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Retention index calculation using Kováts constant model for linear temperature-programmed gas chromatography☆

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Abstract

Retention data from *n*-alkane series were obtained on polar and non-polar capillary columns under different column headpressures and heating rates. In addition to cubic spline polynomials and the equation of Wang–Sun, four models based on the extension of the Kováts equation were tested for direct interpolation of retention index. The quadratic temperature Kováts constant (QTKC) model and cubic spline functions were predictively comparable and provided the most accurate and stable results for the C_7–C_{22} alkane range. The QTKC model is simpler to apply than splines and the parameters to estimate are already known.

Keywords: Retention indices; Thermodynamic parameters

1. Introduction

The need to express gas chromatographic retention data in a standardized system has long been recognized. The translation of such data into a formalized index can serve as a basis for the identification of volatile compounds and the characterization of stationary phases. In 1958, Kováts [1] published a model to generate an isothermal retention index. The Kováts retention index (I) has received wide acceptance and is defined as:

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

where $t'_{R(z)} < t'_{R(i)} < t'_{R(z+1)}$, $t'_{R(i)}$ is the adjusted retention time of a component i, and $t'_{R(z)}$ and $t'_{R(z+1)}$ are the adjusted retention times of *n*-alkanes with z and $z+1$ carbon atoms.

Complex mixtures of volatile compounds are often preferably chromatographed using temperature programming regimes. Van den Dool and Kratz [2] first produced an equation expanding the use of the retention index to linear temperature-programmed gas chromatography (GC):

$$I = 100z + 100\frac{T_{(i)} - T_{(z)}}{T_{(z+1)} - T_{(z)}} \quad (2)$$

where $T_{(z)} < T_{(i)} < T_{(z+1)}$, $T_{(i)}$ is the retention temperature of component i, and $T_{(z)}$ and $T_{(z+1)}$ are the retention temperatures of *n*-alkanes with z and $z+1$ carbon atoms. Retention temperatures can be replaced by corresponding retention

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times. The linear dependence of retention index on temperature has, however, been considered an approximation with potential departure of considerable magnitude, especially in the retention index range near and below 1000 [3]. Several equations have since been reported to improve the prediction of retention index under non-isothermal conditions.

Estimation of temperature-programmed retention indices from isothermal retention data were initially attempted by Giddings [4], Guiochon [5], and Habgood and Harris [3]. Grant and Hollis [6] proposed a simplified theoretical thermodynamic-based model, which was subsequently modified by Curvers et al. [7] to remove some limiting assumptions:

$$\int_{T_0}^{T_R} \frac{dT}{t_m(T)\left[1+\frac{a}{\beta}\exp\left(\frac{\Delta H}{RT}\right)\right]} = r \qquad (3)$$

where T_R of a solute is evaluated as the higher limit of the definite integral, $a = \exp(\Delta S/R)$, a/β and $\Delta H/R$ are entropic and enthalpic parameters, r is the heating rate of the oven and $t_m(T)$ is the time function, usually taken as linear. Fernández-Sanchez et al. [8] found that the model generally predicted the experimental data adequately, except at higher heating rates, where discrepancies were observed.

Zenkevich [9] and Zenkevich and Ioffe [10] proposed the following relationship between retention index and retention data for n-alkanes:

$$I = at + b\log t + c = a(t + q\log t) + c \qquad (4)$$

where

$$q = \frac{(n_2 - n_1)t'_{R1} + (n_3 - n_2)t'_{R3} - (n_3 - n_1)t'_{R2}}{\log(t'^2_{R2}/t'_{R1}t'_{R3})} \qquad (5)$$

a, b, c are constants, and n_1, n_2, and n_3 are the number of carbon atoms of alkane 1, 2, and 3 (not necessarily neighboring). Eqs. 4 and 5 were then incorporated in a 'generalized retention index' for interpolation of n-alkanes with z and $z + k$ carbon atoms as follows:

$$GI_i = 100z + 100k \times \frac{(t'_{R(i)} + q\log t'_{R(i)}) - (t'_{R(z)} + q\log t'_{R(z)})}{(t'_{R(z+k)} + q\log t'_{R(z+k)}) - (t'_{R(z)} + q\log t'_{R(z)})} \qquad (6)$$

where $k \geq 1$. Wang and Sun [11] modified Eq. 6 by replacing Eq. 4 with:

$$I = a_0 + a_1\ln Y + a_2 Y^B = a_0 + a_2(q\ln Y + Y^B) \qquad (7)$$

where $q = a_1/a_2$, a_0, a_1, a_2, and B are constants, and Y represents a retention parameter such as volume or time.

Direct interpolation using curve-fitting equations has also been reported. Many of these equations were based on polynomials varying from the second [12] to the thirteenth degree [13]. The use of cubic functions [14] in computing algorithms is more widespread since higher-degree polynomials do not provide increased precision. Halang et al. [15] considered cubic spline the method of choice to calculate retention indices from temperature-programmed GC data. More accurate results were obtained with cubic spline polynomials compared to the polygon method (linear interpolation), particularly in non-linear regions.

Modeling the proportionality constant (named Kováts constant) derived from the Kováts equation at constant heating rates is another approach that has not been previously investigated. This paper shows that a quadratic temperature Kováts constant model is mathematically simple to use for linear temperature-programmed retention index interpolation and provides results comparable to cubic spline functions.

2. Experimental

2.1. Gas chromatography

Mixtures of C_7–C_{22} n-alkanes (Aldrich Chemical, Milwaukee, WI, USA) dissolved in carbon disulfide were injected (1 μl of 5000 ppm solution) in a Varian Vista 6000 gas chromatograph

(Varian Associates, Walnut Creek, CA, USA) equipped with a flame ionization detector. Chromatograms were obtained with a Varian DS-651 Series Data System. Some of the working conditions remained constant for all tests: carrier gas helium, injector temperature 225°C, detector temperature 225°C, septum purge vent 1 ml/min, split ratio 10:1. The GC oven was programmed to start at 50°C and to increase the temperature at a specified rate to 200°C. Chromatographic separation of alkane mixtures was accomplished with a Supelcowax-10 (60 m × 0.25 mm I.D., 0.25 μm film thickness; Supelco, Bellefonte, PA, USA) and an SPB-1 (30 m × 0.25 mm I.D., 0.25 μm film thickness; Supelco).

2.2. Statistical analysis

Statistical analyses were carried out with SAS software Ver. 6.07 (SAS, Cary, NC, USA). Regression analyses on isothermal data and ANOVA were performed with the GLM procedure. Rate constant models were computed with the NLIN procedure using the secant method [16]. Spline transformations of degree three were carried out with the REG procedure. The selection of spline knots was based on the minimum R^2 improvement method and cross-validation [17]. Cross-validation processes $n-1$ out of n retention data. The functions determined based on these $n-1$ observations are applied to estimate the one observation left out. This procedure is then repeated for all retention data.

3. Results and discussion

This work relied on the hypothesis that an adequate model for linear temperature-programmed retention index prediction could be derived from initial isothermal relationships. The Kováts function (Eq. 1) was used to linearize the isothermal data. Figs. 1 and 2 show logarithmically transformed isothermal curves obtained for Supelcowax-10 and SPB-1 columns held at temperatures ranging from 50°C to 200°C and for various column headpressures. The high coeffi-

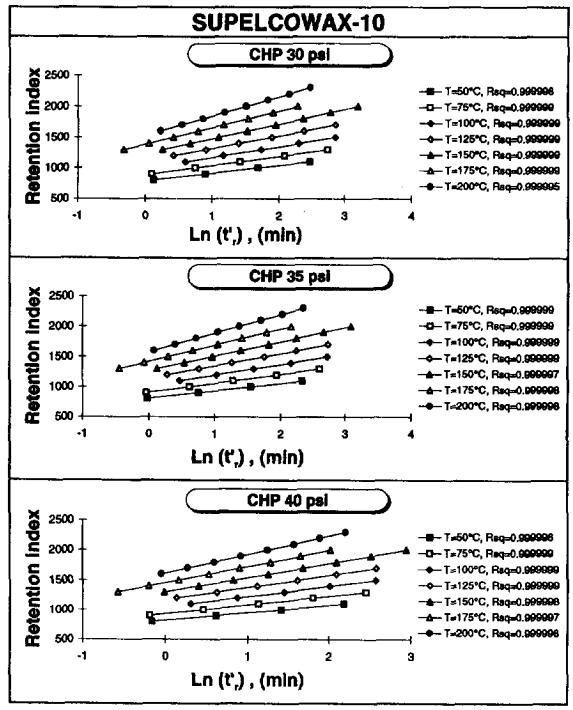

Fig. 1. Logarithmic transformation of n-alkane adjusted retention time for a Supelcowax-10 column held isothermally at different temperatures and column headpressures (CHP) (1 p.s.i. = 6894.76 Pa).

cients of determination demonstrated yet again the reliability of the Kováts equation.

The Kováts proportionality constants (or slopes) of the isothermal curves for both capillary columns were not influenced by column headpressure (Table 1). As expected, Kováts constants were significantly affected by temperature ($P \leq 0.0001$). Combined over column headpressure, Kováts constants appeared to be related in a curvilinear fashion with temperature (Fig. 3).

The following model was then tested:

$$I = a_1 + k \ln(t_R - a_2) \quad (8)$$

with the substitution forms:
logarithmic-linear (LTKC):

$$\ln k = b_0 + b_2 T, \quad k = b_1 + e^{b_2 T} \quad (8a)$$

logarithmic-inverse (ATKC):

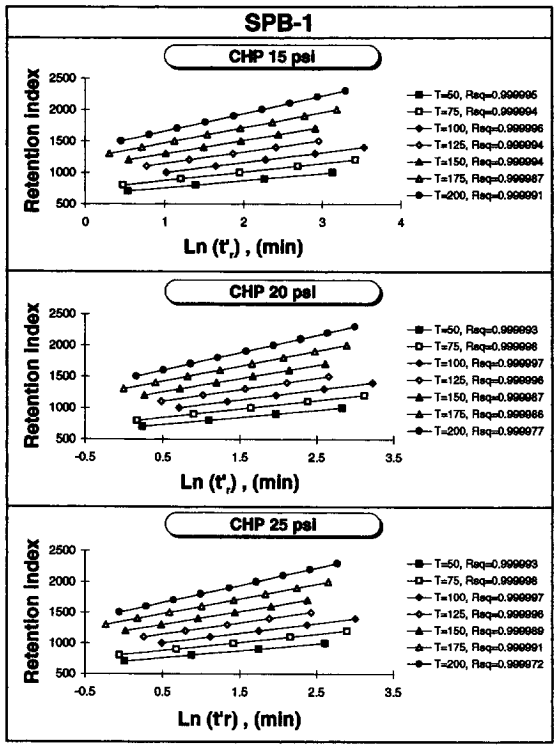

Fig. 2. Logarithmic transformation of *n*-alkane adjusted retention time for an SPB-1 column held isothermally at different temperatures and column headpressures (CHP) (1 p.s.i. = 6894.76 Pa).

$$\ln k = b_0 + b_2/T, \quad k = b_1\, e^{b_2/T} \tag{8b}$$

linear-quadratic (QTKC):

$$k = b_1 + b_2 T + b_3 T^2 \tag{8c}$$

Table 1
Analysis of variance on Kováts constant for different capillary columns

Column	Source of variation[a]	DF	*F* value[b]
Supelcowax-10	CHP	2	2.97 ns
	T	6	33013.16***
	error	12	
SPB-1	CHP	2	1.49 ns
	T	6	31071.06 ***
	error	12	

[a] CHP, column headpressure; *T*, temperature.
[b] *** Significant at 0.0001 level; ns, not significant.

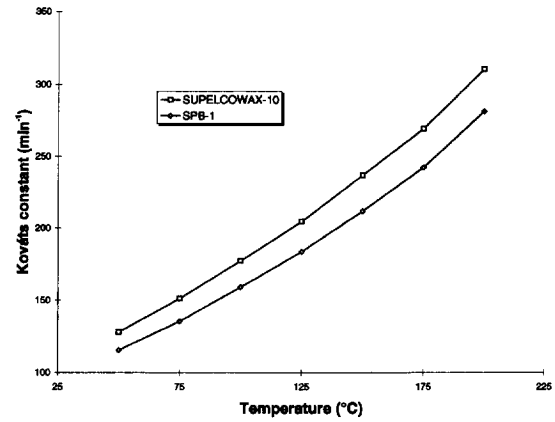

Fig. 3. Relationship between temperature and Kováts constant for Supelcowax-10 and SPB-1 columns.

linear-exponential (ETKC):

$$k = b_1 + b_2 T^{b_3} \tag{8d}$$

where k is the Kováts constant, and a_1, a_2, b_0, b_1, b_2, and b_3 are constants. Eq. 8b corresponds to the Arrhenius equation with $b_2 = -E_a/R$ where E_a is the energy of activation, R the gas constant, and b_1 the Arrhenius factor.

In addition to these equations, the model developed by Wang and Sun (Eq. 7) and the cubic spline functions were tested on retention data obtained for three column headpressures and three flow-rates on both Supelcowax-10 and SPB-1 columns (Figs. 4 and 5, respectively). As indicated in previous reports [6,8,15], the relationships were not linear. All curves had two inflections. There was an initial downward curvature followed by a second upward bend. Both inflections were more pronounced at low temperature-programming rates.

Tables 2 and 3 list the ranges within which the coefficients of each parameter varied for Supelcowax-10 and SPB-1, respectively. Values for both columns were relatively close, as curve configurations were similar. This information provides a starting template when specifying the initial parameter values for the application of the NLIN procedure for future users.

Utilization of spline transformation requires the specifications of at least two basic options, the degree and the knots or interior break points

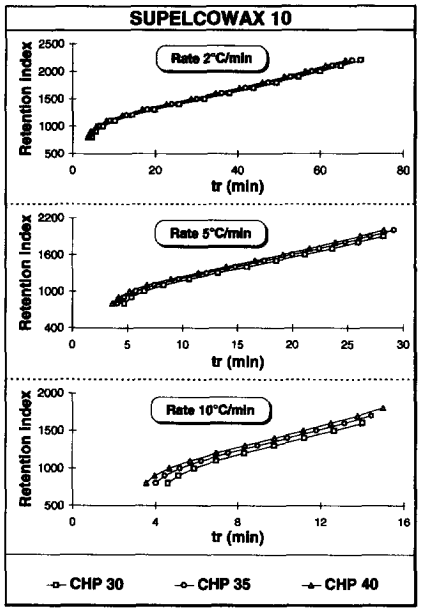

Fig. 4. Relationship between retention time and retention index for a Supelcowax-10 column programmed at different heating rates and column headpressures (CHP) (1 p.s.i. = 6894.76 Pa).

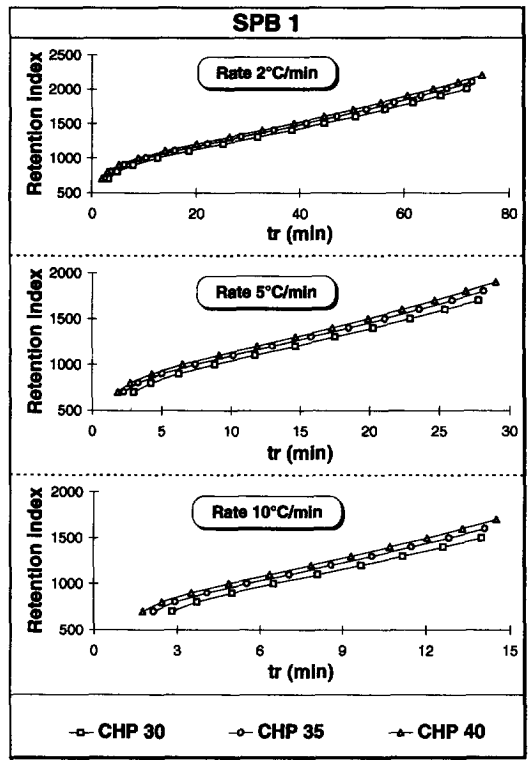

Fig. 5. Relationship between retention time and retention index for SPB-1 column programmed at different heating rates and column headpressures (CHP) (1 p.s.i. = 6894.76 Pa).

[18,19]. Increasing the degree and number of knots gives splines more freedom to bend. However, these numbers should be kept small in order to get stable results. The type of transformation used was a degree-three, piecewise, polynomial spline with continuous first and second derivatives, and discontinuous third derivative at specified knots. Tables 4 and 5 show the coefficients associated with the cubic spline polynomial parameters for Supelcowax-10 and SPB-1, respectively. These parameters were selected for their stability and statistical significance ($P \leq 0.001$). The two columns required the same knots up to $K5$. In the case of SPB-1, the need for higher knots was particularly dependent on heating rate.

The error sums of squares (SSE_c) shown in Figs. 6 and 7 have been summed over column headpressures for each retention index at different heating rates for Supelcowax-10 and SPB-1, respectively. The ATKC model showed the largest errors, followed by the LTKC model. A pattern of peaks and valleys tended to repeat itself at different heating rates for these two models, while no obvious pattern emerged from the other four models. As heating rates increased, SSE_c declined and the differences between these last four remaining models were smaller. Based on 2 and 5°C rates, the QTKC model, the ETKC model, and the spline model generated lower SSE_c than the Wang–Sun model for Supelcowax-10 while the spline and QTKC models, followed by the ETKC model, were superior to the Wang–Sun model for SPB-1. The QTKC, ETKC, and spline models generated coefficients of determination greater than 0.9999999, with error mean squares varying between 0.01 and 0.3 for the C_7–C_{22} alkane range.

Tables 6 and 7 show the error mean squares (MSE) obtained by cross-validation of the models for Supelcowax-10 and SPB-1, respectively. Cross-validation was performed on all data except the extremes in order to allow for true

Table 2
Coefficients of equation parameters in Kováts-constant based models for Supelcowax-10 column

Parameters[a]	Range	Models				
		ETKC	ATKC	LTKC	QTKC	Wang–Sun
a_1	min	$8.1201 \cdot 10^2$	$8.6920 \cdot 10^2$	$8.0250 \cdot 10^2$	$8.1725 \cdot 10^2$	$7.9811 \cdot 10^2$
	max	$9.1903 \cdot 10^2$	$9.4036 \cdot 10^2$	$9.0723 \cdot 10^2$	$9.2027 \cdot 10^2$	$9.0737 \cdot 10^2$
b_1	min	$1.0863 \cdot 10^2$	$4.3111 \cdot 10^3$	$9.8024 \cdot 10^1$	$9.4152 \cdot 10^1$	$1.4604 \cdot 10^2$
	max	$1.4647 \cdot 10^2$	$5.8551 \cdot 10^3$	$1.0582 \cdot 10^2$	$1.0513 \cdot 10^2$	$1.8895 \cdot 10^2$
b_2	min	$2.5301 \cdot 10^{-3}$	$-1.3362 \cdot 10^3$	$6.1242 \cdot 10^{-4}$	$3.6200 \cdot 10^{-1}$	$7.7200 \cdot 10^{-1}$
	max	$2.6280 \cdot 10^{-2}$	$-1.2086 \cdot 10^3$	$6.3960 \cdot 10^{-3}$	$4.7600 \cdot 10^{-1}$	7.1340
b_3	min	1.7235	na[b]	na	$4.0532 \cdot 10^{-3}$	1.6060
	max	2.1200	na	na	$4.4642 \cdot 10^{-3}$	1.8560
a_2	min	2.9368	3.1590	2.8780	$9.8000 \cdot 10^{-1}$	2.8860
	max	3.9770	4.2000	3.9740	3.9920	3.9230

[a] All parameter coefficients were significant at $P \leq 0.001$.
[b] na, not applicable.

interpolation of held-out observations. Lower MSE values were taken as an indication of higher stability and goodness of fit. The ranks were similar to the results with respect to SSE_c. In general, the QTKC, ETKC, and spline models provided a closer and more stable fit than the Wang–Sun model, which in turn drastically surpassed the LTKC and ATKC models. One advantage of Kováts-constant models such as QTKC over cubic splines is that the parameters to be determined are fixed. For situations where the series of *n*-alkanes available for retention

Table 3
Coefficients of equation parameters in Kováts-constant based models for SPB-1 column

Parameters[a]	Range	Models				
		ETKC	ATKC	LTKC	QTKC	Wang–Sun
a_1	min	$6.3838 \cdot 10^2$	$7.1682 \cdot 10^2$	$6.3132 \cdot 10^2$	$6.4807 \cdot 10^2$	$6.1493 \cdot 10^2$
	max	$7.3892 \cdot 10^2$	$7.7455 \cdot 10^2$	$7.0144 \cdot 10^2$	$7.4501 \cdot 10^2$	$7.2409 \cdot 10^2$
b_1	min	$1.0582 \cdot 10^2$	$4.4907 \cdot 10^3$	$1.0188 \cdot 10^2$	$8.2829 \cdot 10^1$	$1.4178 \cdot 10^2$
	max	$1.0925 \cdot 10^2$	$5.8952 \cdot 10^3$	$1.1652 \cdot 10^2$	$9.2066 \cdot 10^1$	$1.5335 \cdot 10^2$
b_2	min	$2.6552 \cdot 10^{-2}$	$-1.3181 \cdot 10^3$	$6.0122 \cdot 10^{-3}$	$4.5520 \cdot 10^{-1}$	$6.3000 \cdot 10^{-1}$
	max	$4.4601 \cdot 10^{-2}$	$-1.2628 \cdot 10^3$	$6.2130 \cdot 10^{-3}$	$6.8890 \cdot 10^{-1}$	6.7730
b_3	min	1.6453	na[b]	na	$3.6488 \cdot 10^{-3}$	1.6540
	max	1.7060	na	na	$3.9965 \cdot 10^{-3}$	1.7320
a_2	min	$9.3964 \cdot 10^{-1}$	1.2214	$6.7145 \cdot 10^{-1}$	$9.9924 \cdot 10^{-1}$	$8.0800 \cdot 10^{-1}$
	max	1.7485	2.3608	1.5903	1.7869	1.6750

[a] All parameter coefficients were significant at $P \leq 0.001$.
[b] na, not applicable.

Table 4
Coefficients of equation parameters in degree-three spline functions for Supelcowax-10 column

CHP (p.s.i.)	Rate (°C/min)	Parameters[a,b]						
		Intercept	Q	C	$K1$	$K3$	$K5$	$K8$
30	2	$1.0004 \cdot 10^{2}$	$6.4931 \cdot 10^{1}$	-7.0846	$1.1278 \cdot 10^{1}$	-4.0638	$-1.2370 \cdot 10^{-1}$	$-5.2460 \cdot 10^{-3}$
	5	$-2.5979 \cdot 10^{2}$	$1.0389 \cdot 10^{2}$	$-1.1878 \cdot 10^{1}$	$2.2498 \cdot 10^{1}$	$-1.0166 \cdot 10^{1}$	$-4.1930 \cdot 10^{-1}$	$-3.0497 \cdot 10^{-2}$
	10	$-5.9620 \cdot 10^{2}$	$1.4353 \cdot 10^{2}$	$-1.6927 \cdot 10^{1}$	$3.7180 \cdot 10^{1}$	$-1.8325 \cdot 10^{1}$	-1.7885	na[c]
35	2	$1.1437 \cdot 10^{2}$	$8.5322 \cdot 10^{1}$	$-1.0773 \cdot 10^{1}$	$1.6967 \cdot 10^{1}$	-6.0204	$-1.6679 \cdot 10^{-1}$	$-6.2570 \cdot 10^{-3}$
	5	$-1.9553 \cdot 10^{2}$	$1.2868 \cdot 10^{2}$	$-1.6855 \cdot 10^{1}$	$3.0990 \cdot 10^{1}$	$-1.3592 \cdot 10^{1}$	$-4.9986 \cdot 10^{-1}$	$-4.0016 \cdot 10^{-2}$
	10	$-6.7963 \cdot 10^{2}$	$2.0311 \cdot 10^{2}$	$-2.7811 \cdot 10^{1}$	$6.1919 \cdot 10^{1}$	$-3.2232 \cdot 10^{1}$	-1.6336	$-1.7456 \cdot 10^{-1}$
40	2	$7.6563 \cdot 10^{1}$	$1.1241 \cdot 10^{2}$	$-1.5913 \cdot 10^{1}$	$2.5327 \cdot 10^{1}$	-9.2051	$-2.0102 \cdot 10^{-1}$	$-7.4980 \cdot 10^{-3}$
	5	$-6.3934 \cdot 10^{1}$	$1.4155 \cdot 10^{2}$	$-2.0723 \cdot 10^{1}$	$3.6172 \cdot 10^{1}$	$-1.4749 \cdot 10^{1}$	$-6.5610 \cdot 10^{-1}$	$-3.8591 \cdot 10^{-2}$
	10	$-5.6933 \cdot 10^{2}$	$2.3711 \cdot 10^{2}$	$-3.6359 \cdot 10^{1}$	$7.7820 \cdot 10^{1}$	$-3.9212 \cdot 10^{1}$	-2.0328	$-1.8551 \cdot 10^{-1}$

[a] All parameter coefficients were significant at $P \leq 0.001$.
[b] Q = quadratic; C = cubic; $K1$–$K8$ = knot number.
[c] na, not applicable.
1 p.s.i. = 6894.76 Pa.

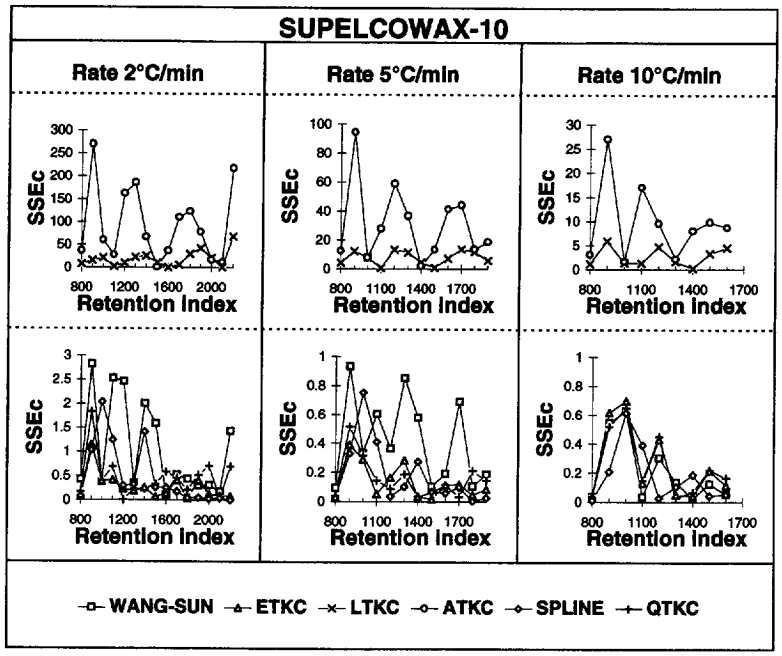

Fig. 6. Error sums of squares across column headpressures (SSE_c) of retention index prediction models for a Supelcowax-10 column programmed at different heating rates.

Table 5
Coefficients of equation parameters in degree-three spline functions for SPB-1 column

CHP (p.s.i.)	Rate (°C/min)	Parameters[a,b]							
		Intercept	Q	C	$K1$	$K3$	$K5$	$K7$	$K9$
15	2	$5.0554 \cdot 10^{2}$	$3.3893 \cdot 10^{1}$	−4.6154	5.2811	$-6.4507 \cdot 10^{-1}$	$-1.8386 \cdot 10^{-2}$	$-1.2330 \cdot 10^{-3}$	$-6.7400 \cdot 10^{-4}$
	5	$4.5458 \cdot 10^{2}$	$4.8637 \cdot 10^{1}$	−7.1627	8.6742	−1.4242	$-7.1400 \cdot 10^{-2}$	$-9.8530 \cdot 10^{-3}$	na[c]
	10	$3.7540 \cdot 10^{2}$	$7.4278 \cdot 10^{1}$	$-1.1937 \cdot 10^{1}$	$1.5711 \cdot 10^{1}$	−3.4316	$-2.8229 \cdot 10^{-1}$	na	na
20	2	$5.1486 \cdot 10^{2}$	$5.6678 \cdot 10^{1}$	$-1.0195 \cdot 10^{1}$	$1.1542 \cdot 10^{1}$	−1.3125	$-3.1648 \cdot 10^{-2}$	$-1.9630 \cdot 10^{-3}$	$-8.8500 \cdot 10^{-4}$
	5	$4.7469 \cdot 10^{2}$	$7.6976 \cdot 10^{1}$	$-1.4813 \cdot 10^{1}$	$1.7540 \cdot 10^{1}$	−2.5977	$-1.0951 \cdot 10^{-1}$	$-1.2377 \cdot 10^{-2}$	na
	10	$4.1712 \cdot 10^{2}$	$1.0921 \cdot 10^{2}$	$-2.2612 \cdot 10^{1}$	$2.8495 \cdot 10^{1}$	−5.4110	$-4.0615 \cdot 10^{-1}$	na	na
25	2	$5.1926 \cdot 10^{2}$	$8.4681 \cdot 10^{1}$	$-1.8815 \cdot 10^{1}$	$2.1184 \cdot 10^{1}$	−2.3176	$-4.7119 \cdot 10^{-2}$	$-3.1960 \cdot 10^{-3}$	$-8.5100 \cdot 10^{-4}$
	5	$4.8725 \cdot 10^{2}$	$1.0945 \cdot 10^{2}$	$-2.5750 \cdot 10^{1}$	$3.0068 \cdot 10^{1}$	−4.1436	$-1.4675 \cdot 10^{-1}$	$-2.0198 \cdot 10^{-2}$	na
	10	$4.8340 \cdot 10^{2}$	$1.5112 \cdot 10^{2}$	$-3.8141 \cdot 10^{1}$	$4.6987 \cdot 10^{1}$	−8.2708	$-4.7125 \cdot 10^{-1}$	$-6.0027 \cdot 10^{-2}$	na

[a] All parameter coefficients were significant at $P \leq 0.001$.
[b] Q = quadratic; C = cubic; $K1$–$K8$ = knot number.
[c] na, not applicable.
1 p.s.i. = 6894.76 Pa.

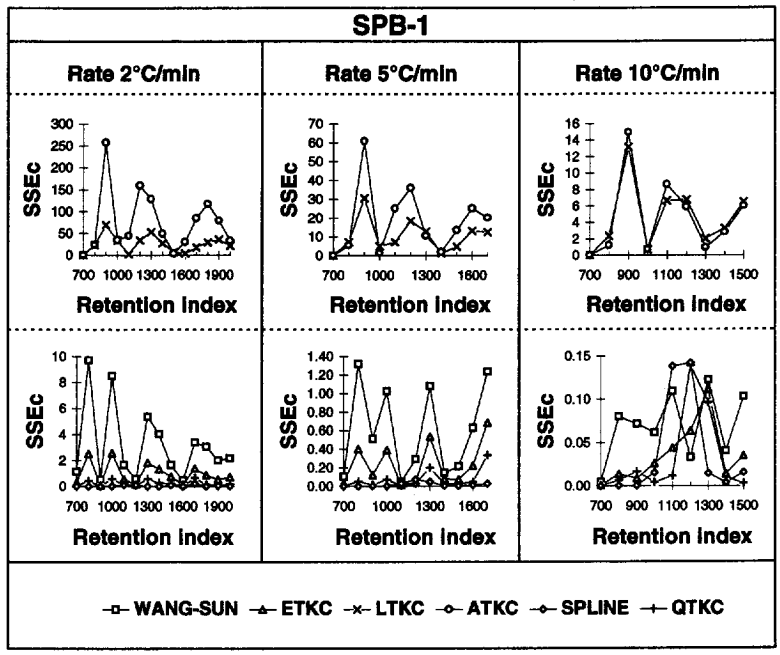

Fig. 7. Error sums of squares across column headpressures (SSE_c) of retention index prediction models for an SPB-1 column programmed at different heating rates.

Table 6
Comparison of temperature-programmed retention index prediction models for Supelcowax-10 column based on cross-validated error mean squares

CHP (p.s.i.)	Rate (°C/min)	Models					
		ETKC	ATKC	LTKC	QTKC	Spline	Wang–Sun
30	2	$3.2400 \cdot 10^{-1}$	$6.4137 \cdot 10^{1}$	8.1845	$7.3831 \cdot 10^{-1}$	2.2131	$4.8400 \cdot 10^{-1}$
	5	$7.8871 \cdot 10^{-2}$	$1.9282 \cdot 10^{1}$	3.7975	$2.7471 \cdot 10^{-2}$	$3.0280 \cdot 10^{-1}$	$6.0703 \cdot 10^{-1}$
	10	2.1580	$1.5490 \cdot 10^{1}$	1.9260	2.5372	4.1700	1.7000
35	2	$2.3196 \cdot 10^{-1}$	$6.0964 \cdot 10^{1}$	8.8064	$6.3620 \cdot 10^{-1}$	2.1141	$5.1220 \cdot 10^{-1}$
	5	$1.7850 \cdot 10^{-1}$	$2.3360 \cdot 10^{1}$	7.3744	$1.2024 \cdot 10^{-1}$	$2.0133 \cdot 10^{-1}$	$8.4925 \cdot 10^{-1}$
	10	$3.8400 \cdot 10^{-2}$	7.1402	1.9180	$5.4800 \cdot 10^{-2}$	$3.7667 \cdot 10^{-1}$	$5.0940 \cdot 10^{-1}$
40	2	$3.7260 \cdot 10^{-1}$	$4.9332 \cdot 10^{1}$	$1.1661 \cdot 10^{1}$	$2.2190 \cdot 10^{-1}$	$8.9643 \cdot 10^{-1}$	2.0321
	5	$3.1125 \cdot 10^{-1}$	$2.9550 \cdot 10^{1}$	5.0855	$5.4000 \cdot 10^{-1}$	1.8653	$2.2250 \cdot 10^{-1}$
	10	$5.9000 \cdot 10^{-2}$	9.6370	3.6796	$5.8333 \cdot 10^{-2}$	$3.1250 \cdot 10^{-1}$	$2.7117 \cdot 10^{-1}$

1 p.s.i. = 6894.76 Pa.

Table 7
Comparison of temperature-programmed retention index prediction models for SPB-1 column based on cross-validated error mean squares

CHP (p.s.i.)	Rate (°C/min)	Models					
		ETKC	ATKC	LTKC	QTKC	Spline	Wang–Sun
15	2	$9.7456 \cdot 10^{-1}$	$4.4931 \cdot 10^{1}$	9.8460	$2.9619 \cdot 10^{-1}$	$3.4567 \cdot 10^{-2}$	2.8491
	5	$7.0000 \cdot 10^{-2}$	$1.2983 \cdot 10^{1}$	4.8514	$1.8333 \cdot 10^{-2}$	$6.5000 \cdot 10^{-2}$	$4.2333 \cdot 10^{-1}$
	10	$3.9000 \cdot 10^{-2}$	4.8384	2.3826	$7.1000 \cdot 10^{-2}$	$1.2333 \cdot 10^{-1}$	$7.8750 \cdot 10^{-2}$
20	2	$9.0700 \cdot 10^{-1}$	$5.3960 \cdot 10^{1}$	$1.5624 \cdot 10^{1}$	$2.0240 \cdot 10^{-1}$	$1.8857 \cdot 10^{-1}$	3.1391
	5	$3.5257 \cdot 10^{-1}$	$1.6470 \cdot 10^{1}$	7.8400	$9.3286 \cdot 10^{-2}$	$4.2000 \cdot 10^{-2}$	$9.7986 \cdot 10^{-1}$
	10	$6.0400 \cdot 10^{-2}$	6.0072	4.4472	$5.4800 \cdot 10^{-2}$	$1.5500 \cdot 10^{-1}$	$1.4320 \cdot 10^{-1}$
25	2	1.1043	$6.3046 \cdot 10^{1}$	$2.3597 \cdot 10^{1}$	$2.1491 \cdot 10^{-1}$	$1.1125 \cdot 10^{-1}$	3.9245
	5	$5.4575 \cdot 10^{-1}$	$2.1446 \cdot 10^{1}$	$1.1651 \cdot 10^{1}$	$1.3875 \cdot 10^{-1}$	$1.0250 \cdot 10^{-1}$	1.4764
	10	$8.1667 \cdot 10^{-2}$	7.1214	7.6486	$2.6667 \cdot 10^{-2}$	$4.2333 \cdot 10^{-1}$	$2.8000 \cdot 10^{-1}$

1 p.s.i. = 6894.76 Pa.

index calculation vary, the number of knots required needs to be tested. This also applies for different types of columns.

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