ELSEVIER

Journal of Chromatography A, 677 (1994) 331–343

JOURNAL OF
CHROMATOGRAPHY A

Fast and accurate method for the automatic prediction of programmed-temperature retention times

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

Istituto di Chimica Industriale, Corso Europa 30, 16132 Genova, Italy

First received 22 February 1994; revised manuscript received 6 April 1994

Abstract

Six calculation methods for the prediction of the retention times in programmed-temperature gas chromatography by starting from isothermal data were applied to capillary column analysis. The minimum number of isothermal runs necessary to obtain accurate results was evaluated. The application of the various methods and the accuracy of the prediction are discussed. A quadratic interpolation method which requires only three isothermal retention values as the starting data was found suitable and easily applied to computer programs.

1. Introduction

The prediction of retention times in programmed-temperature gas chromatography (PTGC) by using computer programs which employ as input data retention values measured under isothermal analytical conditions is a procedure of considerable interest in routine work. To predict the retention times of the component of a sample in all the possible programmed runs permits one to select the best conditions for the separation, mainly when the different polarities of the compounds result in peak coincidence or inversion of the elution order. The conditions yielding the shortest possible analysis time can also be found.

Many methods have been suggested [1–21] and a comparison of the precisions of four of them was published previously [22]. The simplest methods can be easily applied by BASIC programming on a personal computer, by inputting a few initial data: the retention times in few isothermal analyses, the initial temperature of the programmed run, the length of the initial isothermal stage and the temperature gradient.

The increasing computerization of GC instruments, obtained by on-line connection to integrators and data systems or by direct use of built-in microprocessors, nowadays enables one to perform quantitative analysis and to calculate some parameters useful for the correct separation, e.g., the carrier gas velocity and the dead time [23,24]. Dedicated software is also available for this equipment, applied to simulated distillation, retention index calculation, peak deconvolution, gel permeation calculation, etc. It therefore seems possible to add to these software packages some options that automatically predict the PTGC retention times by starting from isothermal runs, whose parameters and results are directly transferred from the data system memory to the input section of the prediction program.

---

* Corresponding author.

0021-9673/94/$07.00
SSDI 0021-9673(94)00375-J

For easy application, such a program should follow a systematic approach, permit the choice of a few initial parameters by the operator, give accurate results and require a limited number of initial isothermal analyses. In order to establish what is the minimum number of isothermal runs that permit a suitable accuracy in the prediction of PTGC retention times, and to select the simplest, most accurate and fastest program, several different prediction methods were tested, by using as the starting values a variable number of isothermal data (from 3 to 25). The results obtained with six methods are discussed and some suggestions on their application to automatic prediction programs are given.

2. 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 (IT) and programmed-temperature (PT) analyses. Fused-silica capillary columns (30 m × 0.32 mm I.D.) were used (Supelco, Bellefonte, PA, USA): a non-polar polydimethylsiloxane (SPB-1), a polar polyglycol (Supelcowax-10) and a carbon layer open-tubular (CLOT) column partially deactivated with polyglycol [20,21].

The analyses were carried out on the three columns in the range 60–190°C, at 10°C intervals for SPB-1 and Supelcowax-10 columns and at 5°C intervals for the CLOT column, by using samples containing all the compounds listed in Tables 2–4. They were selected in order to represent the different polarity classes [25], containing both electron-donor atoms and active hydrogen (chloroanilines), donor atoms but not active hydrogen (nitro- and chloronitrobenzenes), π-electrons of the aromatic ring (naphthalene) more or less influenced by the inductive effect of halogens in different positions (chlorobenzenes). Linear alkanes (C_7–C_{22}) and alcohols (C_5–C_{13}) were also added to the sample to represent the two classes of low-polarity (purely dispersive forces) and high hydrogen bonding capacity, respectively. The presence of linear alkanes and alcohols also permitted the determination of the polarity of the columns with the ΔC method [26,27]. PT analyses were made with different initial temperatures, T_i, initial length of the isothermal stage, t_i, and programming temperature rate, g.

The built-in flow control of the instrument was designed in order to maintain the inlet pressure to the column constant during both isothermal and programmed-temperature analyses. As temperature increases, the gas viscosity and column resistance increase, thus changing the flow-rate. Constant mass flow pneumatic controllers, designed to maintain a constant carrier gas input during the programme, are not reliable in this instance. In fact, differential systems sense the flow-rate and increase the upward pressure on a diaphragm in order to compensate for the increase in column back-pressure with increasing temperature. The available systems installed in many commercial GC instruments can maintain a constant flow-rate over a wide temperature range when packed columns are used at relatively high gas flow-rates (20–60 cm^3 min^{-1}). We checked experimentally that, when wide-bore capillary columns are installed without splitting systems so that all the carrier gas stream is dispatched to the column, commercially available differential controllers can maintain a constant flow-rate as low as 3 cm^3 min^{-1} over the temperature programming range 50–250°C.

However, when narrow-bore columns are used in conjunction with a splitting system, the column back-pressure due to the increase in gas viscosity with temperature has a negligible effect with respect of the prevailing amount of gas flowing through the splitter line. Therefore, the mass flow controllers which keep the overall flow-rate constant do not ensure constancy of the linear velocity into the column.

Further, split–splitless systems, which open and close the split line when the sample is injected, cause fluctuations in the flow regulator that influence the carrier velocity at the beginning of the analysis. It is easier to keep the inlet pressure constant and therefore this solution is generally selected by many producers of capillary GC instruments. When the column inlet and outlet pressures are known, the use of Poiseuille's law permits one to calculate the linear gas velocity in the column at any temperature and to obtain the gas hold-up time which is used in the calculation described below.

The prediction of the PT retention times was carried out by BASIC programming on IBM and COMPAQ personal computers with all the calculation methods described under Theory. As the starting values were used the IT retention times measured with a precision of ±0.001 min, using a Varian DS-650 data system in all the isothermal runs or in three of them selected at the lowest, the highest and one intermediate temperature. The predicted PT values were compared with those measured experimentally during many programmed-temperature runs with different initial temperatures and various programming rates. The built-in BASIC option of the DS-650 can also be programmed in order to capture the raw data recorded by the integration system during isothermal analyses and to apply on-line the prediction procedures.

3. Theory

The general equation used for the prediction of programmed-temperature retention times, PTt_R, is [1,2,7,8]

$$g = \int_{T_i}^{T_f} \frac{\mathrm{d}T}{t_R(T)} \tag{1}$$

where T_i is the initial temperature of the programmed run, T_f is the temperature at which a given compound is eluted from the column, g is the temperature gradient and $t_R(T)$ is the function which represents the dependence of the retention time of that compound on the change in temperature. The main problems of the prediction are to find the function $t_R(T)$ which gives the best approximation to the experimental values of t_R with changing temperature and to solve the integral of Eq. 1 for a value of T_f that satisfies the equation.

For all the methods used, except that suggested by Said [7,8], the integration of Eq. 1 was carried out with the trapezoid method [22,28–31], and the difference between the various procedures is due only to the choice of the function $t_R(T)$. Three different expressions of this function were selected:

$$t_R(T) = A + \exp\left(\frac{B}{T} + C\right) \tag{2}$$

$$t_R(T) = t_M(T)\left[1 + \exp\left(\frac{B'}{T} + C'\right)\right] \tag{3}$$

$$t_R(T) = t_M(T)\left[1 + \exp\left(\frac{A''}{T} + B'' + C''T\right)\right] \tag{4}$$

where $t_M(T)$ is the gas hold-up time (or dead time) necessary for the carrier gas to travel along the column, and introduces into the equations the dependence of the retention time on temperature, through the change of the dynamic viscosity of the carrier gas $\mu(T)$. The different methods that can be used for the determination of $t_M(T)$ were described previously [24,32–36].

The gas hold-up time can be measured by manual or electronic flow meters, deduced by the retention time of methane or calculated theoretically as follows.

When the pressure at the column inlet is constant and exactly known, the application of Poiseuille's law permits one to obtain the $t_M(T)$ (min) value:

$$t_M(T) = \frac{16L^2\mu(T)}{60jr^2} \cdot \frac{P_o}{P_i^2 - P_o^2} \tag{5}$$

where L = column length (cm), r = column radius (cm), P_o = column outlet pressure (absolute) (dyn cm^{-2}), P_i = column inlet pressure (absolute) (dyn cm^{-2}), j = pressure gradient correction factor of James and Martin [37] and $\mu(T)$ = dynamic viscosity of the carrier gas used (poise). $\mu(T)$ depends on temperature and can be obtained from tabulated data or calculated with exponential or quadratic expressions [24,38].

The various procedures used for solving Eq. 1 are briefly described below; for a full description and discussion, the reader should consult the listed references.

3.1. *Said's method*

Said's method [7,8] (indicated with the subscript X in the text and in the tables) is essentially based on the function reported in Eq. 2. The coefficients A, B and C were calculated by using the values of the isothermal retention times (ITt_R) measured at three temperatures only: the lowest, the highest and an intermediate value in the temperature range of the column used.

3.2. *Trapezoids method*

The trapezoids method (subscript T) [22,25–28] also employs the function of Eq. 2 and the same coefficients as in Said's method, but the integral of Eq. 1 was solved by using the trapezoids rule, and ITt_R values measured at three temperatures only were used.

3.3. *Interpolation method*

This method (subscript I) was applied by using the function of Eq. 3 whose coefficients B' and C' were obtained by linear interpolation with the least-squares method of all the experimental ITt_R values obtained at 5 or 10°C intervals within the range 60–190°C. The functions of Eq. 3 and that of Eq. 4 discussed below describe the dependence of the retention time on the values of t_M and of the capacity factor k' [39–46]:

$$t_R(T) = t_M(T)(1 + k') \tag{6}$$

where k' is expressed by

$$k' = \beta \exp(\Delta G/RT) \tag{7}$$

where β is the phase ratio of the column, ΔG is the free energy of solution or partition of a given compound between the gas and liquid phases, R is the universal gas constant and T the absolute temperature. By taking into account the classical thermodynamic equation

$$\Delta G = \Delta H - T\,\Delta S \tag{8}$$

Eq. 7 can be rewritten as

$$k' = \exp\left(\ln \beta + \frac{\Delta H}{RT} - \frac{\Delta S}{R}\right) \tag{9}$$

The term β can be considered as a constant while both ΔH and ΔS depend on temperature [40,41,47,48]. If these thermodynamic parameters are taken as constants, the combination of Eqs. 6 and 9 is equivalent to the function of Eq. 3. The values of PTt_R predicted with method I differ from the experimental values more that those obtained with the Said (X) and trapezoids (T) methods, notwithstanding the greater number of ITt_R values used for interpolation. This confirms that the hypothesis of ΔH and ΔS being completely independent of temperature cannot be accepted. One can suppose that this dependence can be neglected for small temperature intervals and, by using a great number of isothermal runs differing by only 5 or 10°C, calculate the values of the coefficients B' and C' for every small temperature interval. The integral of Eq. 1 was therefore solved by using for each temperature step the corresponding pair of B' and C' coefficients. This procedure, differing from the linear interpolation method (I), is indicated with the subscript S (step) and, as shown below, predicts PTt_R with a good approximation to the experimental results.

Further, as the procedure yields a large number of B' and C' pairs, each of them corresponding to a narrow temperature range or, to a first approximation, to the average temperature for that interval, their values can be correlated with thermodynamic functions, with the polarity of the column and with its dependence on temperature. The main difficulty in the application of the step interpolation method (S) for routine work is that it requires a large number of isothermal runs and therefore is more time consuming than the Said and trapezoids methods.

Our experimental results, however, show that the ΔH and ΔS can be considered with a suitable approximation to depend linearly on temperature. Fig. 1 shows for some compounds taken as examples the linear dependence of B' and C' on temperature. As these coefficients are proportional to ΔH and ΔS, respectively, as follows:

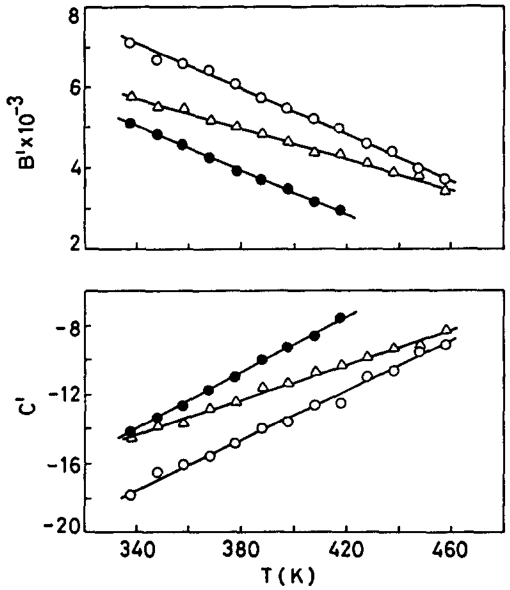

Fig. 1. Experimental values of the coefficients of Eq. 3, B' (upper graph) and C' (lower graph), as a function of temperature, for (●) n-dodecane, (○) n-octanol and (△) 1,4-dichlorobenzene on a Supelcowax 10 column. The slope of the regression lines are given in Table 1.

$$B' = \Delta H/R \tag{10}$$

$$C' = \ln \beta - (\Delta S/R) \tag{11}$$

β and R being constants, the thermodynamic parameters also vary linearly with the column temperature.

Table 1 shows the values of the slope and of the correlation coefficient of B' and C' versus absolute temperature for eight compounds representative of the various polarity classes on the three columns. The linearity is fair and the slopes depend on the polarity of the compound and of the column. All the other compounds tested show linear behaviour. Therefore, by taking into account the linear dependence of ΔH and ΔS on temperature, by combination of Eqs. 6 and 9 an equation equivalent to the function of Eq. 4 is obtained. The method, indicated as QI (quadratic interpolation), employs the function of Eq. 4, whose coefficients A'', B'' and C'' were obtained by interpolating with the least-squares method all the experimental values of ITt_R obtained in the range 60–190°C.

These coefficients are valid within the whole temperature range of the column, while those obtained with the S method change for every temperature interval of the programmed run. This method has the same disadvantage as the S method, because a large number of isothermal runs are used in order to obtain the coefficients A'', B'' and C''. However, by taking into account the linearity of the coefficients B' and C', an attempt was made to obtain the coefficients of Eq. 4 by using the same three ITt_R values used for the calculation with the Said and trapezoids methods. This procedure, indicated as the Q (quadratic) method, allows one to predict the PTt_R values with an approximation nearly equivalent to that obtained with the more complex and time-consuming QI method and is therefore suitable for routine use.

4. Results and discussion

Tables 2, 3 and 4 show examples of the results obtained by predicting the PTt_R on the three columns: in the first column of each table all the compounds contained in the samples are listed in order of increasing retention times obtained in isothermal analysis at 60°C on the three columns. The experimental retention times PTt_R(exp) obtained in a programmed-temperature run taken as an example (initial temperature T_i = 60°C; initial isothermal time t_i = 2 min; programming rate g = 5°C min^{-1}, and the same for the three columns, are listed. The percentage differences between the predicted and experimental PTt_R values, calculated with the equation

$$E = \frac{\mathrm{PT}t_R(\mathrm{calc}) - \mathrm{PT}t_R(\mathrm{exp})}{\mathrm{PT}t_R(\mathrm{exp})} \cdot 100 \tag{12}$$

are reported for all the calculation methods used. The subscripts refer to the various methods described in the Theory section, as follows: three methods use the ITt_R of all the isothermal runs in the range 60–190°C: I = linear interpolation method, S = step method and QI = quadratic interpolation method.

The other methods use as the starting data

Table 1
Slope, *s*, and correlation coefficient, *r*, of the straight lines showing the dependence of the coefficients B' and C' of Eq. 3 on the absolute temperature of the column for various compounds (see also Fig. 1)

Compound	Coefficient	SPB-1		Supelcowax-10		CLOT	
		s	*r*	*s*	*r*	*s*	*r*
n-Dodecane	B'	−24.10	0.996	−27.74	0.997	−27.40	0.993
	C'	0.061	0.995	0.080	0.998	0.066	0.997
n-Octanol	B'	−30.43	0.991	−28.87	0.990	−16.37	0.986
	C'	0.077	0.993	0.071	0.992	0.039	0.993
Naphthalene	B'	−20.11	0.994	−15.22	0.996	−7.51	0.951
	C'	0.052	0.995	0.038	0.995	0.017	0.966
1,4-Dichlorobenzene	B'	−24.30	0.991	−19.24	0.996	−11.49	0.974
	C'	0.062	0.993	0.050	0.996	0.029	0.972
1,3,5-Trichlorobenzene	B'	−21.45	0.997	−17.62	0.998	−13.25	0.997
	C'	0.055	0.998	0.045	0.998	0.031	0.997
Nitrobenzene	B'	−23.31	0.994	−15.67	0.994	−21.49	0.977
	C'	0.060	0.995	0.038	0.994	0.050	0.979
1-Chloro-4-nitrobenzene	B'	−21.24	0.984	−14.56	0.992	−24.02	0.994
	C'	0.054	0.987	0.635	0.990	0.055	0.995
4-Chloroaniline	B'	−24.37	0.995	−10.89	0.999	−26.96	0.999
	C'	0.062	0.995	0.025	0.999	0.062	0.997

three isothermal runs at the lowest, the highest and an intermediate temperature: X = Said's method [7,8], T = trapezoid method [22,28–31] and Q = quadratic method.

The average errors $E_{\mathrm{ave}}(\mathrm{tot})$ and the absolute average errors $E_{\mathrm{abs}}(\mathrm{tot})$ are also reported, taking into account all the compounds contained in the sample, and calculated as

$$E_{\mathrm{ave}}(N) = \frac{\sum_{0}^{n} E_M(N)}{N} \tag{13}$$

$$E_{\mathrm{abs}}(N) = \frac{\sum_{0}^{n} |E_M(N)|}{N} \tag{14}$$

where the subscript M refers to the symbols of the methods listed above. Table 5 shows the values of $E_{\mathrm{ave}}(N)$ and $E_{\mathrm{abs}}(N)$ for programmed runs with different T_i, t_i and g and the overall averages of all these runs for each method, $E_{\mathrm{ave}}(\mathrm{tot})$ and $E_{\mathrm{abs}}(\mathrm{tot})$, calculated with the same method shown in Eqs. 13 and 14. The values of $E_{\mathrm{abs}}(\mathrm{tot})$ in Table 5 are plotted in Fig. 2 for the various prediction methods, indicated on the abscissa.

The data in Tables 2–4 show that the three columns tested elute the analysed compounds in different orders. The elution order in various isothermal analyses does not change on the gas–liquid SPB-1 and Supelcowax-10 columns, whereas some inversions were observed on the gas–liquid–solid CLOT column [20,21]. This is due to the polarity of the column, which, calculated with the ΔC method [26,27], is constant in the range 60–190°C for GLC columns (2.70 for SPB-1 and 7.52 for Supelcowax-10) but changes linearly from 6.00 to 6.45 for the CLOT column.

Notwithstanding the different characteristics of the columns and their dependence on temperature, the prediction methods tested permitted an acceptable approximation to the experimental results. In fact, the values of the deviation between the predicted and calculated $\mathrm{PT}t_{\mathrm{R}}$ values are small for the methods tested, excluding the linear interpolation (I) method (see Fig. 2).

Table 2
Percentage difference between predicted and experimental PTt_R values, E, calculated by Eq. 11 for the SPB-1 column

No. Compound	PTt_r (min)	E_X	E_T	E_I	E_S	E_{QI}	E_Q
1 n-C_7	1.177	−0.93	−0.93	−0.34	−0.93	−0.99	−0.93
2 n-C_8	1.658	−0.72	−0.72	4.40	−0.72	−0.79	−0.72
3 Chlorobenzene	1.904	−0.16	−0.16	5.88	−0.16	−0.17	−0.16
4 n-C_9	2.683	−0.79	−0.26	8.42	−0.75	−0.97	−0.67
5 Bromobenzene	2.825	−0.20	−0.18	7.58	−0.14	−0.35	−0.07
6 1,3-Dichlorobenzene	4.049	−0.04	−0.02	9.53	−0.30	0.30	−0.44
7 1,4-Dichlorobenzene	4.148	0.09	−0.05	9.43	−0.36	0.07	−0.36
8 n-C_{10}	4.409	−0.45	−0.93	7.08	−1.00	−1.04	−0.82
9 1,2-Dichlorobenzene	4.571	0.14	0.02	8.58	−0.35	0.00	−0.39
10 Nitrobenzene	5.404	0.48	−0.11	7.75	−0.31	−0.20	−0.17
11 2-Chloroaniline	6.491	0.26	−0.29	5.73	−0.25	−0.12	−0.09
12 n-C_{11}	6.702	−0.32	−1.01	4.61	−0.82	−0.67	−0.73
13 1,3,5-Trichlorobenzene	6.842	−0.08	−0.70	4.52	−0.42	−0.37	−0.34
14 1,2,4-Trichlorobenzene	7.825	0.00	−0.58	2.84	−0.20	−0.13	−0.03
15 Naphthalene	7.945	0.06	−0.57	2.84	−0.20	−0.05	0.08
16 3-Chloroaniline	8.117	−0.19	−0.90	3.01	−0.10	0.00	−0.10
17 4-Chloroaniline	8.191	0.09	−0.48	2.93	−0.07	0.05	0.20
18 1,2,3-Trichlorobenzene	8.636	0.05	−0.39	2.00	−0.15	0.01	0.24
19 1-Chloro-3-nitrobenzene	8.723	−0.16	−0.77	2.02	−0.11	0.02	0.07
20 1-Chloro-4-nitrobenzene	8.914	−0.03	−0.63	1.76	−0.10	0.06	0.24
21 1-Chloro-2-nitrobenzene	9.080	−0.33	−0.77	1.40	−0.12	−0.03	−0.06
22 n-C_{12}	9.271	−0.41	−1.07	0.91	−0.47	−0.30	−0.04
23 n-C_{13}	11.874	2.02	1.38	0.43	0.67	1.19	2.42
$E_{ave}(N)$		−0.07	−0.44	4.49	−0.32	−0.20	−0.13
$T_{abs}(N)$		0.35	0.56	4.52	0.38	0.34	0.41

Analytical parameters of the temperature-programmed run: $T_i = 60°C$; $t_i = 2$ min; $g = 5°C\ min^{-1}$. The values averaged over all the compounds are also shown (see Eqs. 12 and 13). Subscripts to E refer to the prediction methods.

Further, by comparing the values of E for the various compounds obtained with many temperature programs and the average values in Table 5, one can see that the deviations between the predicted and experimental PTt_R values are stochastic and do not depend on the method used or on the compound analysed. The greater values of the deviation for the linear interpolation method (E_I) are due, as seen in the Theory section, to the hypothesis applied for the calculation that ΔH and ΔS values do not depend on temperature. On the contrary, as shown in Fig. 1 and Table 1, both thermodynamic functions depend linearly on the column temperature.

This is better shown by Fig. 3, where the Arrhenius plots ($\ln k'$ vs. $1/T$) for n-nonanol on the three columns of different polarity are reported (upper graph). All these plots show an appreciable curvature, greater for the SPB-1 column, as confirmed by the behaviour of the first derivative (lower graph), i.e., of the slope of the various tracts. Therefore, the linear interpolation of method I predicts PTt_R values differing from the experimental values to an extent depending on the curvature of the Arrhenius plot. The same behaviour was observed for all the compounds tested, as shown by the greater values in the E_I column in Tables 2–5. Fig. 3 shows that the best linearity of the $\ln k'$ vs. $1/T$ plot was given by the CLOT column, notwithstanding its change of polarity with temperature. The other prediction methods, which are independent of the linearity of the Arrhenius plot or interpolate step by step by taking into account its curvature, are therefore more accurate than the I method,as shown in Fig. 2.

Table 3

Percentage difference between predicted and experimental PTt_R values, E, calculated by Eq. 11 for the Supelcowax-10 column

No. Compound	PTt_r (min)	E_X	E_T	E_I	E_S	E_{QI}	E_Q
22 n-C_{12}	2.901	−1.03	−1.00	5.58	−0.97	−0.76	−0.90
3 Chlorobenzene	3.152	−0.85	−0.57	7.14	−0.79	−0.79	−0.73
23 n-C_{13}	4.440	−1.08	−1.58	5.43	−1.60	−1.46	−1.37
5 Bromobenzene	5.229	−1.37	−1.93	4.40	−1.30	−1.11	−1.76
24 n-C_{14}	6.394	−1.40	−2.13	3.24	−1.64	−1.49	−1.67
6 1,3-Dichlorobenzene	6.597	−1.30	−1.71	2.82	−1.36	−1.18	−1.55
7 1,4-Dichlorobenzene	7.224	−1.39	−2.02	1.87	−1.34	−1.20	−1.51
9 1,2-Dichlorobenzene	8.108	−1.51	−2.00	0.43	−1.27	−1.25	−1.49
25 n-C_{15}	8.556	−1.98	−2.73	−0.41	−1.62	−1.60	−1.81
13 1,3,5-Trichlorobenzene	8.683	−1.61	−2.15	−0.44	−1.20	−1.27	−1.57
26 n-C_{16}	10.798	0.25	−0.48	5.25	−0.31	−0.82	−0.95
14 1,2,4-Trichlorobenzene	11.432	0.08	−0.33	3.26	−0.22	−0.55	−0.62
18 1,2,3-Trichlorobenzene	13.229	−0.25	−0.61	1.19	−0.48	−0.62	−0.68
10 Nitrobenzene	13.542	−0.26	−0.50	0.92	−0.45	−0.58	−0.63
15 Naphthalene	13.542	−0.26	−0.50	0.92	−0.45	−0.58	−0.63
27 n-C_{18}	15.168	−0.32	−1.07	−0.51	−0.88	−0.89	−0.82
19 1-Chloro-3-nitrobenzene	17.073	−0.23	−0.57	0.01	−0.47	−0.62	−0.64
20 1-Chloro-4-nitrobenzene	17.902	−0.27	−0.72	−0.32	−0.53	−0.65	−0.69
11 2-Chloroaniline	18.045	−0.10	−0.69	−0.35	0.50	−0.62	−0.64
21 1-Chloro-2-nitrobenzene	19.237	−0.11	−0.59	−0.50	−0.41	−0.51	−0.55
28 n-C_{20}	19.237	−0.02	−0.90	−1.05	−0.74	−0.80	−0.81
17 4-Chloroaniline	22.659	0.76	0.13	0.48	0.22	−0.05	−0.05
16 3-Chloroaniline	22.833	0.73	0.10	0.45	0.19	−0.07	−0.07
29 n-C_{22}	23.062	0.75	−0.21	0.05	−0.12	−0.38	−0.38
$E_{ave}(N)$		−0.53	−1.03	1.66	−0.76	−0.83	−0.94
$E_{abs}(N)$		0.75	1.05	1.96	0.79	0.83	0.94

Analytical parameters of the temperature-programmed run: $T_i = 60°C$; $t_i = 2$ min; $g = 5°C\ min^{-1}$. The values averaged over all the compounds are also shown (see Eqs. 12 and 13). Subscripts to E refer to the prediction methods.

The two methods QI and Q, which both apply the expression of Eq. 4, and whose coefficients A'', B'' and C'' are obtained by using many ITt_R values at small temperature intervals (QI) or three ITt_R values only (Q), show a comparable accuracy (Fig. 2). The exponential section of Eq. 4 containing the three coefficients is similar to the familiar Van Deemter expression; in fact, the dependence of the exponent on temperature follows the same behaviour as the dependence of HETP on the gas velocity: a constant value (B''), a linear dependence ($C''T$) and an hyperbolic function (A''/T). Fig. 4 shows as an example the dependence of A'', B'' and C'' for linear alkanes on SPB-1, Supelcowax-10 and CLOT columns. The trend for the last column differs markedly from that observed on gas–liquid partition systems, and this difference was also observed for other homologous series tested.

5. Application of Q method to automatic prediction

As shown above, the Q method permits the prediction of PTt_R values to be carried out by starting from three isothermal runs, with an accuracy similar to that given by the more complex S and QI methods. Its application, which can be off-line, by manually transferring

Table 4
Percentage difference between predicted and experimental PTt_R values, E, calculated by Eq. 11 for the CLOT column

No. Compound	PTt_r (min)	E_X	E_T	E_I	E_S	E_{QI}	E_Q
8 n-C_{10}	3.990	−0.98	−1.50	3.38	0.83	−0.53	−1.38
12 n-C_{11}	6.266	−1.68	−2.30	2.19	1.36	−1.29	−2.70
3 Chlorobenzene	5.545	−0.58	−1.17	2.13	1.01	−1.08	−1.51
22 n-C_{12}	8.870	−3.03	−3.83	−1.05	1.48	−1.72	−3.12
5 Bromobenzene	8.482	−2.22	−2.45	−1.38	1.73	−1.92	−2.86
23 n-C_{13}	11.527	−1.22	−1.93	0.83	1.13	−1.18	−1.74
6 1,3-Dichlorobenzene	10.455	−1.97	−2.25	−1.59	1.28	−1.30	−1.74
7 1,4-Dichlorobenzene	11.154	−1.05	−1.40	0.58	1.10	−1.21	−1.34
9 1,2-Dichlorobenzene	12.184	−1.23	−1.53	−0.11	1.16	−1.24	−1.39
24 n-C_{14}	14.109	0.02	−0.57	2.35	0.44	−0.72	−0.89
13 1,3,5-Trichlorobenzene	13,451	−0.51	−0.74	1.81	0.58	−1.03	−1.04
25 n-C_{15}	16,601	1.04	0.43	2.70	−0.59	0.00	0.02
14 1,2,4-Trichlorobenzene	16,402	−0.07	−0.29	1.88	0.08	−0.75	−0.71
10 Nitrobenzene	17.665	−0.32	−0.48	0.93	0.38	−0.82	−0.80
26 n-C_{16}	18.977	0.29	−0.49	0.66	0.37	−0.73	−0.74
18 1,2,3-Trichlorobenzene	18.319	−0.40	−0.61	0.72	0.52	−0.92	−0.93
15 Naphthalene	18.319	−0.34	−0.50	0.68	0.41	−0.78	−0.79
19 1-Chloro-3-nitrobenzene	21.403	−1.30	−1.62	−1.03	0.80	−2.04	−1.81
11 2-Chloroaniline	21.799	0.01	−0.42	0.22	−0.02	−0.83	−0.68
20 1-Chloro-4-nitrobenzene	22.533	−0.11	−0.43	0.01	−0.01	−0.79	−0.70
21 1-Chloro-2-nitrobenzene	23.485	−0.20	−0.53	−0.28	0.19	−0.79	−0.70
27 n-C_{18}	23.457	0.24	−0.82	−0.40	0.57	−0.99	−0.99
17 4-Chloroaniline	26.431	0.06	−0.60	−0.53	0.53	−0.75	−0.75
16 3-Chloroaniline	26.562	0.05	−0.63	−0.56	0.48	−0.78	−0.78
28 n-C_{20}	27.605	0.24	−0.96	−0.89	0.96	−1.10	−1.03
$E_{ave}(N)$		−0.61	1.11	0.53	0.67	−1.01	−1.24
$E_{abs}(N)$		0.77	1.14	1.16	0.72	1.01	1.25

Analytical parameters of the programmed-temperature run: $T_i = 60°C$; $t_i = 2$ min; $g = 5°C\ min^{-1}$. The values averaged over all the compounds are also shown (see Eqs. 12 and 13). Subscripts to E refer to the prediction methods.

the ITt_R values to a personal computer, or on-line, if the integrator used is directly programmable in BASIC or is interfaced to a separate computer, require the following steps.

(a) Three isothermal runs covering the expected temperature range of the programmed-temperature analysis are carried out. Automatic samplers can be employed in order to repeat the injection three or four times at every temperature.

(b) The average ITt_R values at the three temperatures are used to solve a system of three equations deduced from Eq. 4, in order to calculate the values of A'', B'' and C'':

$$\ln k'_{(i)} = \frac{A''}{T_i} + B'' + C''T_i \tag{15}$$

where i refers to the different isothermal runs.

(c) The values of the coefficients are substituted in the integral

$$g = \int_{T_i}^{T_f} \frac{\mathrm{d}T}{t_M(T)\left[1 + \exp\left(\frac{A''}{T} + B'' + C''T\right)\right]}$$

which is solved with the trapezoids method [22,28–31]. The values of T_f (elution temperature of every compound) are obtained and, the

Table 5

Average and absolute average percentage differences between predicted and calculated PTt_R values, E, calculated with Eqs. 12 and 13 for various programmed-temperature runs on the three columns

Column	T_i (°C)	t_i (min)	g (°C min^{-1})	E_X	E_T	E_I	E_S	E_{QI}	E_Q
SPB-1	45	0	4	0.89	1.23	7.03	0.69	0.76	0.76
	50	0	2	1.04	0.46	10.27	0.56	0.38	0.41
	80	0	3	0.90	0.95	1.27	0.45	0.68	0.80
	50	3	5	0.80	1.30	7.44	1.02	0.87	0.87
	60	2	5	0.35	0.56	4.52	0.38	0.34	0.41
	60	6	2	0.56	0.59	10.19	0.47	0.52	0.52
E_{abs}(tot)				0.76	0.85	6.79	0.60	0.59	0.63
	45	0	4	−0.15	−1.12	7.03	−0.25	−0.65	−0.56
	50	0	2	0.49	−0.09	10.27	0.54	0.23	0.34
	80	0	3	0.90	0.50	−1.16	0.41	0.66	0.71
	50	3	5	−0.66	−1.24	7.44	−0.23	−0.73	−0.64
	60	2	5	−0.07	−0.44	4.49	−0.32	−0.20	−0.13
	60	6	2	0.33	0.30	10.19	0.42	0.46	0.50
E_{ave}(tot)				0.14	−0.35	6.38	0.10	−0.04	0.04
Supelcowax-10	45	0	4	1.03	1.05	3.19	0.75	0.91	1.01
	60	0	4	0.87	1.14	1.44	0.85	0.86	0.98
	80	0	3	1.36	1.40	2.45	0.75	0.79	0.96
	45	2	5	0.94	1.30	3.04	0.92	1.26	1.36
	60	2	5	0.75	1.05	1.96	0.79	0.83	0.94
	100	4	2	1.26	1.00	3.46	0.66	0.32	0.57
E_{abs}(tot)				1.04	1.16	2.59	0.79	0.83	0.97
	45	0	4	0.42	−1.00	3.12	−0.66	−0.91	−1.01
	60	0	4	−0.60	−1.11	1.13	−0.80	−0.87	−0.98
	80	0	3	−1.36	−1.24	−1.43	−0.68	−0.79	−0.94
	45	2	5	−0.13	−1.30	2.77	0.92	−1.27	−1.36
	60	2	5	−0.53	−1.03	1.66	−0.76	−0.83	−0.94
	100	4	2	−1.12	−0.73	−2.71	0.13	−0.20	−0.36
E_{ave}(tot)				−0.55	−1.07	0.76	−0.31	−0.81	−0.93
CLOT	45	0	4	0.98	1.01	1.57	0.74	0.98	1.15
	70	0	5	0.97	0.97	1.53	0.72	0.52	0.88
	80	0	3	1.30	1.24	2.18	0.79	0.87	1.29
	60	2	5	0.77	1.14	1.16	0.72	1.01	1.25
	80	2	7	0.96	0.95	1.57	0.80	0.60	0.91
	90	10	10	1.44	1.43	2.68	1.03	0.78	1.28
E_{abs}(tot)				1.07	1.12	1.78	0.80	0.79	1.13
	45	0	4	0.37	1.00	1.22	−0.59	−0.95	−1.11
	70	0	5	0.00	−0.29	0.64	−0.35	0.01	0.40
	80	0	3	−1.17	−1.02	0.23	0.20	0.80	−1.21
	60	2	5	−0.61	−1.11	0.53	0.67	−1.01	−1.24
	80	2	7	0.22	0.09	0.60	−0.67	0.33	−0.03
	90	10	10	−0.22	−0.23	0.57	0.64	0.21	−0.34
E_{ave}(tot)				−0.23	−0.26	0.63	−0.02	−0.10	−0.59

The overall averages are also shown. Subscripts to E refer to the prediction methods.

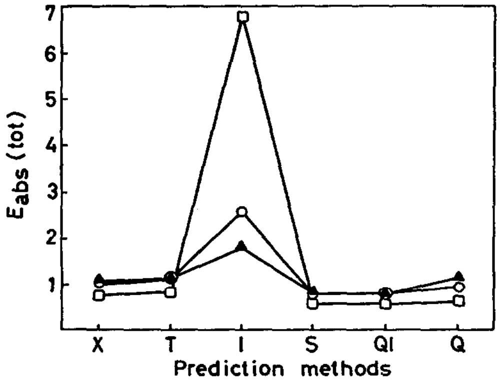

Fig. 2. Absolute percentage difference between predicted and experimental PTt_R values, averaged over all the analysed compounds and different programmed runs, E_{abs}(tot), for the various calculation methods (see Table 5).

programming rate g and the initial temperature T_i being known, permit the calculation of the retention time:

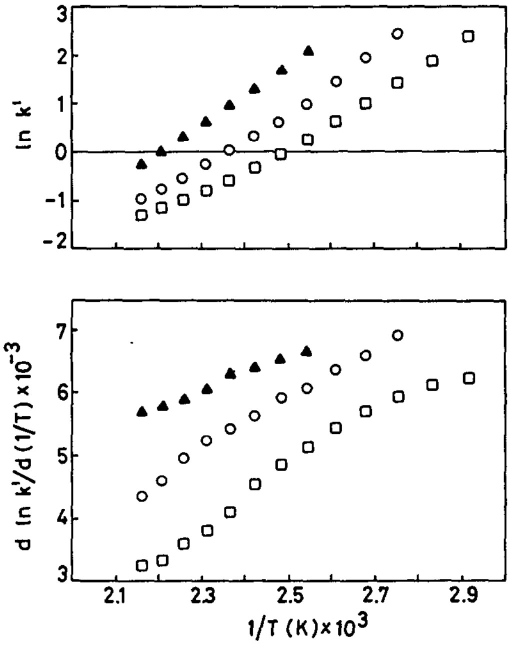

Fig. 3. Upper graph: Arrhenius plots (ln k' vs. $1/T$) for n-nonanol on the three columns (□ = SPB-1; ○ = Supelcowax-10; ▲ = CLOT). Lower graph: values of the first derivative that show the change of slope of the upper curves with temperature.

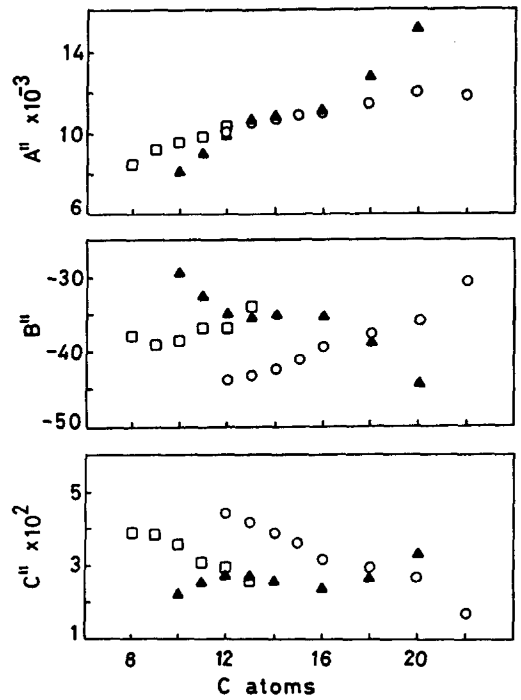

Fig. 4. Values of the coefficients of Eq. 4, A'', B'' and C'', for linear alkanes on (□) SPB-1, (○) Supelcowax-10 and (▲) CLOT columns.

$$PTt_R(\text{calc}) = (T_f - T_i)/g \tag{16}$$

6. Conclusions

The comparison of the various prediction methods tested showed that, for some of them, an increase in the number of starting isothermal data results in a better approximation of predicted to experimental PTt_R values, whereas for others, when the linearity is poor, appreciable deviations are observed. The step (S), quadratic interpolation (QI) and quadratic (Q) methods permit the same degree of confidence to be obtained as found previously with the Said and trapezoids methods. A further advantage of the Q method is that it can be applied by using only three isothermal data and is suitable of easy application to automatic data acquisition and calculation. The constants of Eqs. 3 and 4, which can be calculated by using experimental isothermal retention values, are correlated with the classical thermodynamic functions and may therefore be used to obtain their values and to investigate the solute–solvent interaction mechanism.

Acknowledgements

This research was supported by the Italian Ministry of University and Scientific Research (MURST). The authors thank Miss Carla Parodi for her help in preparing the manuscript.

References

[1] H.W. Habgood and W.E. Harris, *Anal. Chem.*, 32 (1960) 450.
[2] W.E. Harris and H.W. Habgood, *Programmed Temperature Gas Chromatography*, Wiley, New York (1966).
[3] D.W. Grant and M.G. Hollis, *J. Chromatogr.*, 158 (1978) 3.
[4] J. Culvers, J. Rijks, C. Cramers, K. Knauss and P. Larson, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 607.
[5] E.E. Akporhonor, S. Le Vent and D.R. Taylor, *J. Chromatogr.*, 405 (1987) 67.
[6] P.Y. Shrotri, A. Mokashy and D. Hukesh, *J. Chromatogr.*, 387 (1987) 399.
[7] A.S. Said, in P. Sandra (Editor), *Proceedings of the 8th International Symposium on Capillary Chromatography, Riva del Garda, Italy*, Vol. I, 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, Italy*, Hüthig, Heidelberg, 1989, p. 163.
[9] F. Helaimiam, M. Bourmahraz, H. Sissaoni and M.D. Messadi, *Analysis*, 17 (1989) 596.
[10] E.E. Akporhonor, S. Le Vent and D.R. Taylor, *J. Chromatogr.*, 463 (1989) 271.
[11] J.Y. Zhang, G.M. Wang and R. Qian, *J. Chromatogr.*, 521 (1990) 71.
[12] Y. Guan and L. Zhou, *J. Chromatogr.*, 552 (1991) 187.
[13] L.H. Wright and J.F. Walling, *J. Chromatogr.*, 540 (1991) 311.
[14] Y. Guan, P. Zheng and L. Zhou, *J. High Resolut. Chromatogr.*, 15 (1992) 18.
[15] N.H. Snow and H.M. McNair, *J. Chromatogr. Sci.*, 30 (1992) 271.
[16] T.C. Gerbino and C. Castello, in P. Sandra (Editor), *Proceedings of the 14th International Symposium on Capillary Chromatography, Baltimore, MD, 1992*, Foundation for the International Symposium on Capillary Chromatography, Miami, FL, 1992, p. 70.
[17] T.C. Gerbino and G. Castello, *J. High Resolut. Chromatogr.*, 16 (1993) 46.
[18] T.C. Gerbino, G. Castello and G. Pettinati, *J. Chromatogr.*, 634 (1993) 338.
[19] T.C. Gerbino and G. Castello, in P. Sandra (Editor), *Proceedings of the 15th International Symposium on Capillary Chromatography, Riva del Garda, Italy*, Hüthig, Heidelberg, 1993, p. 60.
[20] G. Castello and S. Vezzani, in P. Sandra (Editor), *Proceedings of the 15th International Symposium on Capillary Chromatography, Riva del Garda, Italy*, Hüthig, Heidelberg, 1993, p. 68.
[21] G. Castello, S. Vezzani and P. Moretti, *J. High Resolut. Chromatogr.*, 17 (1994) 31.
[22] G. Castello, P. Moretti and S. Vezzani, *J. Chromatogr.*, 635 (1993) 103.
[23] S.S. Stafford (Editor), *Electronic Pressure Control in Gas Chromatography*, Hewlett-Packard, Wilmington, DE, 1993.
[24] G. Castello, S. Vezzani and P. Moretti, *J. Chromatogr. A*, 677 (1994) 95.
[25] R.H. Ewell, J.M. Harrison and L. Berg, *Ind. Eng. Chem.*, 36 (1944) 871.
[26] G. Castello and G. D'Amato, *J. Chromatogr.*, 623 (1992) 289.
[27] G. Castello, G. D'Amato and S. Vezzani, *J. Chromatogr.*, 646 (1993) 361.
[28] C. Caratheodory, *Algebraic Theory of Measure and Integration*, Chelsea, New York, 1963.
[29] F. Ayres, Jr., *Theory and Problems of Differential and Integral Calculus*, Schaum, New York, 1964.
[30] E.J. McShane, *Unified Integration*, Academic Press, Orlando, FL (1983).
[31] J.L. Kelley and T.P. Srinmivasan, *Measure and Integral*, Springer, New York, 1988.
[32] L.S. Ettre, *Chromatographia*, 13 (1980) 73.
[33] M.S. Wainwright and J.K. Haken, *J. Chromatogr.*, 184 (1980) 1.
[34] M.S. Wainwright, C.S. Nieass, J.K. Haken and R.P. Chaplin, *J. Chromatogr.*, 321 (1985) 287.
[35] R.J. Smith, J.K. Haken, M.S. Wainwright and B.G. Madden, *J. Chromatogr.*, 328 (1985) 11.
[36] B. Koppenhoefer, G. Laupp and M. Humel, *J. Chromatogr.*, 547 (1991) 239.
[37] A.P. James and A.J.P. Martin, *Biochem. J.*, 50 (1952) 679.
[38] L.S. Ettre, *Chromatographia*, 18 (1984) 243.
[39] R. Kaiser, *Gas Phase Chromatography*, Vol. 1, Butterworths, London, 1963.
[40] M.H. Guermouches and J.M. Vergnaud, *J. Chromatogr.*, 94 (1971) 169.

[41] M.H. Guermouches and J.M. Vergnaud, *J. Chromatogr.*, 94 (1974) 25.
[42] R.L. Grob, *Modern Practice of Gas Chromatography*, Wiley, New York, 1977.
[43] L. Podmaniczky, L. Szepesy, K. Lakzner and G. Schomburg, *Chromatographia*, 20 (1985) 591.
[44] L. Podmaniczky, L. Szepesy, K. Lakzner and G. Schomburg, *Chromatographia*, 20 (1985) 623.
[45] K. Kuningas, S. Rang and T. Kailas, *Chromatographia*, 27 (1989) 544.
[46] H. Rotzsche, *Stationary Phases in Gas Chromatography*, Elsevier, Amsterdam, 1991.
[47] R.W. Dwyer, *J. Chromatogr. Sci.*, 15 (1977) 450.
[48] A.N. Korol and T.I. Dovbush, *J. Chromatogr.*, 209 (1981) 21.