

## Live retention database for identification in multi-step temperature-programmed capillary gas chromatography

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### ABSTRACT

A calculation procedure for multi-step temperature programmed gas chromatographic retention times and that was investigated over diverse temperature programme conditions is described. Thermodynamic parameters of components, calculated from their Kováts retention indices and the isothermal retention times of *n*-alkanes, are utilized in the procedure. The influence of column dead time and variations of Kováts retention indices is examined. The calculation accuracies are better than 1% in most instances. A live retention time database for multi-step temperature programming was constructed using this procedure.

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### INTRODUCTION

Calculation of temperature-programmed retention times or indices from isothermal data has been reported in the past using different approaches [1–9]. The correct way for such a conversion is through thermodynamic theory [1–4]. The ultimate goal of the calculation is to replace standard samples in qualitative analysis using capillary gas chromatography. It is therefore critical that the calculation accuracy is compatible with the overall accuracy of the gas chromatograph. It is also vitally important that the isothermal retention data used for the calculation are easy to measure and to document, and to be transferrable between laboratories.

The type of isothermal retention data and their accuracy will undoubtedly affect the calculation accuracy. The thermodynamic quantities  $\Delta S$  and  $\Delta H$  of a component on a given stationary phase have been proposed as basic data for intercolumn data transfer [1,3]. It was found, unfortunately, that  $\Delta S$  and  $\Delta H$  are dependent on the stationary phase film thickness, phase ratio ( $\beta$ ) and column temperature [1,4], although the agreement between Kováts retention indices on the columns tested is better than  $\pm 0.5$  index unit.

Calculation of linear temperature-programmed retention indices with high accuracy had been described in a previous paper [4]. As most of the temperature-programmed analyses involve initial and final hold times, or even several programming steps, the calculation of retention time in multi-step temperature programming is more demanding.

In this work, Kováts retention indices at two temperature were chosen as the basic data. Retention times of *n*-alkanes at two temperatures were used to characterize the column and carrier gas flow. They were also used to calculate, in combination with Kováts retention indices, the thermodynamic parameters of components. The calculation accuracies for different classes of compounds under diverse temperature-programmed conditions were demonstrated.

#### CALCULATION

The entropy and enthalpy terms of each component on a column are determined by

$$-\frac{\Delta H}{R} = [\ln k(i, T_1) - \ln k(i, T_2)] \left( \frac{T_1 T_2}{T_2 - T_1} \right) \quad (1)$$

$$\frac{\alpha}{\beta} = \exp \left[ \ln k(i, T) - \frac{\Delta H}{RT} \right] \quad (2)$$

where  $\alpha = \exp(\Delta S/R)$ .

The deduction of eqns. 1 and 2 is the same as described previously [4], the film thickness or phase ratio dependence of the thermodynamic parameters being corrected automatically without the need to know them.

The calculation of the multi-step temperature-programmed retention time of each component is achieved by solving the following numerical integration equation:

$$\int_0^{t_i} \frac{dt}{t_0 [T(t)] \left[ 1 + \frac{\alpha}{\beta} \exp \left( \frac{-\Delta H}{RT(t)} \right) \right]} = 1 \quad (3)$$

where  $T(t) = T_0 + \sum r(i)t(i)$ ;  $i = 0, 1, 2, \dots$

The  $r(i)$  value can be positive, negative or zero, corresponding to upward temperature programming, downward programming and a plateau, respectively. There is no limitation to the number of steps or the function type of the programming rate. To ensure calculation accuracy, the time interval of the integration should be  $\leq 0.005t_0(T)$ .

When a series of *n*-alkanes can be mixed into the sample, a temperature-programmed retention index, as defined by Van den Dool and Kratz [10], can provide better accuracy for compound identification, as it tolerates instability of the gas chromatograph to a greater extent.

#### EXPERIMENTAL

A Model GC-R1A gas chromatograph (Shimadzu, Kyoto, Japan) was used for all experiments. An external thermometer was used to calibrate the oven temperature under isothermal conditions. Four cross-linked fused-silica columns coated with

TABLE I  
COLUMN SPECIFICATIONS

Column No.	Stationary phase	Length (m)	I.D. (mm)	Film thickness ( $\mu\text{m}$ )	Manufacturer
1	OV-1	50	0.31	0.52	Hewlett-Packard
2	SE-54	25	0.25	0.3	Dalian Institute of Chemical Physics
3	PEG-20M	25	0.25	0.2	Dalian Institute of Chemical Physics
4	FFAP	30	0.20	0.32	Lanzhou Institute of Chemical Physics

different stationary phases from different manufacturers were randomly selected for the test. Their specifications are listed in Table I.

Samples containing hydrocarbon, phenols, alcohols, esters, ketones, aromatic hydrocarbons and amines were used in the experiments. Hydrogen was used as the carrier gas. The splitting ratio of the injection was 1:50. The temperatures of the injection port and detector block were 250°C. An IBM AT-class microcomputer with math coprocessor was used for computation. Software was written in Quick-Basic V.4.0 (Micro-Soft). The typical calculation time for a 22-component sample with a 35-min chromatogram was 13–20 s.

## RESULTS AND DISCUSSION

The calculation accuracy of the retention time, according to eqn. 3, is affected by the errors of thermodynamic parameters, column dead time and temperature. We use  $\Delta S/R - \ln \beta$  as one term (entropy term) instead of  $\Delta S$ . For columns with the same stationary phase and reproducible Kováts retention indices but different film thicknesses and dimensions, their entropy and enthalpy terms  $\Delta H/R$  are different [1,4]. One way to obtain accurate values of these terms is to measure all the components on the column used [1–3,5]. It is a tedious task and often impossible to carry out. Another procedure, as we propose, is to use the Kováts retention indices, either measured or published, to calculate the isothermal terms. The only additional experimental data needed in the calculation are the retention times of *n*-alkanes measured at two temperatures on the column to be used.

The calculated and experimental results are given in Table II for an OV-1 column. There is excellent agreement for even multi-step temperature programming. The chromatographic conditions are listed in Table III. Tabulated Kováts retention indices, most of them from published data [11], were used in the calculation as this column was well defined.

Tables IV, VI and VIII further demonstrate the fitness of the calculation and observed results for three columns with different polarities and under diverse temperature programming conditions. The differences between the calculated and measured retention times is less than 1%, regardless of the steps of temperature programming and the properties of the stationary phases.

For polar phase columns from different manufacturers, the reproducibility of the Kováts retention indices is poor and published data can hardly be used at the

TABLE II  
RETENTION TIME CALCULATION FOR COLUMN 1

Component	Programme A		Programme B		Programme C		Programme D	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
Decane	5.78	5.73	8.57	8.55	6.11	6.13	5.98	5.96
<i>o</i> -Cresol	6.29	6.26	9.17	9.21	6.75	6.80	6.50	6.50
<i>p</i> -Cresol	6.71	6.68	9.68	9.68	7.33	7.30	6.94	6.94
2,6-Xylenol	7.55	7.51	10.48	10.41	8.51	8.53	7.84	7.82
Undecane	7.95	7.92	10.90	10.82	9.19	9.21	8.30	8.28
2,4-Xylenol	8.44	8.40	11.32	11.26	10.02	10.03	8.87	8.86
2,5-Xylenol	8.48	8.45	11.36	11.30	10.10	10.12	8.93	8.92
3,5-Xylenol	8.90	8.87	11.72	11.66	10.87	10.89	9.45	9.44
2,3-Xylenol	9.13	9.10	11.91	11.84	11.26	11.26	9.75	9.74
3,4-Xylenol	9.48	9.45	12.19	12.12	11.89	11.90	10.21	10.20
Dodecane	10.35	10.34	12.87	12.79	13.51	13.48	11.46	11.45
<i>o</i> - <i>tert.</i> -Butylphenol	11.45	11.45	13.70	13.65	15.56	15.47	13.07	13.05
1-Decanol	11.67	11.66	13.87	13.80	16.11	16.04	13.40	13.37
2,3,5-Trimethylphenol	11.95	11.97	14.09	14.06	16.64	16.55	13.76	13.75
Tridecane	12.76	12.79	14.77	14.75	18.20	18.14	14.84	14.83
2- <i>tert.</i> -Butyl-4-cresol	13.43	13.46	15.35	15.38	19.31	19.26	15.69	15.69
6- <i>tert.</i> -Butyl-3-cresol	13.70	13.74	15.59	15.64	19.70	19.67	16.01	16.03
Tetradecane	15.53	15.53	17.18	17.27	22.24	22.22	17.94	18.01
Pentadecane	10.43	19.35	20.55	20.87	—	—	21.05	21.25

TABLE III  
TEMPERATURE PROGRAMMING CONDITIONS FOR COLUMN 1

Condition	Step No.	Temperature (°C)	Hold time (min)	Programming rate (°C/min)
A	1	97.5	3.0	6.0
	2	155.0	Hold	
B	1	77.0	5.0	10.0
	2	158.0	Hold	
C	1	97.5	2.0	2.0
	2	109.0	2.0	4.0
	3	125.0	2.0	6.3
	4	150.0	2.0	8.0
	5	220.0	Hold	
D	1	77.5	0.0	10.0
	2	98.0	0.0	4.0
	3	118.0	0.0	2.0
	4	128.0	0.0	8.0
	5	144.0	0.0	4.0
	6	164.0	0.0	2.0
	7	170.0	0.0	3.0
	8	200.0	Hold	

TABLE IV  
RETENTION TIME CALCULATION FOR COLUMN 2

For temperature programming conditions see Table V.

Component	Programme A		Programme B		Programme C		Programme D	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
Decane	2.32	2.35	—	—	1.88	1.90	2.60	2.63
<i>o</i> -Cresol	3.57	3.50	3.53	3.50	2.68	2.62	4.04	4.05
<i>p</i> -Cresol	4.10	4.04	3.95	3.94	3.01	2.94 <sup>a</sup>	4.60	4.62
Undecane	3.91	3.92	3.81	3.81	2.91	2.94 <sup>a</sup>	4.39	4.39
Dodecane	6.59	6.60	5.54	5.55	4.88	4.88	7.33	7.34
1-Decanol	8.55	8.53	6.85	6.84	7.12	7.13	10.57	10.56
Tridecane	9.07	9.09	7.22	7.22	7.84	7.90	11.48	11.49
Tetradecane	11.21	11.20	8.76	8.76	11.15	11.21	15.82	15.82
Methyl undecanoate	11.76	11.75	9.15	9.15	12.06	12.09	16.75	16.73
Pentadecane	13.53	13.52	10.17	10.17	14.74	14.79	18.72	18.72
Methyl dodecanoate	14.31	14.29	10.55	10.57	15.97	15.99	19.33	19.34
Hexadecane	16.98	16.94	11.78	11.81	20.23	20.22	20.80	20.84

<sup>a</sup> Peaks overlap.

present stage. In view of this difficulty, measured Kováts retention indices were used in the calculations for columns 3 and 4. The data in Tables VI and VIII demonstrate the accuracy of the procedure for polar phase columns. Their temperature programming conditions are listed in Tables VII and IX, respectively.

For apolar stationary phases, columns with highly reproducible Kováts retention indices are commercially available. It is feasible to use published standard Kováts retention indices for the calculations. However, for each individual column, its Kováts retention indices will certainly show some deviation from the standard values. To simulate the real situation, the Kováts retention indices of some arbitrarily selected compounds were varied deliberately by  $\pm 0.5$  index unit and were used for the

TABLE V  
TEMPERATURE PROGRAMMING CONDITIONS FOR COLUMN 2

Condition	Step No.	Temperature (°C)	Hold time (min)	Programming rate (°C/min)
A	1	87.0	5.0	8.0
	2	137.0	Hold	
B	1	87.0	3.0	10.0
	2	157.0	Hold	
C	1	97.5	5.0	4.0
	2	127.5	Hold	
D	1	82.5	2.0	2.0
	2	90.0	2.0	4.2
	3	107.0	2.0	8.0
	4	200.0	Hold	

TABLE VI  
RETENTION TIME CALCULATION FOR COLUMN 3

Component	Programme A		Programme B		Programme C		Programme D	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
Decane	1.33	1.34	1.39	1.40	1.29	1.29	1.29	1.17
Ethylbenzene	1.53	1.53	1.62	1.62	1.50	1.50	1.36	1.33
Undecane	1.67	1.69	1.82	1.83	1.68	1.69	1.47	1.45
Dodecane	2.24	2.25	2.61	2.60	2.41	2.44	1.98	1.97
2-Octanone	2.33	2.34	2.70	2.71	2.50	2.52	2.08	2.04
Tridecane	3.11	3.29	3.81	3.77	3.58	3.57	2.85	2.81
Octyl acetate	4.21	4.20	5.35	5.33	5.01	5.00	3.97	3.90
Tetradecane	4.29	4.24	5.52	5.47	5.17	5.15	4.06	4.03
1-Octanol	5.37	5.31	7.22	7.20	6.74	6.69	5.20	5.13
Pentadecane	5.73	5.66	7.70	7.66	7.20	7.18	5.59	5.62
1-Pentadecene	6.50	6.42	8.65	8.62	8.08	8.03	6.47	6.45
1-Nonanol	7.00	6.92	9.35	9.32	8.65	8.57	7.01	6.97
Hexanecane	7.33	7.27	9.87	9.84	9.05	9.03	7.38	7.45
1-Decanol	8.70	8.64	12.04	12.04	10.79	10.72	8.76	8.74
Heptadecane	8.99	9.06	12.52	12.53	11.18	11.19	9.03	9.10
2,6-Xylidine	10.22	10.22	14.60	14.68	12.70	12.67	10.10	10.07
Octadecane	10.62	10.66	15.80	15.91	13.34	13.40	10.46	10.51

TABLE VII  
TEMPERATURE PROGRAMMING CONDITIONS FOR COLUMN 3

Condition	Step No.	Temperature (°C)	Hold time (min)	Programming rate (°C/min)
A	1	85.0	0.0	6.0
	2	220.0	Hold	
B	1	81.5	2.0	6.5
	2	94.5	2.0	9.5
	3	113.5	2.0	4.0
	4	122.0	2.0	1.5
	5	125.0	2.0	5.0
	6	200.0	Hold	
C	1	82.0	2.0	6.0
	2	94.0	0.0	2.0
	3	98.0	0.0	9.5
	4	117.0	0.0	2.0
	5	121.0	0.0	4.0
	6	129.0	0.0	6.0
	7	200.0	Hold	
D	1	91.0	2.0	6.5
	2	104.0	0.0	4.0
	3	112.0	0.0	7.0
	4	126.0	0.0	9.0
	5	143.0	0.0	7.0
	6	200.0	Hold	

TABLE VIII  
RETENTION TIME CALCULATION FOR COLUMN 4

Component	Programme A		Programme B		Programme C	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
Decane	1.11	1.12	1.06	1.06	1.08	1.07
Ethylbenzene	1.34	1.33	1.28	1.25	1.31	1.27
Dodecane	2.01	2.03	1.91	1.91	1.96	1.94
Tridecane	2.97	2.96	2.78	2.75	2.84	2.80
Octyl acetate	4.30	4.24	3.77	3.74	3.85	3.79
Tetradecane	4.58	4.61	3.96	3.96	4.03	4.03
1-Octanol	5.99	6.00	4.89	4.89	5.01	4.98
Pentadecane	6.87	6.90	5.61	5.60	5.81	5.80
1-Pentadecene	7.79	7.82	6.52	6.53	6.80	6.80
1-Nonanol	8.16	8.17	6.94	6.94	7.19	7.18
Hexadecene	8.92	8.94	7.92	7.86	8.01	8.02
1-Decanol	10.05	10.08	9.58	9.59	9.44	9.44
Heptadecane	10.68	10.72	10.59	10.56	10.47	10.46
2-Ethylhexanoic acid	11.39	11.42	11.64	11.64	11.66	11.60
Octadecane	12.23	12.30	13.20	13.18	13.70	13.66
2,6-Xylidine	12.96	13.00	14.30	14.30	15.52	15.42

TABLE IX  
TEMPERATURE PROGRAMMING CONDITIONS FOR COLUMN 4

Condition	Step No.	Temperature (°C)	Hold time (min)	Programming rate (°C/min)
A	1	99.5	5.0	7.9
	2	200.0	Hold	
B	1	99.5	2.0	6.0
	2	111.5	0.0	1.9
	3	119.0	0.0	4.0
	4	137.0	0.0	7.5
	5	152.0	0.0	3.0
	6	158.0	0.0	8.5
	7	175.0	0.0	5.0
	8	200.0	Hold	
C	1	99.5	2.0	6.0
	2	111.5	2.0	7.8
	3	127.0	2.0	2.0
	4	131.0	2.0	4.5
	5	140.0	2.0	6.0
	6	200.0	Hold	

TABLE X  
EFFECT OF VARIATION OF KOVÁTS RETENTION INDEX ON CALCULATED RESULTS  
Calculated on column 1 with temperature programme C.

Component	Increment of all Kováts retention indices					
	0 i.u.		-0.5 i.u.		+0.5 i.u.	
	Meas.	Calc.	Calc.	Calc.	Calc.	Calc.
<i>o</i> -Cresol	6.80	6.75	6.72	6.77		
<i>p</i> -Cresol	7.30	7.33	7.30	7.34		
2,6-Xylenol	8.53	8.51	8.48	8.53		
2,4-Xylenol	10.03	10.02	9.98	10.04		
2,5-Xylenol	10.12	10.10	10.06	10.13		
3,5-Xylenol	10.89	10.87	10.83	10.90		
2,3-Xylenol	11.26	11.26	11.22	11.29		
3,4-Xylenol	11.90	11.89	11.85	11.92		
<i>o</i> - <i>tert.</i> -Butylphenol	15.47	15.56	15.51	15.59		
1-Decanol	16.04	16.11	16.06	16.13		
2,3,5-Trimethylphenol	16.64	16.55	16.59	16.66		
2- <i>tert.</i> -Butyl-4-cresol	19.26	19.31	19.27	19.33		
6- <i>tert.</i> -Butyl-3-cresol	19.67	19.70	19.66	19.72		

calculation of retention time. A comparison between the calculated values using the standard and varied Kováts retention indices and the measured values is shown in Table X. The results show that the relative deviations of the calculated retention times and the Kováts retention indices are of the same order of magnitude.

In the measurement of *n*-alkane retention times at two isothermal states, the retention times of methane are used as the column dead time [ $t_0(T)$ ], which always has the highest relative deviation. The error in the  $t_0(T)$  determination will influence the

TABLE XI  
CALCULATION USING DIFFERENT  $t_0$  VALUES ON COLUMN 2

Component	Programme C		Programme D	
	Measured $t_0$	Extrapolated $t_0$	Measured $t_0$	Extrapolated $t_0$
Decane	1.88	1.79	2.60	2.16
<i>o</i> -Cresol	2.68	2.55	4.04	3.41
<i>p</i> -Cresol	3.01	2.87	4.60	3.94
Undecane	2.91	2.78	4.39	3.76
Dodecane	4.85	4.65	7.33	6.63
1-Decanol	7.12	6.96	10.57	10.03
Tridecane	7.84	7.70	11.48	11.03
Tetradecane	11.15	11.12	15.82	15.67
Methyl undecanoate	12.06	12.05	16.75	16.65
Pentadecane	14.74	14.76	18.72	18.68
Methyl dodecanoate	15.97	16.01	19.33	19.30
Hexadecane	20.23	20.30	20.80	20.73



calculated results, particularly the earlier eluting components. Table XI gives the calculated results on column 2 using measured and extrapolated [12] column dead times. The influence is dependent on the programming conditions.

The above procedure leads to an easy and reliable database for identification in multi-step temperature-programmed capillary gas chromatography. Isothermal runs and linear temperature programming are the simplest forms or a step unit in multi-step programming, and are included in the procedure and the database.

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