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Optimization of temperature-programmed gas chromatographic separations
I. Prediction of retention times and peak widths from retention indices

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Abstract

A numerical method is described to predict retention times and peak widths of a mixture containing components with known identities in capillary gas chromatography. The procedure is based on extracting thermodynamic values (enthalpy and entropy terms) from Kováts retention indices. Next, a numerical procedure is developed that uses these data to calculate retention times and peak widths on any capillary column containing the same stationary phase but with a different phase ratio. The estimations are based on a sound theoretical basis. The predictions can be performed either in the isothermal or temperature-programmed (single- or multi-ramp) mode. In the temperature programs, which cover a broad temperature range, isothermal plateaus are allowed. Errors in the predictions of retention times are generally less than 4%. Prediction of peak widths under the same conditions can be performed with errors of about 10%. An attractive feature of the approach is, that once the thermodynamic values of the solutes of interest are known, future optimizations can be performed without the need to perform experimental input runs. This indicates that the concept can be used for complete off-line simulations and/or optimizations of gas chromatographic separations.

1. Introduction

Gas chromatography (GC) is nowadays widely used for the analysis of a wide variety of samples containing substances with a broad range of boiling points and/or polarities. The technique is performed either isothermal or temperature-programmed. The use of temperature programming has the advantage of decreasing the analysis time, while providing improved resolution for later-eluting compounds.

The optimization (i.e. achieving acceptable resolution in the shortest possible analysis time) of temperature-programmed GC separations is often a tedious and time-consuming task and is usually performed on a trial and error basis. Optimization of separations can be very important, considering the increasing complexity of samples and/or the high demands which are put on the sample throughput in contemporary GC practice.

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To circumvent labour intensive trial and error optimizations, many authors have tried to simulate the chromatographic process for optimization purposes. Various calculation methods have been suggested to predict retention times in linear temperature-programmed GC [1–6], multi-ramp temperature-programmed GC [7,8] either in single-column systems or for serially linked capillary columns [9,10]. For the purpose of prediction of separations, however, the peak width of the solutes of interest must be known as well. This problem has received much less attention in literature. When both the retention time and the peak width are available, the resolution of adjacent peaks can be calculated. The computer-assisted prediction and subsequent optimization of temperature-programmed separations has been addressed by several authors. Dose [11,12] proposed a method based upon thermodynamic quantities. Bautz et al. [13] have presented a method based upon an approximation similar to the linear solvent strength model for gradient HPLC. In addition, other approaches have been followed to simulate and optimize temperature-programmed GC separations as a function of experimental conditions [14–19].

A typical feature of all these simulations is the need for performing several input runs (either isothermal or temperature programmed) of the sample or, in some cases, of other standards as part of the optimization procedure. The data of those runs are then used to carry out the final optimization. Although these optimizations often yield satisfactory results, a disadvantage of the methods is the need for performing experimental runs prior to the true optimization. Apart from the time-consuming nature of these experiments, a change in the analytical system (e.g. changing the column) often requires renewed on-line optimization. In addition, incorporation of isothermal plateaus in the temperature program is often not allowed or the experimental data cover only a limited temperature range. Moreover, the calculation methods are often based on a less sound theoretical background.

The main aim of this work is to describe a method to predict (truly off-line) linear temperature-programmed retention times and peak widths of a mixture containing components with known identities. A method will be described that allows extracting thermodynamic values (entropy and enthalpy terms) from published Kováts retention indices. Next, a numerical procedure is presented, that uses these thermodynamic values to calculate linear (single- or multi-ramp) temperature-programmed retention times and peak widths on any capillary GC column containing the same stationary phase. In this method ideal gas behaviour and constant inlet pressure operation are assumed. For peak width calculations a new numerical approach is developed. Retrieval of the thermodynamic values from Kováts retention indices is mandatory, since the peak data cannot be predicted directly from the retention index itself. Moreover, it will be shown that, once the thermodynamic values of the solutes of interest are known, they can be stored in a database and future optimizations can be performed without the need to perform any experimental input run. The only additional parameter to be measured is the dead time of the column on which the retention times and peak widths are to be predicted. This implies that complete off-line simulation and subsequent optimization of GC separations is now possible.

2. Theory

2.1. Calculation of enthalpy- and entropy terms from Kováts retention indices

The retention index, introduced by Kováts in 1958 [20], is undoubtedly the most widely adapted retention index system available in contemporary GC practice. Kováts indices for a large number of compounds are nowadays available (either in private laboratory data, publications or in commercially available libraries such as the Sadtler Library [21]). Unfortunately, retention times and peak widths cannot be calculated directly from a solute's retention index. For this purpose thermodynamic values (entropy and enthalpy term) must be known. Kováts indices contain this information in an indirect manner. In this section it will be demonstrated how the

thermodynamic parameters can be extracted from Kováts retention indices.

The Kováts retention index expresses the retention of a given compound relative to a homologous series of *n*-alkanes measured under the same isothermal conditions. The Kováts index depends only on the temperature and stationary phase employed. For a given solute *i*, it can be calculated from:

$$I(i) = 100z + 100\frac{\log t'_{R,i} - \log t'_{R,z}}{\log t'_{R,z+1} - \log t_{R,z}} \quad (1)$$

where z is the carbon number of the *n*-alkane eluting before the solute. $t'_{R,i}$, $t'_{R,z}$ and $t'_{R,z+1}$ are the adjusted retention times of the solute and the *n*-alkanes eluting before and after the solute, respectively. Making this equation explicit in $\log t'_{R,i}$ gives:

$$\log t'_{R,i} = -\frac{(100z - I(i))(\log t'_{R,z+1} - \log t'_{R,z})}{100} + \log t'_{R,z} \quad (2)$$

From Eq. 2 it can be seen that if the Kováts index of the compound is known, the only additional information needed to calculate the adjusted retention time of the solute is the adjusted retention times of two *n*-alkanes at the same temperature. From the adjusted retention time of the solute, its retention factor, k, can be calculated once the column dead time is available. Finally, from retention factors determined at two different isothermal temperatures, enthalpy and entropy terms can be obtained as demonstrated by, for example, Guan et al. [22]. For this purpose the following well-known relationship is used:

$$\ln k = \ln\frac{a}{\beta} + \frac{\Delta H}{RT} \quad (3)$$

where $a = \exp(\Delta S/R)$, β is the column phase ratio, R the universal gas constant, T the absolute temperature, ΔH the molar enthalpy of solution (expressed positive) and ΔS the molar entropy of solution. By plotting $\ln k$ versus the reciprocal of the absolute temperature, the entropy term (a/β) and the enthalpy term ($\Delta H/R$) can be obtained from the intercept and the slope, respectively. Both terms can then be used to calculate the retention factor of the solute as a function of temperature. In principle, the entropy and enthalpy terms can be transferred from one column to another column containing the same stationary phase but having different column dimensions. In this respect it is important to realize that the entropy term depends on the column phase ratio. Hence, a correction should be applied by multiplying the entropy term with the phase ratio. Moreover, for some compounds it is observed experimentally that the enthalpy term can depend on the phase ratio as well [23].

If the adjusted retention times of the *n*-alkanes on any capillary column, containing the given stationary phase, are known, no additional measurements are needed to calculate entropy and enthalpy terms for any arbitrary component. The only additional information needed is the solute's Kováts index at two temperatures. This means that entropy and enthalpy terms can be calculated directly for numerous components without performing any additional measurements.

In the next sections it will be shown how these data can be used to predict temperature-programmed retention times and peak widths.

2.2. Prediction of retention times

In capillary GC the basic equation of the retention time t_R of a solute is given by:

$$t_R = t_M(1 + k) = \frac{L}{\bar{u}}(1 + k) \quad (4)$$

where t_M is the column dead time, L equals the column length and $\bar{u}$ is the average linear carrier gas velocity.

In isothermal GC, the retention time can be calculated in a straightforward manner from Eqs. 3 and 4, when t_M, β, the entropy term and the enthalpy term are known. When temperature programming is applied, however, the velocity of the solute changes continuously, since both the gas velocity and the retention factor are temperature dependent. Therefore, in the temperature-programmed mode, the retention time

must be calculated by applying a numerical method. In short, the solute's chromatographic process is modelled in segments corresponding to very small time intervals Δt. If the time intervals are chosen sufficiently small, both the retention factor and the carrier gas velocity can be assumed constant within one interval. If, further, the actual temperature in a given segment is known (which is the case when the applied temperature program is known), the distance ΔL_x the solute travels in the time interval Δt can be calculated from:

$$\Delta L_x = \frac{\Delta t u_x}{1 + k_x} \tag{5}$$

where the subscript x indicates that the values of these parameters pertain to the conditions in the time interval under consideration. To calculate k_x Eq. 3 can be applied, since the temperature in the segment is known. To calculate u_x, however, one has to realize that the carrier gas velocity varies both with temperature and pressure (or location). Due to the temperature increase during the run, the carrier gas viscosity increases, which results in a decrease of the average mobile phase velocity. The pressure dependence is reflected by the compressibility of the mobile phase. Therefore a correction for both quantities has to be applied in every time interval. The requirement of temperature correction is fulfilled when in a given segment the following adjustment is applied (for constant column inlet pressure):

$$u_x = u_o \frac{\eta_0}{\eta_x} \tag{6}$$

where η_0 is the carrier gas viscosity at the initial column temperature and η_x is the carrier gas viscosity in the xth time interval. In this paper, carrier gas viscosities are calculated according to Hawkes [24]. In Eq. 6 u_o equals the linear carrier gas velocity at the column outlet, which is related to the experimentally more readily available average linear gas velocity $\bar{u}$ via:

$$u_o = \frac{\bar{u}}{j} = \frac{L}{t_M} j \tag{7}$$

where j is the carrier gas compressibility correction factor according to James and Martin [25]. Defining $P = p_i/p_o$ as the ratio of column inlet over outlet pressure, this factor is given by:

$$j = \frac{3(P^2 - 1)}{2(P^3 - 1)} \tag{8}$$

Apart from the viscosity dependence of the velocity, the mobile phase compressibility has to be taken into account. Therefore, a pressure correction has to be applied to every segment during the calculations. The pressure p_x at any position z in the column can be calculated from:

$$p_x = \sqrt{P^2 - \frac{z}{L}(P^2 - 1)} \tag{9}$$

The pressure and temperature-corrected velocity in the xth segment, u_x, can now be obtained from:

$$u_x = \frac{u_o}{p_x} \frac{\eta_0}{\eta_x} \tag{10}$$

The total distance a solute travelled can be calculated by summation of the distances travelled in the individual time segments. Upon elution, this sum equals the column length:

$$\sum_{x=1}^{n} \frac{\Delta t u_x}{1 + k_x} = L \tag{11}$$

Finally, the retention time is governed by keeping track of the number of time intervals the analyte needs to pass through the column. Summation yields the retention time:

$$\sum_{x=1}^{n} \Delta t = t_R \tag{12}$$

2.3. Prediction of peak widths

In the literature only a few models for the estimation of peak widths in temperature-programmed GC have been published. Most of these methods are based on a less sound theoretical basis. Here a numerical approach for the calculation of temperature-programmed peak widths is developed, starting from basic chromatographic theory. As before, the chromatographic process of the analyte is divided into very short time intervals (segments). Within a

segment again all relevant properties are assumed to be constant.

In this respect it is important to realize that equal time segments must be chosen for the calculation instead of dividing the column into segments of equal length. This can be explained as follows. In Fig. 1 graphs are presented of the retention factor of several *n*-alkanes at different temperatures. The retention factors can be obtained by using Eq. 3. From the figure it can be seen that at low temperatures the retention factors of the *n*-alkanes with high carbon number are extremely high. At the low initial column temperature under temperature-programmed conditions these components are almost completely cold-trapped. For numerical calculations, the column could, in principle, also be divided into segments of equal length. Due to the long residence times of later-eluting components in a segment, however, the temperature within one segment will change before the solute moves to the next segment. This means that the assumption of equal conditions within one segment no longer applies. This, in turn, implies that erroneous results will be obtained when calculating retention times or peak widths. Only if the length of the segments is chosen infinitesimal, correct results can be expected. This would, however, lead to unacceptably long calculation times and probably to gross computer rounding errors. Hence, the better approach is dividing the chromatographic process into intervals of equal time.

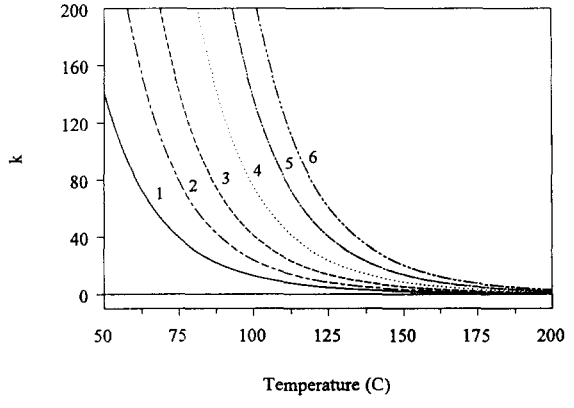

Fig. 1. Plot of k versus temperature of several *n*-alkanes; $\beta = 153$. Lines: 1 = *n*-C_{13}; 2 = *n*-C_{14}; 3 = *n*-C_{15}; 4 = *n*-C_{16}; 5 = *n*-C_{17}; 6 = *n*-C_{18}.

Under isothermal conditions, the chromatographic band broadening (in time units), σ_t^2, can be obtained from:

$$\sigma_t^2 = \frac{t_R^2}{N} = \frac{Ht_R^2}{L} = \frac{Ht_M^2(1+k)^2}{L} = \frac{HL(1+k)^2}{\bar{u}^2} \quad (13)$$

where N and H are the column plate number and plate height, respectively. Since the numerical process is performed by using segments of equal time, this equation must be converted to length units. For a given segment this can be realized by applying the following correction:

$$\sigma_{L,x}^2 = \frac{\sigma_{t,x}^2 u_x^2}{(1+k_x)^2} \quad (14)$$

where $\sigma_{L,x}^2$ is the increment in the peak variance in length units in the xth time segment. Analogously, $\sigma_{t,x}^2$ is the increment in the peak variance in time units. Calculation of peak variances rather then peak standard deviations enables the application of the rule of additivity of variances. Combining Eq. 14 with Eqs. 4 and 13 leads to:

$$\sigma_{L,x}^2 = H_x \Delta L \quad (15)$$

where H_x is the local plate height. For columns with a coating efficiency of 100%, H_x equals $H_{x,th}$, the minimal theoretically attainable plate height given by the well-known Golay equation for open tubular columns:

$$H_{x,th} = \frac{2D_{G,x}}{u_x} + \frac{f(k_x)d_c^2 u_x}{D_{G,x}} + \frac{2k_x d_f^2 u_x}{3(1+k_x)^2 D_{L,x}} \quad (16)$$

where d_c and d_f are the column inner diameter and stationary phase film thickness, respectively. $D_{G,x}$ is the binary diffusion coefficient of the solute in the mobile phase in the xth segment. Throughout this paper diffusion coefficients will be calculated according to the method developed by Fuller et al. [26]. For this calculation the molecular formula of the solute must be known.

$D_{L,x}$ is the diffusion coefficient in the stationary phase. The value of this parameter can be estimated using the approximation:

$$D_{L,x} = \frac{D_{G,x}}{5 \times 10^4} \tag{17}$$

The function $f(k_x)$ is given by:

$$f(k_x) = \frac{1 + 6k_x + 11k_x^2}{96(1 + k_x)^2} \tag{18}$$

The value for k_x can be calculated by applying Eq. 3; u_x is governed by Eq. 10. Since not every column generates the maximal theoretically attainable plate number, a correction for the column coating efficiency, CE, is applied to every segment and H_x is given by:

$$H_x = H_{x,\mathrm{th}}/CE \tag{19}$$

The mobile phase compressibility again has to be taken into account. This requirement is fulfilled by applying a pressure correction to the actual sum of the local peak variances. In this way expansion of the solute band due to the pressure decrease along the column is taken into account. The summation which yields the actual peak variance during the process is then given by:

$$\sum_{x=1}^{n} \sigma_{L,x}^2 = \left(\sum_{x=1}^{n-1} \sigma_{L,x}^2 \right) \frac{p_{x-1}^2}{p_x^2} + H_x \Delta L \tag{20}$$

p_x can be obtained from Eq. 9.

The residence time of the component can be calculated by the methods described in the previous section. Upon elution, the summation of Eq. 20 yields the band width in length units. Converting this to time units finally yields the chromatographic band broadening:

$$\sigma_t = \sqrt{\frac{\left(\sum_{x=1}^{n} \sigma_{L,x}^2 \right)(1 + k_n)^2}{u_n^2}} \tag{21}$$

where k_n and u_n are the retention factor and the mobile phase velocity in the last segment, respectively.

From σ_t, the peak width at half height w_h, or the peak width at the base w_b, can be obtained from the well-known relationships $w_h = 2.354\sigma_t$ and $w_b = 4\sigma_t$, respectively.

2.4. Calculation of inlet pressure from the column dead time

The most attractive feature of the approach presented above is that once the thermodynamic values of the solutes are known, no additional experimental measurements are needed to predict retention times and peak widths on any other column containing the same stationary phase.

To assure reliable predictions, however, the column dead time must be known accurately. In principle it is possible to calculate this quantity from the known column inlet pressure by using the Poiseuille equation. To maximize the accuracy of the predicted retention data, however, we chose in this work for actual measurement of the column dead time. This quantity was then used to calculate the column inlet pressure p_i.

Using the Poiseuille equation, the column outlet velocity, u_o, can be obtained (for ambient outlet pressure) from:

$$u_o = \frac{d_c^2(p_i^2 - 1)}{64\eta L} \tag{22}$$

Further, u_o is related to the average linear velocity $\bar{u}$ by the gas compressibility factor j:

$$\bar{u} = u_o j = \frac{3d_c^2(p_i^2 - 1)^2}{128\eta L(p_i^3 - 1)} \tag{23}$$

Also, $\bar{u}$ can be calculated using the observed column dead time:

$$\bar{u} = L/t_M \tag{24}$$

Once the average linear velocity is known, p_i can be calculated from Eq. 23 by using an iterative method. Here we use the bisection method [27], which requires two initial estimates of p_i bracketing the root.

The method of t_M determination through methane injections is chosen deliberately since this method is very simple and straightforward. Care should be taken, however, when this ap-

proach is applied to columns with a low phase ratio (high retention power). In those situations, methane can show significant retention, leading to erroneous (too high) t_M values. In those cases (or in cases of detector incompatibility, e.g. when ECD detection is applied), other methods of t_M determination can be employed [28,29]. Those methods can, however, be more tedious and/or time-consuming.

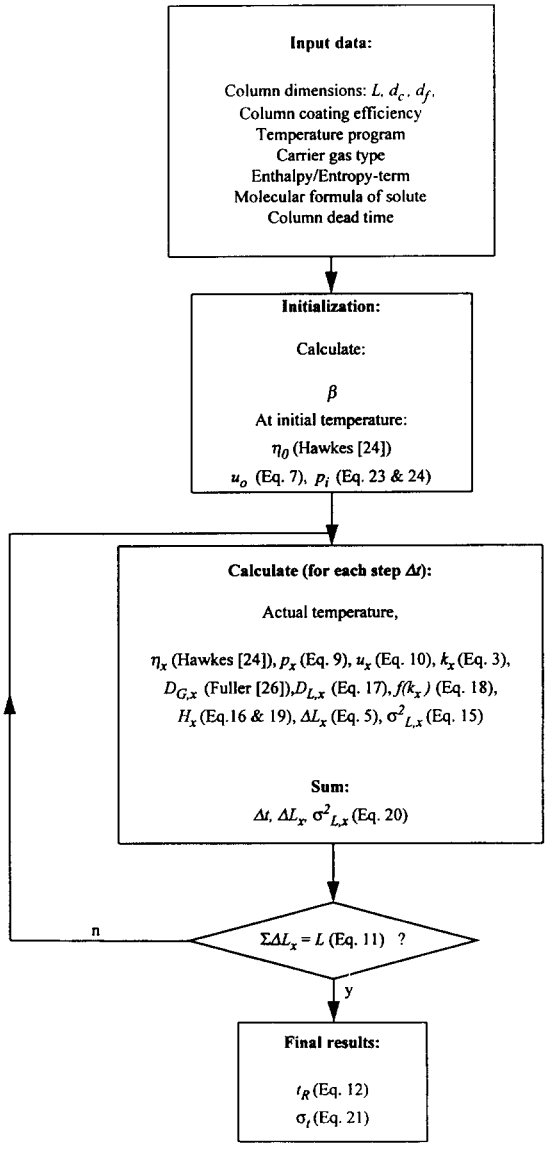

Fig. 2. Algorithm for the prediction of retention times and peak standard deviations of a given solute.

The final algorithm to predict retention times and peak standard deviations of the solutes of interest is presented in Fig. 2.

3. Experimental

3.1. Instrumentation

Gas chromatography was performed on an HP 5890 gas chromatograph equipped with a split–splitless injector and a flame-ionization detector (FID) (Hewlett-Packard, Wilmington, DE, USA). Two columns were used in this study: (A) 25 m × 0.32 mm I.D., film thickness 0.52 μm ($\beta = 153$); (B) 25 m × 0.32 mm I.D., film thickness 0.17 μm ($\beta = 470$), both coated with 100% methyl silicone, HP-1, (Hewlett-Packard). The coating efficiency of both columns was assumed to be 90%. Injections were performed in the split mode (split ratio 1:100) to minimize injection band broadening. The instrument was operated in the constant pressure mode. For the calculations it was assumed that the column outlet pressure equals 100 kPa (abs.). Carrier gas (helium) pressure was adjusted to the optimal column inlet pressure using the approach presented by Leclercq and Cramers [30]. Both injector and detector temperature were held constant at 300°C during the experimental work. The make-up gas flow-rate (nitrogen) was maintained at 30 ml min^{-1}. Methane was used as the column dead time marker. An Omega data system (Perkin-Elmer, Norwalk, CT, USA) was used for data acquisition and processing. Retention times were extracted from the data system's report. Peak widths were determined directly from the observed chromatogram. All computations were carried out on a 486-DX2/66 MHz personal computer. Software was written in Turbo Pascal 6.0 (Borland, USA). Data entry is arranged through filed input.

3.2. Test mixture and *n*-alkane solution

To determine the applicability of the procedures presented above, a test mixture was compiled, containing eleven components of different

functionality. *p*-Chlorotoluene, *sec.*-butyl-benzene, diphenyl ether, anthracene, pyrene and hexadecene were purchased from Janssen Chimica (Geel, Belgium). Methyl esters of myristic acid, palmitic acid and oleic acid were obtained from Polyscience (Niles, IL, USA). Hexachlorobenzene was purchased from Merck (Darmstadt, Germany). 1-Chlorotetradecane was obtained from Humphrey Wilkinson (North Haven, CT, USA).

For the determination of the entropy and enthalpy terms of the test components, a mixture was prepared, containing the *n*-alkanes in the range *n*-C_9 through *n*-C_{23}. The purity of all analytes was at least 98%. The solvent used to prepare both mixtures was analytical grade *n*-hexane (Merck).

Kováts retention indices of the test components were obtained from the Sadtler retention index library [21].

4. Results and discussion

The determination of the entropy and enthalpy terms of the test components was performed on column A. For this purpose the *n*-alkane mixture was analyzed under isothermal conditions at the temperatures corresponding to the temperatures at which the retention indices are listed [21]. Using the approach described in Section 2.1, entropy and enthalpy terms were calculated. The results of this calculation are presented in Table 1. The entropy and enthalpy terms obtained this way were now used for the prediction of retention times and peak widths applying the approach presented in the Theory section. To assure reliable predictions of these parameters, a careful selection of the magnitude of the stepwidth Δt is extremely important. Too high values of Δt can result in inaccurate predictions. Decreasing Δt will most probably increase the accuracy, but only at the expense of extremely long calculation times. In practice a compromise has to be made. To get an impression of the magnitude of the optimal value of Δt, predictions of retention time and peak standard deviation were performed for naphthalene under temperature-programmed conditions. A series of predictions was carried out with decreasing values of Δt. In Fig. 3A the percentage difference of subsequent predictions of the retention time of naphthalene versus the stepwidth Δt is presented. In Fig. 3B this is repeated for the prediction of the peak standard deviation. From the figures it can be observed that, according to expectations, the accuracy improves with decreasing stepwidth Δt. Moreover, it can be seen that both figures are very similar. In practice, calculation accuracies of 0.1% or less are acceptable. This demand is fulfilled, for the prediction of both retention times and peak standard deviations, when Δt is selected at 1000 ms (see Fig. 3A,B). For all predictions presented in this paper this value of Δt was used to perform the corresponding calculations. This resulted in calculation times for the prediction of both retention time and peak standard deviation for a given solute in the range of 10 s to 1 min, depending on the residence time of the solute in the column. Obviously, a higher residence time leads to an increased calculation time.

Using the entropy and enthalpy data from Table 1, the retention times and peak standard deviations of the solutes in the test mixture are calculated under different isothermal conditions on column A. The data from these calculations are compared with experimentally observed data

Table 1
Entropy and enthalpy terms of the test solutes determined on column A

Compound	Entropy term a/β ($\times 10^{-7}$)	Enthalpy term $\Delta H/R$ (K)
p-Chlorotoluene	83.0	4558
sec.-Butylbenzene	53.3	4861
Diphenylether	48.5	5678
1-Hexadecene	11.5	6696
1-Chlorotetradecane	39.8	6189
Myristic acid, methyl ester	18.0	6632
Hexachlorobenzene	84.7	5952
Anthracene	84.1	6066
Palmitic acid, methyl ester	8.0	7360
Oleic acid, methyl ester	6.3	7751
Pyrene	51.3	6766

Kováts indices were obtained from Ref. [21].

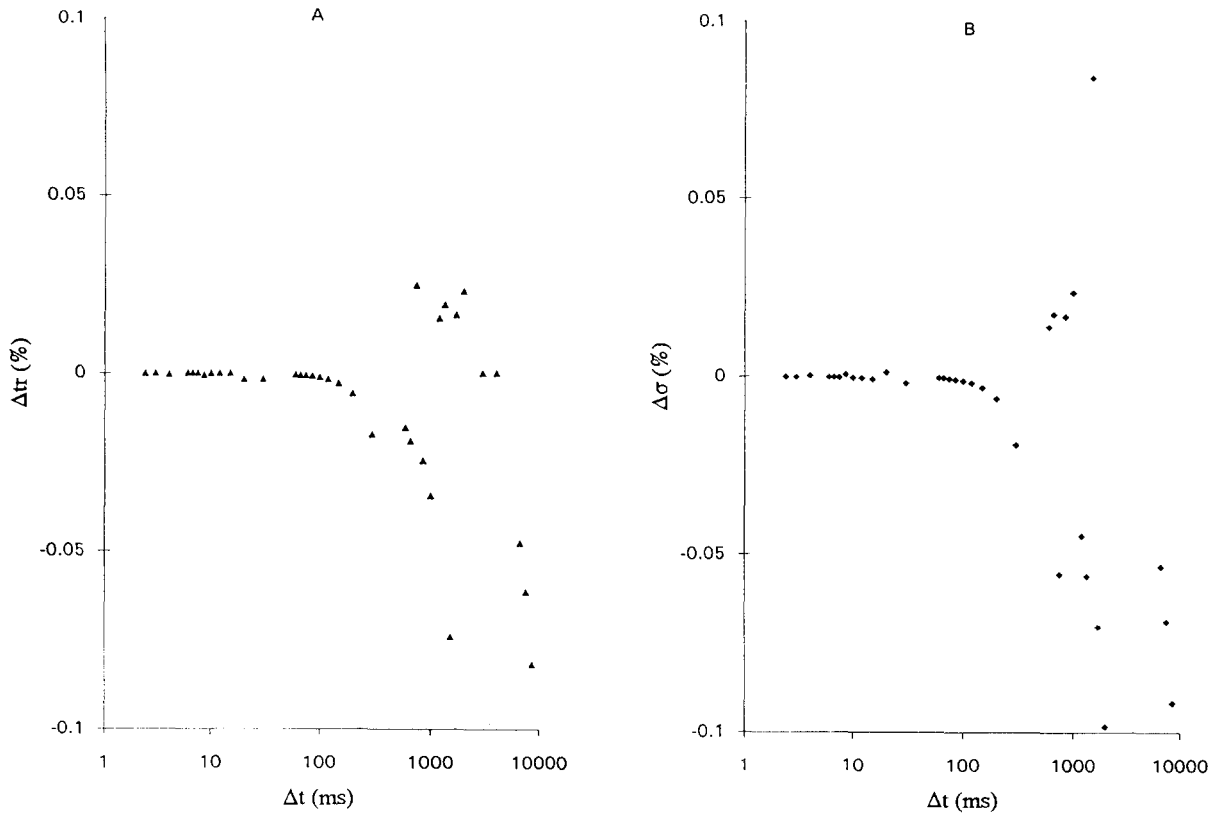

Fig. 3. Percentage difference for subsequent predictions versus stepwidth Δt. Component: anthracene. (A) t_R (28.928 min); (B) σ ($28.26 \cdot 10^{-3}$ min). Temperature program: 50°C (1 min) → 5°C min^{-1} → 300°C. Column A. t_m (50°C) = 1.081 min. For entropy and enthalpy terms refer to Table 1.

in Tables 2 (retention times) and 3 (standard deviations). From the tables a number of interesting conclusions can be drawn. Firstly, for most components a good agreement between experimental and predicted data is observed. Secondly, for certain components (e.g. diphenyl ether at 100°C or hexachlorobenzene at 150°C) large differences are sometimes observed between predicted and experimental data. A possible explanation for this behaviour can be found in the determination of the entropy and enthalpy terms of those solutes. The retention indices, used for those determinations, for example for diphenyl ether, are listed to be 140 and 220°C [21]. This means that when retention times are predicted at temperatures outside this range, extrapolation takes place in the $\ln k$ versus $1/T$ plot. This leads to larger prediction errors as compared to the situation where the prediction takes place within the temperature range (e.g. the data of diphenyl ether at 200°C show good agreement). The extrapolation errors observed are most likely due to non-linearity of the $\ln k$ versus $1/T$ plot, as observed by, for example, Kozloski [31] and Hawkes [32]. An other source of errors can be a slight deviation of the listed retention indices from the true values.

In Table 3 a comparison of the peak standard deviations is presented. From this table it is clear that the accuracy of prediction is acceptable. The prediction of peak standard deviations is slightly worse than the accuracy of the retention time predictions from Table 2. In general, the magnitude of the errors follows the trend observed for the retention time predictions. This is not unexpected since both calculation procedures are

Table 2
Comparison of experimental, $t_{R,e}$, and calculated, $t_{R,c}$, retention times (min) for different isothermal analyses of the test mixture on column A. $\Delta(\%) = 100(t_{R,e} - t_{R,c})/t_{R,c}$

Compound	50°C			100°C			150°C			200°C			250°C		
	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)
p-Chlorotoluene	13.363	13.071	2.23	3.137	3.192	−1.72	1.820	1.803	0.94	1.588	1.562	1.69			
sec.-Butylbenzene	21.263	20.723	2.61	3.980	4.082	−2.50	1.983	1.963	1.02	1.635	1.599	2.25			
Diphenyl ether				27.799	24.686	12.61	5.445	5.506	−1.11	2.473	2.481	−0.32	1.872	1.851	1.12
1-Hexadecene							12.240	12.379	−1.12	3.459	3.619	−4.42	2.081	2.097	−0.76
1-Chlorotetradecane							16.687	12.861	29.75	4.177	4.032	3.60	2.265	2.289	−1.05
Myristic acid, methyl ester							17.743	16.223	9.37	4.566	4.443	2.77	2.326	2.335	−0.39
Hexachlorobenzene							20.350	15.363	32.46	4.888	4.800	1.83	2.570	2.576	−0.23
Anthracene							22.821	19.574	16.59	5.788	5.697	1.60	2.814	2.832	−0.64
Palmitic acid, methyl ester										7.963	7.717	3.19	2.985	3.009	−0.80
Oleic acid, methyl ester										13.334	12.813	4.07	3.964	4.023	−1.47
Pyrene										13.566	12.934	4.89	4.571	4.623	−1.12
Mean error (%, abs.)			2.42			5.61			11.54			2.78			0.84

t_M: 50°C: 1.081 min; 100°C: 1.193 min; 150°C: 1.292 min; 200°C: 1.386 min; 250°C: 1.480 min.

interrelated. When the prediction of the retention time shows a strong deviation, the standard deviation prediction will as well. Prediction of too low retention times leads to the prediction of too low peak standard deviations, vice versa. This is logical since at shorter residence times, reduced chromatographic band broadening is expected and, consequently, predicted.

The results presented in Tables 2 and 3 were obtained for the column that was utilized for entropy and enthalpy term determination (column A). Applying the same entropy/enthalpy

Table 3
Comparison of experimental, σ_e, and calculated, σ_c, peak standard deviations (10^{-3} min) for different isothermal analyses of the test mixture on column A. $\Delta(\%) = 100(\sigma_e - \sigma_c)/\sigma_c$

Compound	50°C			100°C			150°C			200°C			250°C		
	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)
p-Chlorotoluene	47.94	48.75	−1.66	10.64	11.07	−3.88	6.84	6.21	10.14	6.96	5.79	20.19			
sec.-Butylbenzene	78.11	79.88	−2.22	13.74	14.29	−3.85	7.11	6.53	8.88	6.90	5.57	23.88			
Diphenyl ether				9.69	9.14	6.02	18.49	19.90	−7.09	8.99	9.01	−0.22	7.45	7.10	4.93
1-Hexadecene							43.66	45.37	−3.77	11.39	12.62	−9.75	7.19	7.23	−0.55
1-Chlorotetradecane							58.85	47.10	24.95	13.92	14.23	−2.18	7.96	8.07	−1.36
Myristic acid, methyl ester							61.63	59.72	3.20	15.34	15.75	−2.60	7.92	8.20	−3.41
Hexachlorobenzene							71.69	56.72	26.39	17.06	17.93	−4.85	9.44	9.99	−5.51
Anthracene							79.61	72.59	9.67	20.57	21.51	−4.37	10.41	11.13	−6.47
Palmitic acid, methyl ester										26.44	27.89	−5.20	9.66	10.64	−9.21
Oleic acid, methyl ester										46.44	46.91	−1.00	12.84	14.06	−8.68
Pyrene										46.74	49.27	−5.13	16.30	18.32	−11.03
Mean error (%, abs.)			1.94			4.58			11.76			7.22			5.68

t_M: 50°C: 1.081 min; 100°C: 1.193 min; 150°C: 1.292 min; 200°C: 1.386 min; 250°C: 1.480 min.

Table 4
Comparison of experimental, $t_{R,e}$, and calculated, $t_{R,c}$ retention times (min) for different isothermal analyses of the test mixture on column B. $\Delta(\%) = 100(t_{R,e} - t_{R,c})/t_{R,c}$

Compound	50°C			100°C			150°C			200°C			250°C		
	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)
p-Chlorotoluene	4.810	4.597	4.63	1.683	1.692	−0.53									
sec.-Butylbenzene	7.245	6.894	5.09	1.942	1.958	−0.82									
Diphenyl ether				9.346	8.115	15.17	2.458	2.453	0.20	1.599	1.606	−0.44			
1-Hexadecene							4.534	4.514	0.44	1.901	1.948	−2.41			
1-Chlorotetradecane							5.903	4.659	26.70	2.121	2.072	2.36			
Myristic acid, methyl ester							6.245	5.667	10.20	2.241	2.196	2.05			
Hexachlorobenzene							7.034	5.409	30.04	2.343	2.303	1.74			
Anthracene							7.835	6.672	17.43	2.623	2.572	1.98	1.767	1.763	0.23
Palmitic acid, methyl ester							16.159			3.284	3.178	3.34	1.818	1.816	0.11
Oleic acid, methyl ester							23.530			4.959	4.708	5.33	2.119	2.121	−0.09
Pyrene										5.001	4.745	5.40	2.309	2.299	0.43
Mean error (%, abs.)			4.86			5.51			11.54			2.25			0.22

t_M: 50°C: 0.996 min; 100°C: 1.094 min; 150°C: 1.189 min; 200°C: 1.277 min; 250°C: 1.358 min.

values to another column (containing the same stationary phase), a correction for differences in phase ratio should be made. To test the applicability of the method, predictions were also performed on column B (different phase ratio from column A), using the entropy and enthalpy terms determined on column A. The comparison with experimentally observed data is presented in Tables 4 (retention times) and 5 (standard deviations). From both tables it can be concluded that the observed errors are of the same magnitude as those observed on column A. This

Table 5
Comparison of experimental, σ_e, and calculated, σ_c, peak standard deviations (10^{-3} min) for different isothermal analyses of the test mixture on column B. $\Delta(\%) = 100(\sigma_e - \sigma_c)/\sigma_c$

Compound	50°C			100°C			150°C			200°C			250°C		
	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)
p-Chlorotoluene	17.27	16.02	7.80	6.47	5.03	28.63									
sec.-Butylbenzene	28.70	25.59	12.15	7.13	5.84	22.09									
Diphenyl ether				35.38	28.97	22.13	8.86	7.87	12.58	5.72	5.25	8.95			
1-Hexadecene							16.67	15.25	9.31	5.94	5.87	1.19			
1-Chlorotetradecane							21.03	15.78	33.27	6.76	6.37	6.12			
Myristic acid, methyl ester							22.62	19.58	15.53	7.19	6.79	5.89			
Hexachlorobenzene							26.13	18.75	39.36	8.15	7.73	5.43			
Anthracene							28.99	23.48	23.47	9.12	8.78	3.87	6.53	6.31	3.49
Palmitic acid, methyl ester							63.56			10.96	10.28	6.61	5.78	5.67	1.94
Oleic acid, methyl ester							91.38						6.74	6.38	5.64
Pyrene													8.45	8.29	1.93
Mean error (%, abs.)			9.98			14.28			11.76			5.44			3.25

t_M: 50°C: 0.996 min; 100°C: 1.094 min; 150°C: 1.189 min; 200°C: 1.277 min; 250°C: 1.358 min.

Table 6
Single- and multi-ramp temperature programs used for comparison of experimental and calculated retention times and peak standard deviations

Symbol	Temperature program
A	50°C → 5°C min^{-1} → 300°C
B	50°C → 10°C min^{-1} → 300°C
C	50°C → 15°C min^{-1} → 300°C
D	50°C → 20°C min^{-1} → 300°C
E	50°C → 10°C min^{-1} → 100°C (2 min) → 20°C min^{-1} → 300°C
F	50°C → 20°C min^{-1} → 100°C (2 min) → 10°C min^{-1} → 300°C
G	50°C → 10°C min^{-1} → 100°C (2 min) → 20°C min^{-1} → 200°C (2 min) → 10°C min^{-1} → 300°C
H	50°C → 20°C min^{-1} → 100°C (2 min) → 10°C min^{-1} → 200°C (2 min) → 20°C min^{-1} → 300°C

means that the entropy and enthalpy terms can easily be transferred from one column to another containing the same stationary phase but with a different phase ratio.

The numerical procedure was also evaluated for application in the (practically more important) temperature-programmed mode. Several single- and multi-ramp (either two-stage or three-stage) temperature programs, covering a broad temperature range, were arbitrarily selected (see Table 6). A comparison of experimental and predicted data (for both column A and column B) is presented in Tables 7–14. From the tables it can be concluded that the errors in retention time predictions are generally less than 4%. The errors in the predictions of the peak standard deviations are in the order of about 10%. Again, no large discrepancies between the two columns are observed. Even for the three-stage multi-ramp temperature programs (identified by the symbols G and H) a good agreement is observed between predicted and ex-

Table 7
Comparison of experimental, $t_{R,e}$, and calculated, $t_{R,c}$, retention times (min) for different single-ramp linear temperature programs of the test mixture on column A. $\Delta(\%) = 100(t_{R,e} - t_{R,c})/t_{R,c}$

Compound	Temp. prog. A			Temp. prog. B			Temp. prog. C			Temp. prog. D		
	$t_{R,e}$	$t_{R,c}$	$\Delta(\%)$	$t_{R,e}$	$t_{R,c}$	$\Delta(\%)$	$t_{R,e}$	$t_{R,c}$	$\Delta(\%)$	$t_{R,e}$	$t_{R,c}$	$\Delta(\%)$
p-Chlorotoluene	7.631	7.620	0.14	6.055	6.048	0.11	5.257	5.236	0.40	4.760	4.727	0.70
sec.-Butylbenzene	9.373	9.403	−0.32	7.069	7.081	−0.17	5.983	5.971	0.20	5.333	5.302	0.58
Diphenyl ether	20.413	20.011	2.01	13.009	12.879	1.01	10.111	10.028	0.83	8.529	8.453	0.90
1-Hexadecene	26.066	25.953	0.44	15.807	15.840	−0.21	11.965	11.996	−0.26	9.913	9.925	−0.12
1-Chlorotetradecane	27.810	26.118	6.48	16.738	16.085	4.06	12.615	12.232	3.13	10.418	10.146	2.68
Myristic acid, methyl ester	28.280	27.618	2.40	17.190	16.771	2.50	13.011	12.781	1.80	10.770	10.449	3.07
Hexachlorobenzene	28.830	27.283	5.67	17.228	16.811	2.48	12.934	12.660	2.16	10.651	10.595	0.53
Anthracene	29.807	29.930	−0.41	17.998	17.680	1.80	13.572	13.381	1.43	11.206	11.057	1.35
Palmitic acid, methyl ester	33.204	32.508	2.14	19.479	19.237	1.26	14.465	14.314	1.05	11.821	11.697	1.06
Oleic acid, methyl ester	36.392	36.100	0.81	21.265	21.090	0.83	15.687	15.846	−1.00	13.038	12.659	2.99
Pyrene	36.639	35.941	1.94	21.452	21.301	0.71	15.955	15.576	2.43	12.760	12.937	−1.37
Mean error (%, abs.)			2.07			1.38			1.34			1.40

For identifying symbols of temperature programs refer to Table 6. t_M (50°C): 1.081 min.

Table 8
Comparison of experimental, σ_e, and calculated, σ_c, peak standard deviations (10^{-3} min) for different single-ramp linear temperature programmed analyses of the test mixture on column A. $\Delta(\%) = 100(\sigma_e - \sigma_c)/\sigma_c$

Compound	Temp. prog. A			Temp. prog. B			Temp. prog. C			Temp. prog. D		
	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_c	σ_c	Δ(%)
p-Chlorotoluene	15.27	16.76	−8.89	10.71	11.34	−5.56	8.91	9.09	−1.98	7.64	7.87	−2.92
sec.-Butylbenzene	17.33	18.29	−5.25	11.29	11.77	−4.08	8.99	9.24	−2.71	7.70	7.92	−2.78
Diphenyl ether	19.77	22.91	−13.71	12.33	13.94	−11.55	10.19	10.82	−5.82	8.60	9.26	−7.13
1-Hexadecene	20.04	22.89	−12.45	12.23	13.68	−10.60	9.74	10.53	−7.50	7.94	8.97	−11.48
1-Chlorotetradecane	20.67	24.49	−15.60	12.33	14.67	−15.95	9.66	11.30	−14.51	8.80	9.61	−8.43
Myristic acid, methyl ester	22.44	23.81	−5.75	14.75	14.28	3.29	9.51	11.01	−13.62	8.28	9.38	−11.73
Hexachlorobenzene	20.36	26.02	−21.77	12.82	15.90	−19.37	11.04	12.39	−10.90	9.42	10.63	−11.38
Anthracene	23.24	26.65	−12.80	14.12	16.34	−13.59	11.39	12.76	−10.74	9.59	10.97	−12.58
Palmitic acid, methyl ester	21.48	23.97	−10.39	12.44	14.41	−13.67	9.66	11.15	−13.36	8.86	9.53	−7.03
Oleic acid, methyl ester	25.42	24.61	3.29	12.42	14.67	−15.32	10.10	11.28	−10.46	8.28	9.60	−13.75
Pyrene	20.57	28.40	−27.57	15.46	17.52	−11.76	12.07	13.74	−12.15	10.79	11.85	−8.95
Mean error (%, abs.)			12.50			11.34			9.43			8.92

For identifying symbols of temperature programs refer to Table 6. t_M (50°C): 1.081 min.

Table 9
Comparison of experimental, $t_{R,e}$, and calculated, $t_{R,c}$, retention times (min) for different single-ramp linear temperature programs of the test mixture on column B. $\Delta(\%) = 100(t_{R,e} - t_{R,c})/t_{R,c}$

Compound	Temp. prog. A			Temp. prog. B			Temp. prog. C			Temp. prog. D		
	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)
p-Chlorotoluene	4.009	3.887	3.14	3.568	3.502	1.88	3.312	3.252	1.85	3.125	3.074	1.66
sec.-Butylbenzene	5.207	5.084	2.42	4.389	4.331	1.34	3.945	3.896	1.26	3.648	3.607	1.14
Diphenyl ether	14.787	13.849	6.77	9.799	9.422	4.00	7.780	7.553	3.01	6.655	6.492	2.51
1-Hexadecene	20.469	19.761	3.58	12.651	12.428	1.79	9.682	9.572	1.15	8.085	8.015	0.87
1-Chlorotetradecane	21.967	19.482	12.76	13.498	12.406	8.80	10.268	9.610	6.85	8.537	8.074	5.73
Myristic acid, methyl ester	22.064	21.152	4.31	13.615	13.204	3.11	10.417	10.124	2.89	8.691	8.450	2.85
Hexachlorobenzene	23.154	20.259	14.29	14.029	12.902	8.74	10.617	9.989	6.29	8.796	8.386	4.89
Anthracene	23.403	21.773	7.49	14.366	13.702	4.85	10.936	10.541	3.75	9.090	8.810	3.18
Palmitic acid, methyl ester	27.376	25.980	5.37	16.195	15.563	3.46	12.087	11.772	2.68	9.916	9.696	2.27
Oleic acid, methyl ester	29.568	29.413	0.53	17.588	17.424	0.94	13.146	12.978	1.29			
Pyrene	30.631	28.450	7.67	17.885	17.158	4.24	13.241	12.895	2.68			
Mean error (%, abs.)			6.21			3.92			3.06			2.79

For identifying symbols of temperature programs refer to Table 6. t_M (50°C): 0.996 min.

Table 10
Comparison of experimental, σ_e, and calculated, σ_c, peak standard deviations (10^{-3} min) for different single-ramp linear temperature programmed analyses of the test mixture on column B. $\Delta(\%) = 100(\sigma_e - \sigma_c)/\sigma_c$

Compound	Temp. prog. A			Temp. prog. B			Temp. prog. C			Temp. prog. D		
	σ_e	σ_c	$\Delta(\%)$	σ_e	σ_c	$\Delta(\%)$	σ_e	σ_c	$\Delta(\%)$	σ_e	σ_c	$\Delta(\%)$
p-Chlorotoluene	11.13	10.41	6.92	8.74	8.11	7.77	7.38	6.88	7.27	6.48	6.11	6.06
sec.-Butylbenzene	13.57	12.66	7.19	9.25	9.05	2.21	8.01	7.35	8.98	6.74	6.38	5.64
Diphenyl ether	19.14	19.22	−0.42	11.47	11.49	−0.17	8.61	8.76	−1.71	7.66	7.40	3.51
1-Hexadecene	20.68	20.10	2.89	11.08	11.64	−4.81	8.41	8.77	−4.10	7.24	7.34	−1.36
1-Chlorotetradecane				11.33	12.36	−8.33	8.76	9.30	−5.81	6.95	7.78	−10.67
Myristic acid, methyl ester				12.42	12.05	3.07	9.39	9.09	3.30	8.15	7.62	6.96
Hexachlorobenzene	21.39	21.76	−1.70	11.08	12.89	−14.04	8.50	9.84	−13.62	7.25	8.32	−12.86
Anthracene	20.19	22.15	−8.85	11.85	13.16	−9.95	9.36	10.07	−7.05	8.24	8.53	−3.40
Palmitic acid, methyl ester	19.24	20.88	−7.85	11.85	12.14	−2.39	8.74	9.18	−4.79	7.35	7.73	−4.92
Oleic acid, methyl ester	21.87	21.75	0.55	14.34	12.53	14.45	10.36	9.42	9.98			
Pyrene	20.82	23.36	−10.87	11.94	13.97	−14.53	8.62	10.75	−19.81			
Mean error (%, abs.)			5.25			7.43			7.86			6.15

For identifying symbols of temperature programs refer to Table 6. t_M (50°C): 0.996 min.

Table 11
Comparison of experimental, $t_{R,e}$, and calculated, $t_{R,c}$, retention times (min) for different multi-ramp linear temperature programs of the test mixture on column A. $\Delta(\%) = 100(t_{R,e} - t_{R,c})/t_{R,c}$

Compound	Temp. prog. E			Temp. prog. F			Temp. prog. G			Temp. prog. H		
	$t_{R,e}$	$t_{R,c}$	$\Delta(\%)$	$t_{R,e}$	$t_{R,c}$	$\Delta(\%)$	$t_{R,e}$	$t_{R,c}$	$\Delta(\%)$	$t_{R,e}$	$t_{R,c}$	$\Delta(\%)$
p-Chlorotoluene	6.064	6.049	0.25	5.027	4.999	0.56	6.057	6.048	0.15	5.021	4.999	0.44
sec.-Butylbenzene	7.203	7.217	−0.19	6.014	6.022	−0.13	7.195	7.217	−0.30	6.008	6.022	−0.23
Diphenyl ether	12.749	12.626	0.97	12.375	12.233	1.16	12.749	12.626	0.97	12.371	12.233	1.13
1-Hexadecene	14.353	14.339	0.10	15.275	15.293	−0.12	14.616	14.636	−0.14	15.273	15.293	−0.13
1-Chlorotetradecane	14.877	14.541	2.31	16.217	15.532	4.41	15.459	14.932	3.53	16.262	15.532	4.70
Myristic acid, methyl ester	15.122	14.881	1.62	16.661	16.234	2.63	15.899	15.528	2.39	16.781	16.285	3.05
Hexachlorobenzene	15.215	14.996	1.46	16.715	16.262	2.79	15.979	15.664	2.01	16.858	16.314	3.33
Anthracene	15.665	15.483	1.18	17.480	17.143	1.97	16.763	16.503	1.58	17.849	17.409	2.53
Palmitic acid, methyl ester	16.313	16.175	0.85	18.978	18.724	1.36	18.167	17.969	1.10	19.547	19.291	1.33
Oleic acid, methyl ester	17.256	17.149	0.62	20.767	20.584	0.89	20.040	19.892	0.74	21.071	20.888	0.88
Pyrene	17.530	17.418	0.64	20.951	20.791	0.77	20.260	20.136	0.62	21.201	21.041	0.76
Mean error (%, abs.)			0.93			1.52			1.23			1.68

For identifying symbols of temperature programs refer to Table 6. t_M (50°C): 1.081 min.

Table 12
Comparison of experimental, σ_e, and calculated, σ_c, peak standard deviations (10^{-3} min) for different multi-ramp linear temperature programmed analyses of the test mixture on column A. $\Delta(\%) = 100(\sigma_e - \sigma_c)/\sigma_c$

Compound	Temp. prog. E			Temp. prog. F			Temp. prog. G			Temp. prog. H		
	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)
p-Chlorotoluene	10.69	11.44	−6.56	10.79	11.31	−4.60	10.71	11.44	−6.38	10.44	11.31	−7.69
sec.-Butylbenzene	14.02	14.77	−5.08	12.76	13.01	−1.92	13.80	14.77	−6.57	12.04	13.01	−7.46
Diphenyl ether	9.33	9.96	−6.33	13.27	14.30	−7.20	9.29	9.96	−6.73	13.16	14.30	−7.97
1-Hexadecene	8.41	9.17	−8.29	12.42	13.81	−10.07	11.56	13.17	−12.22	12.58	13.81	−8.91
1-Chlorotetradecane	8.67	9.85	−11.98	13.19	14.82	−11.00	13.48	14.78	−8.80	14.77	14.90	−0.87
Myristic acid, methyl ester	8.22	9.54	−13.84				12.41	14.79	−16.09	16.91	16.40	−3.11
Hexachlorobenzene	9.67	10.82	−10.63	12.66	16.02	−20.97	13.96	16.34	−14.57	16.26	18.17	−10.51
Anthracene	10.40	11.10	−6.31	14.47	16.43	−11.93	14.87	16.86	−11.80	17.98	21.77	−17.41
Palmitic acid, methyl ester	8.39	9.58	−12.42	12.44	14.44	−13.85	13.48	15.05	−10.43	11.07	13.65	−18.90
Oleic acid, methyl ester	8.61	9.62	−10.50	12.71	14.69	−13.48	14.37	15.15	−5.15	10.44	11.53	−9.45
Pyrene	10.78	11.88	−9.26	14.87	17.54	−15.22	16.24	17.96	−9.58	12.54	13.88	−9.65
Mean error (%, abs.)			9.20			11.02			9.84			9.27

For identifying symbols of temperature programs refer to Table 6. t_M (50°C): 1.081 min.

Table 13
Comparison of experimental, $t_{R,e}$, and calculated, $t_{R,c}$, retention times (min) for different multi-ramp linear temperature programs of the test mixture on column B. $\Delta(\%) = 100(t_{R,e} - t_{R,c})/t_{R,c}$

Compound	Temp. prog. E			Temp. prog. F			Temp. prog. G			Temp. prog. H		
	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)	$t_{R,e}$	$t_{R,c}$	Δ(%)
p-Chlorotoluene	3.571	3.502	1.97	3.124	3.074	1.63	3.574	3.502	2.06	3.125	3.074	1.66
sec.-Butylbenzene	4.388	4.331	1.32	3.650	3.608	1.16	4.393	4.331	1.43	3.651	3.608	1.19
Diphenyl ether	10.403	10.051	3.50	8.952	8.553	4.67	10.405	10.051	3.52	8.952	8.553	4.67
1-Hexadecene	12.411	12.268	1.17	12.040	11.797	2.06	12.412	12.268	1.17	12.040	11.797	2.06
1-Chlorotetradecane	12.920	12.275	5.25	12.915	11.759	9.83	12.921	12.275	5.26	12.916	11.759	9.84
Myristic acid, methyl ester	13.032	12.755	2.17	13.016	12.600	3.30	13.034	12.755	2.19	13.017	12.600	3.31
Hexachlorobenzene	13.212	12.607	4.80	13.467	12.268	9.77	13.219	12.607	4.85	13.469	12.268	9.79
Anthracene	13.477	13.101	2.87	13.790	13.098	5.28	13.507	13.102	3.09	13.792	13.098	5.30
Palmitic acid, methyl ester	14.393	14.134	1.83	15.671	15.116	3.67	14.752	14.361	2.72	15.676	15.116	3.70
Oleic acid, methyl ester				17.061	16.907	0.91	16.245	16.042	1.27	17.332	17.149	1.07
Pyrene				17.372	16.627	4.48	16.435	15.879	3.50	17.822	16.761	6.33
Mean error (%, abs.)			2.76			4.25			2.82			4.45

For identifying symbols of temperature programs refer to Table 6. t_M (50°C): 0.996 min.

Table 14
Comparison of experimental, σ_e, and calculated, σ_c, peak standard deviations (10^{-3} min) for different multi-ramp linear temperature programmed analyses of the test mixture on column B. $\Delta(\%) = 100(\sigma_e - \sigma_c)/\sigma_c$

Compound	Temp. prog. E			Temp. prog. F			Temp. prog. G			Temp. prog. H		
	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)	σ_e	σ_c	Δ(%)
p-Chlorotoluene	8.47	8.12	4.31	6.33	6.11	3.60	8.67	8.11	6.91	6.44	6.11	5.40
sec.-Butylbenzene	9.49	9.05	4.86	6.87	6.56	4.73	9.59	9.05	5.97	6.94	6.56	5.79
Diphenyl ether	9.50	10.18	−6.68	12.52	12.42	0.81	9.42	10.18	−7.47	12.17	12.42	−2.01
1-Hexadecene	7.47	8.06	−7.32	11.56	12.03	−3.91	8.07	8.06	0.12	11.62	12.03	−3.41
1-Chlorotetradecane	7.28	8.64	−15.74	11.65	12.78	−8.84	7.58	8.64	−12.27	12.04	12.78	−5.79
Myristic acid, methyl ester	8.46	8.17	3.55	12.23	12.36	−1.05	8.61	8.17	5.39	12.62	12.36	2.10
Hexachlorobenzene	7.29	9.00	−19.00	11.56	13.25	−12.75	7.79	9.00	−13.44	11.47	13.25	−13.43
Anthracene	8.39	9.02	−6.98	12.27	13.44	−8.71	9.67	9.24	4.65	12.72	13.44	−5.36
Palmitic acid, methyl ester	7.28	7.90	−7.85	11.65	12.26	−4.98	11.65	11.05	5.43	12.35	12.26	0.73
Oleic acid, methyl ester				13.38	12.60	6.19	14.73	13.23	11.34	19.15	17.09	12.05
Pyrene				12.33	14.05	−12.24	14.16	14.64	−3.28	15.84	17.43	−9.12
Mean error (%, abs.)			8.48			6.16			6.93			5.93

For identifying symbols of temperature programs refer to Table 6. t_M (50°C): 0.996 min.

perimental data. Note that the applied temperature programs contain isothermal plateaus as well, which is normally not allowed when other optimization procedures are used.

5. Conclusions

With the numerical methods derived it is possible to accurately predict retention times and peak widths in temperature-programmed GC separations (either single- or multi-ramp). Incorporation of isothermal plateaus in the program is allowed.

The errors in the prediction of retention times are below 4%. Peak width predictions can be performed with errors of about 10%.

An attractive feature of the approach is that, once the thermodynamic values of the solutes of interest are known, future optimizations can be performed without the need to perform experimental input runs. This feature makes the approach presented here very suitable for complete off-line simulation/optimization of capillary GC separations.

References

[1] G. Anders, M. Scheller, C. Schuhler and H.G. Struppe, Chromatographia, 15 (1982) 43.
[2] A.S. Said, in P. Sandra (Editor), Proceedings of the 8th International Symposium on Capillary Chromatography, Riva del Garda, Italy, Huethig, Heidelberg, 1987, p. 85.
[3] P.Y. Shrotri, A. Mokashi and D. Mukesh, J. Chromatogr., 387 (1987) 399.
[4] E.E. Akporhonor, S. Le Vent and D.R. Taylor, J. Chromatogr., 463 (1989) 271.
[5] G. Castello, P. Moretti and S. Vezzani, J. Chromatogr., 635 (1993) 103.
[6] S. Vezzani, P. Moretti and G. Castello, J. Chromatogr. A, 677 (1994) 331.
[7] N.H. Snow and H.M. McNair, J. Chromatogr. Sci., 30 (1992) 271.
[8] E.E. Akporhonor, S. Le Vent and D.R. Taylor, J. Chromatogr., 405 (1987) 67.
[9] L.H. Wright and J.F. Walling, J. Chromatogr., 540 (1991) 311.
[10] T.C. Gerbino and G. Castello, J. High Resolut. Chromatogr., 17 (1994) 597.
[11] E. Dose, Anal. Chem., 59 (1987) 2414.
[12] E. Dose, Anal. Chem., 59 (1987) 2420.
[13] D.E. Bautz, J.W. Dolan, W.D. Raddatz and L.R. Snyder, Anal. Chem., 62 (1990) 1560.
[14] E.M. Sibley, C. Eon and B.L. Karger, J. Chromatogr. Sci., 11 (1973) 309.
[15] V. Bártů and S. Wičar, Anal. Chim. Acta, 150 (1983) 245.

[16] L. Peichang, L. Bingcheng, C. Xinhua, L. Chunrong, L. Guangda and L. Haochun, J. High Resolut. Chromatogr. Chromatogr. Commun., 9 (1986) 702.
[17] M. Wernekenschnieder and P. Zinn, Chromatographia, 28 (1989) 241.
[18] T.I. Al-Bajjari, S. Le Vent and D.R. Taylor, J. Chromatogr. A, 683 (1994) 367.
[19] T.I. Al-Bajjari, S. Le Vent and D.R. Taylor, J. Chromatogr. A, 683 (1994) 377.
[20] E. Kováts, Helv. Chim. Acta, 41 (1958) 1915.
[21] The Sadtler Standard Gas Chromatography Retention Index Library, Sadtler Research Laboratories, Philadelphia, PA, USA, 1985.
[22] Y. Guan, J. Kiraly and J.A. Rijks, J. Chromatogr., 472 (1989) 129.
[23] J. Curvers, J. Rijks, C. Cramers, K. Knauss and P. Larson, J. High Resolut. Chromatogr. Chromatogr. Commun., 8 (1985) 611.
[24] S.J. Hawkes, Chromatographia, 37 (1993) 399.
[25] A.T. James and A.J.P. Martin, J. Biochem., 50 (1952) 679.
[26] E.N. Fuller, P.D. Schettler and J.C. Giddings, Ind. Eng. Chem., 58 (1966) 19.
[27] A.C. Norris, Computational Chemistry–An introduction to numerical methods, John Wiley, New York, 1981, p. 74.
[28] R.J. Smith, J.K. Haken and M.S. Wainwright, J. Chromatogr., 334 (1985) 95.
[29] G. Castello, S. Vezzani and P. Moretti, J. Chromatogr. A, 677 (1994) 95.
[30] P.A. Leclercq and C.A. Cramers, J. High Resolut. Chromatogr. Chromatogr. Commun., 8 (1985) 764.
[31] R.P. Kozloski, Chromatographia, 21 (1986) 397.
[32] S.J. Hawkes, Anal. Chem., 61 (1989) 88.