cross symbol) and therefore this deviation from linearity at the beginning of the program has a small influence on the PTt_R prediction. Greater influence is connected to the overheating at the end of the linear tract of the programmed run, due to the equilibration of the oven and column temperature after the heater shut-off. The amount of the overheating depends on the geometry of the column oven, on the position of the temperature control probes, etc. In type B and D programmed

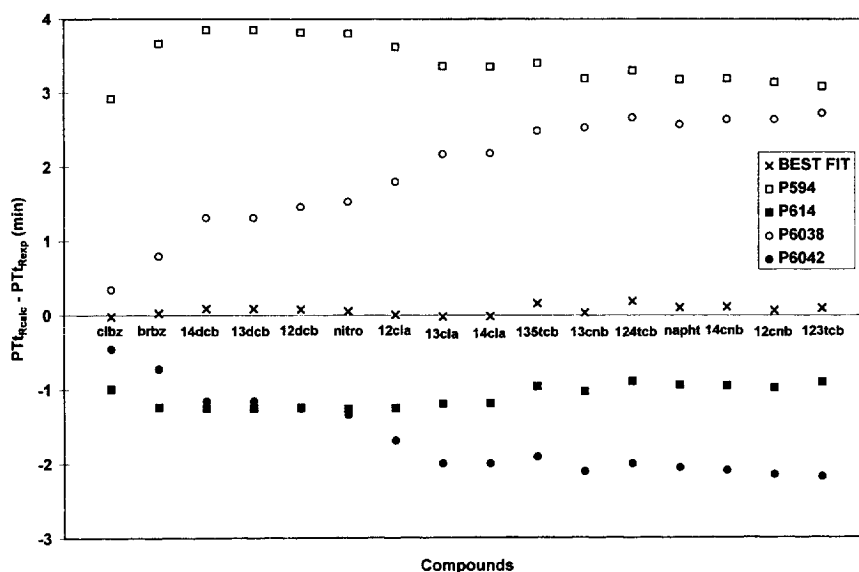


Fig. 2. Effects of uncertainty in the determination of initial temperature and programming gradient on the calculation of PT_{t_R} . The zero line represents the experimental PT_{t_R} . (×) True values 60.5°C and 4.01°C/min; (□) 59°C and 4.01°C/min; (■) 61°C and 4.01°C/min; (○) 60.5°C and 3.8°C/min; (●) 60.5°C and 4.2°C/min. Column: SPB-octyl.

runs, the compounds eluted during the upper isothermal tract are slightly accelerated in the time interval from t_f to t_{f+x} , and $PT_{t_{Rexp}}$ values smaller than the $PT_{t_{Rcalc}}$ may be found. A correction is possible by using in type B and D programmed runs, the values of t_{f+x} and t_x respectively, instead of t_f and T_f , but, of course, the best solution is to use instruments calibrated carefully and with the smallest possible difference between the temperatures and gradient set and the actual ones. The difference between predicted and experimental values can be used in order to check the accuracy of the temperature readout of the gas chromatograph; as an example, in type A programmed run of Table 2, if a T_i value of 60.4°C is used instead of the actual 60.5°C, the $E\%_{abs}$ changes from 0.072 to 0.239.

5. Conclusions

The method described permits one to predict with a suitable accuracy the retention times of compounds

having different polarities analysed with capillary columns. The results obtained during temperature-programmed analyses with complex temperature profiles depend on the exact knowledge of the analytical parameters, mainly the column internal diameter, the initial and final temperature and the gradient and linearity of temperature increase. The work has determined quantitatively the incidence of the discrepancy between *assumed* $T(t)$ vs. *real* $T(t)$ on the calculated retention, and the accuracy of the method is confirmed by the fact that any error in the calibration of the thermocouples of the gas chromatograph can be detected and corrected by comparison of experimental with predicted retention times. The average errors between calculated and experimental retention time can be reduced to insignificant aleatory values (less than 1%) by means of precise temperature monitoring. This result confirms that any calculation method for the theoretical evaluation and prediction of data in gas chromatography, that on the basis of existing literature can have a great precision, strongly depends on the correct calibration of the instruments and on the

Table 4
Effect of changing the various parameters of the analysis on the accuracy of the prediction of PT_{iR}

| Parameters | Symbols | Nominal value | Actual value | $E\%_{ave}$ |
|----------------------|------------------|---------------|--------------|-------------|
| Length | L (cm) | 3000 | 3010 | -0.045 |
| | | | 2990 | -0.069 |
| Diameter | d (mm) | 0.32 | 0.34 | -0.122 |
| | | | 0.30 | 0.025 |
| Viscosity constant | α | 5.024 | 5.050 | -0.046 |
| | | | 5.000 | -0.061 |
| Viscosity constant | β | 0.648 | 0.655 | -0.015 |
| | | | 0.640 | -0.095 |
| Atmospheric pressure | p_a (mmHg) | 770 | 790 | -0.047 |
| | | | 750 | -0.050 |
| Inlet pressure | p_i (p.s.i.g.) | 21.7 | 22.0 | -0.057 |
| | | | 21.5 | -0.056 |
| Outlet pressure | p_o (p.s.i.g.) | 0.20 | 1.00 | -0.027 |
| | | | 0.01 | -0.065 |
| Initial temperature | T_i (°C) | 60.2 | 61.0 | -2.185 |
| | | | 59.0 | 3.157 |
| Gradient | g_1 (°C/min) | 2.03 | 2.10 | -0.663 |
| | | | 1.90 | 1.061 |
| Final temperature | T_f (°C) | 80.1 | 81 | -0.361 |
| | | | 79 | 0.340 |

1 mmHg = 133.322 Pa; 1 p.s.i. = 6894.76 Pa.

By using the nominal values an average percentage error, $E\%_{ave}$, of -0.032 was obtained. By using the value of column 4 the $E\%_{ave}$ values listed in column 5 were found.

knowledge, as accurate as possible, of the analytical parameters that have to be used as the input data for calculations.

Therefore, further improvement to the accuracy in the prediction of retention values should be rather instrumental than theoretical. It has been shown in previously published papers the importance, for the calculation of retention times, of the exact knowledge of the capillary column diameter, which should be given by the producer with great accuracy. Moreover, the manufacturers of gas chromatographic instrumentations, which may think to improve easily the performance of their products by simply adding to the existing built-in softwares some programs for automatic calculation of carrier gas velocity, retention times, retention indices etc., must take into account that the validity of the results greatly depend

on the accuracy of the data inputted. Temperature and pressure in the various points of the system have to be monitored with suitable transducer, corrected to room temperature and atmospheric pressure, and inputted to the computer of the instrument with a sufficient approximation degree. Only if this condition is satisfied will theoretical prediction of retention values in different analytical conditions become a standard feature of the next generation of chromatographic instruments.

Acknowledgments

The research was supported by the Italian Ministry of University and Research (MURST).

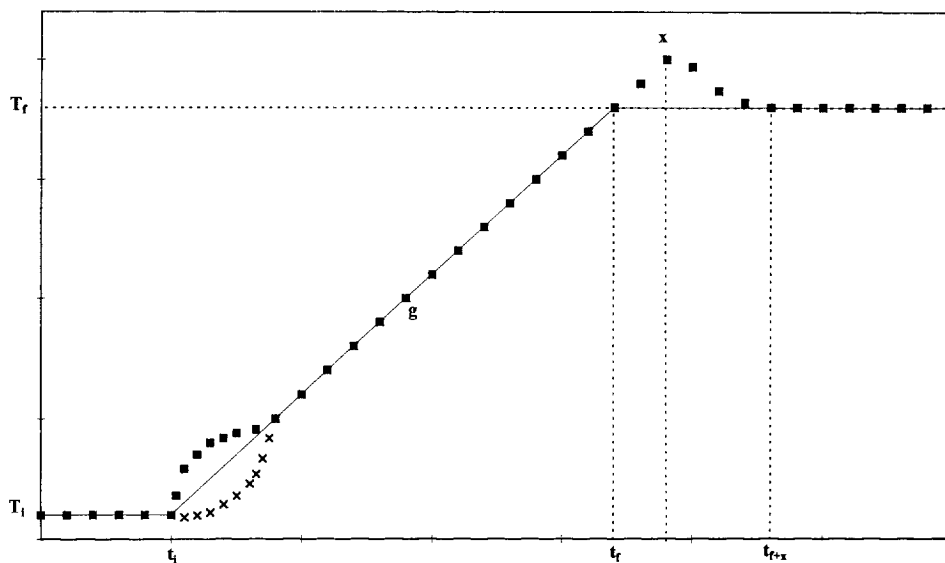


Fig. 3. Behaviour of temperature, T , as a function of time, t , in ideal programmed run with initial and final isothermal tract (full line) and actual values of the column oven temperature (points) due to delay in the equilibration of the heating system. The delayed initial heating of the column due to its thermal inertia is also shown (cross symbols). See text.

References

- [1] S. Vezzani, P. Moretti and G. Castello, *J. Chromatogr. A*, 677 (1994) 331.
- [2] G. Castello, G. D'Amato and S. Vezzani, *J. Chromatogr.*, 646 (1993) 361.
- [3] G. Castello, S. Vezzani and P. Moretti, *J. High Resolut. Chromatogr.*, 17 (1994) 31.
- [4] G. Castello and S. Vezzani, in P. Sandra (Editor), *Proceedings of the 15th International Symposium on Capillary Chromatography*, Riva del Garda, Hüthig, Heidelberg, 1993, p. 68.
- [5] H.W. Habgood and W.E. Harris, *Anal. Chem.*, 32 (1960) 450.
- [6] W.E. Harris and H.W. Habgood, *Programmed Temperature Gas Chromatography*, Wiley, New York, 1966.
- [7] A.S. Said, in P. Sandra (Editor), *Proceedings of the 8th International Symposium on Capillary Chromatography*, Vol. 1, Riva del Garda, Hüthig, Heidelberg, 1987, p. 85.
- [8] A.S. Said, in P. Sandra and G. Redant (Editors), *Proceedings of the 10th International Symposium on Capillary Chromatography*, Riva del Garda, Hüthig, Heidelberg, 1989, p. 163.
- [9] T.C. Gerbino and G. Castello, *J. High Resolut. Chromatogr.*, 16 (1993) 46.
- [10] T.C. Gerbino, G. Castello and G. Pettinati, *J. Chromatogr.*, 634 (1993) 338.
- [11] G. Castello, P. Moretti and S. Vezzani, *J. Chromatogr.*, 635 (1993) 103.
- [12] R. Kaiser, *Gas Phase Chromatography*, Vol. 1, Butterworths, London, 1963.
- [13] M.H. Guermouches and J.M. Vergnaud, *J. Chromatogr.*, 94 (1971) 169.
- [14] M.H. Guermouches and J.M. Vergnaud, *J. Chromatogr.*, 94 (1974) 25.
- [15] R.L. Grob, *Modern Practice of Gas Chromatography*, Wiley, New York, 1977.
- [16] L. Podmaniczky, L. Szepeszy, K. Lakzner and G. Schomburg, *Chromatographia*, 20 (1985) 591.
- [17] L. Podmaniczky, L. Szepeszy, K. Lakzner and G. Schornburg, *Chromatographia*, 20 (1985) 623.
- [18] K. Kuningas, S. Rang and T. Kailas, *Chromatographia*, 27 (1989) 544.
- [19] H. Rotzsche, *Stationary Phases in Gas Chromatography*, Elsevier, Amsterdam, 1991.
- [20] H. Snijders, H.-G. Janssen and C. Cramers, in P. Sandra (Editor), *Proceedings of the 18th International Symposium on Capillary Chromatography*, Riva del Garda, Hüthig, Heidelberg, 1996, p. 365.
- [21] H. Snijders, H.-G. Janssen and C. Cramers, *J. Chromatogr. A*, 718 (1995) 339.
- [22] T. Hevesi and J. Krupcik, in P. Sandra (Editor), *Proceedings of the International Symposium on Capillary Chromatography*, Riva del Garda, Hüthig, Heidelberg, 1994, p. 365.
- [23] T.C. Gerbino and G. Castello, *J. High Resolut. Chromatogr.*, 17 (1994) 597.
- [24] G. Castello, S. Vezzani and P. Moretti, *J. Chromatogr. A*, 677 (1994) 95.
- [25] C. Caratheodory, *Algebraic Theory of Measure and Integration*, Chelsea Pub. Co., New York, 1963.
- [26] F. Ayres Jr., *Theory and Problems of Differential and Integral Calculus*, Schaum, New York 1964.
- [27] G. Castello, S. Vezzani and P. Moretti, *J. Chromatogr. A*, 742 (1996) 151.

- [28] L.S. Ettre, *Chromatographia*, 18 (1984) 243.
- [29] S.S. Stafford (Editor), *Electronic Pressure Control in Gas Chromatography*, Hewlett–Packard, Wilmington, DE, 1993.
- [30] J.O. Hirschfelder, C.F. Curtiss and R. Byron-Bird, *Molecules Theory of Gases and Liquids*, Wiley, New York, 1964.
- [31] E. Marchi and A. Rubatta, *Meccanica dei Fluidi*, UTET, Milano, 1976, Ch. 13, 14.
- [32] R.H. Ewell, J.M. Harrison and L. Bers, *Ind. Eng. Chem.*, 36 (1944) 871.
- [33] G. Castello and G. D'Amato, *J. Chromatogr.*, 623 (1992) 289.