INTERACTIVE RETENTION INDEX DATABASE FOR COMPOUND IDENTIFICATION IN TEMPERATURE-PROGRAMMED CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

A procedure is described and evaluated that allows the calculation of linear temperature-programmed retention indices from accurate Kováts retention indices on a given stationary phase and their temperature variation coefficients. The influence of experimental factors such as column film thickness, phase ratio and variation of Kováts retention indices, column dead time and carrier gas flow-rates are examined. The calculation accuracies are ≤ 0.5 retention index units in most instances. The applicability and limitations of the procedure are discussed.

INTRODUCTION

Large numbers of isothermal gas chromatographic retention data have been published as Kováts retention indices. The use of Kováts retention indices has a great advantage over relative retention times, retention volumes or capacity ratios in that they are independent of the film thickness, column dimensions and phase ratio. Owing to the advances in column technology, highly reproducible (expressed as Kováts' indices) columns are commercially available for non-polar and some polar stationary phases.

The prediction or calculation of linear temperature-programmed retention indices (LTPRI) from isothermal data has been explored in the past[1–6] and different approaches were proposed and evaluated. Owing to the difference between the LTPRI and Kováts systems in the definition of retention index, the correct way to convert isothermal retention data to LTPRI is through the thermodynamic parameters of components as established by Curvers *et al.*[1]. It is feasible in theory to transfer the isothermal data (capacity ratios or Kováts retention indices) in terms of entropy and enthalpy of each component from one column to another for columns with the same stationary phase but different dimensions. However, in practice, this is not as easy as it may seem. The entropy term $[\exp(\Delta S/R)/\beta]$ is dependent on the phase ratio (β) and is difficult to determine accurately owing to the uncertainty in the measurement of the phase ratio. It has been observed experimentally that the enthalpy terms are also

dependent on the phase ratio[1]. Some of them are unexpectedly large, whereas theoretically they should remain constant.

The objectives of the study reported here were (a) direct utilization of Kováts retention indices, either measured or published, for calculating LTPRI; and (b) to find a means of eliminating the necessity to determine the film thickness or phase ratio and the corresponding changes in entropy and enthalpy.

THEORY

Calculation

For a given component i at a given temperature T, the Kováts retention index is

$$I(i) = 100z + 100 \cdot \frac{\log t'_R(i) - \log t'_R(z)}{\log t'_R(z + 1) - \log t'_R(z)} \tag{1}$$

Substitution of $t'_R(i)/t'_R(j) = k(i)/k(j)$ in eqn. 1 and rearranging yields

$$\log k(i) = \frac{I(i) - 100z}{100} \cdot \log\left[\frac{k(z + 1)}{k(z)}\right] + \log k(z) \tag{2}$$

Converting both sides of the equation into natural logarithm gives

$$\ln k(i) = \frac{I(i) - 100z}{100} \cdot \ln\left[\frac{k(z + 1)}{k(z)}\right] + \ln k(z) \tag{3}$$

One should bear in mind that all variables in eqns. 1–3 are temperature dependent. To make it explicit, $k(i,T)$ is used instead of $k(i)$ in the following equations.

Using the well known equation

$$\ln k(i,T) = \ln\left[\frac{\alpha(i)}{\beta}\right] - \frac{\Delta H(i)}{RT} \tag{4}$$

where $\alpha = \exp[\Delta S(i)/R]$, together with eqn. 3, we obtain the desired equations:

$$-\frac{\Delta H(i)}{R} = \left[\ln k(i,T_1) - \ln k(i,T_2)\right]\left(\frac{T_1 T_2}{T_2 - T_1}\right) \tag{5}$$

and

$$\frac{\alpha(i)}{\beta} = \exp\left[\ln k(i,T) - \frac{\Delta H(i)}{RT}\right] \tag{6}$$

where T can be T_1 or T_2.

Apart from the Kováts retention index of components at two temperatures, the only additional information needed for the calculation of the entropy and enthalpy terms is the adjusted retention time (or capacity ratio) of *n*-alkanes measured at two

corresponding temperatures on the column used for analysis. Subsequent calculations of the temperature-programmed retention temperature or retention time of each component use the well defined relationship[1]

$$\int_{T_0}^{T_R} \frac{dT}{t_0(T)\left[1 + \frac{a}{\beta}\exp\left(\frac{-\Delta H}{RT}\right)\right]} = r \tag{7}$$

Van den Dool and Kratz's[7] definition of the LTPRI is used in the final calculation.

EXPERIMENTAL

A Model 5790A gas chromatograph (Hewlett-Packard, Avondale, PA, U.S.A.) equipped with an HP 7672A auto-sampler was used for column testing. The instrument was provided with a two-point temperature calibration at 130.0 and 320.0°C. The temperature control was better than 0.1°C. An external high-precision pressure gauge was installed to allow pressure readings of 0.001 bar. An HP Model 3388 computer integrator was used for data handling.

A Mega Series 5300 gas chromatograph (Carlo Erba, Milan, Italy) was used for testing squalane columns. An external quartz thermometer (Type 2801, Hewlett-Packard) was used to correct the oven temperature under isothermal operation. A Spectra-Physics (Santa Clara, CA, U.S.A.) SP4290 integrator was used for data handling.

Four different cross-linked columns were randomly selected from the Ultra Performance series of Hewlett-Packard and two from Chrompack (Middelburg, The Netherlands). Their characteristics are given in Table I.

Helium was used as the carrier gas. The septum-flush flow-rate was 15 ml/min; the splitting ratio was set at 1:100 for the HP 5790A and 1:200 for the Mega Series 5300 instruments.The temperatures of the injection port and detector block were set at 250°C for the HP 5790A and 200°C for the Mega Series 5300 instruments.

Samples containing hydrocarbons, aromatics, ketones, esters and alcohols were used with both non-polar and weakly polar columns. AT-class microcomputers with math coprocessors were used for all computations. Software was written in Quick-Basic (Micro-Soft).

TABLE I

COLUMN CHARACTERISTICS

Column No.	Stationary phase	Length (m)	I.D. (mm)	Film thickness (μm)	Manufacturer
1	Squalane	50	0.22	0.21	Chrompack
2	OV-1	25	0.31	0.52	Hewlett-Packard
3	SE-54	25	0.31	0.52	Hewlett-Packard
4	OV-1	20	0.32	1.2	Chrompack
5	OV-1	25	0.31	0.52	Hewlett-Packard
6	SE-54	25	0.31	0.52	Hewlett-Packard

RESULTS AND DISCUSSION

The reliability of the calculated LTPRI is influenced by several factors, *viz.*, $\Delta H/RT$, $\Delta S/R$, β, $t_0(T)$ and the accuracy of the isothermal data used for the calculation; for clarity, we discuss them separately.

Temperature dependence of entropy and enthalpy terms

As both the entropy and enthalpy terms (*cf.*, eqns. 5 and 6) are temperature dependent, their values determined according to the procedure used in refs. 1–3 and the approach proposed in this paper are actually average values between the two temperatures of the isothermal measurements. The values of both terms depend not only on the temperatures of the isothermal measurements, but also on the difference between the two temperatures. When the elution temperature of a component is much higher than the upper isothermal measurement temperature, the term $\alpha/\beta \exp[-\Delta H/(RT)]$ will be smaller than it should be (*cf.*, data in ref. 1, Table 3), and the calculated T_r will be lower than the experimental value. Therefore, the optimum temperatures for measuring the isothermal retention indices should be selected as discussed by Curvers *et al.*[1], in order to obtain a better fit with the calculated and experimental LTPRIs.

The influence of the selected isothermal temperatures on the calculated LTPRI is different in both concepts. The retention temperatures of components and the adjacent *n*-alkanes are calculated using entropy and enthalpy terms obtained under identical conditions. In our approach, this is accomplished by using (a) the Kováts retention indices at two isothermal temperatures (which are known to have very good column-to-column reproducibility) and (b) the adjusted retention times of *n*-alkanes at two corresponding isothermal temperatures measured on the column to be used.

Systematic errors are partially cancelled in the calculation of LTPRI, because the shifts of the calculated T_r for a given component and the adjacent *n*-alkanes are in the same direction and of a similar magnitude. A comparison of calculated and measured LTPRIs is presented in Tables II–V for four columns differing either in stationary phase or film thickness, with different programming rates. The differences between the measured and calculated retention indices are within 0.5 retention index units (i.u.) in all instances, except for 1-butanol, for which there is a non-linear relationship between ln k and $1/T$. Note that the elution temperatures of some components (in the bottom parts of Tables III and IV at a programming rate of 8°C/min) are much higher than the temperatures in the isothermal measurements, and these do not cause an additional error in the calculated LTPRI. Unlike in the former approach[1], the choice of temperature in isothermal measurements is not so critical with the procedure presented here. Considering both the analysis time and the accuracy of the measurement, a capacity ratio (k') between 0.5 and 30 should be satisfactory. The temperature difference between the two measurements should be as large as possible.

Effect of film thickness and phase ratio

The entropy and enthalpy terms of some components on columns 2 and 4 are given in Table VI. The values were calculated using tabulated Kováts retention indices measured on column 2 at two temperatures and the adjusted retention times of *n*-alkanes obtained from two isothermal runs for each column. The agreement of the

TABLE II

COMPARISON OF CALCULATED AND MEASURED LTPRI VALUES ON COLUMN 1 (SQUALANE)

$T_0 = 40.0°C.$

Component	Isothermal (°C)		Programming rate (°C/min)			
	50.0	70.0	1.5		2.5	
			$I_{calc.}$[a]	ΔI[a]	$I_{calc.}$[a]	ΔI[a]
2,2-Dimethylpentane	625.6	626.9	617.8	−0.1	618.6	−0.1
2,4-Dimethylpentane	629.8	630.5	621.4	0.0	622.2	0.0
Benzene	637.2	641.8	626.7	−0.3	628.1	−0.3
3,3-Dimethylpentane	658.9	661.5	648.0	0.0	649.5	0.1
2-Methylhexane	666.6	666.9	657.0	−0.2	658.1	−0.1
1-cis, 3-Dimethylcyclopentane	682.7	686.0	675.6	0.3	676.9	0.3
3-Ethylpentane	686.0	687.1	680.4	0.0	681.2	−0.1
2,5-Dimethylhexane	728.4	729.0	722.5	−0.1	723.7	−0.1
2,4-Dimethylhexane	731.9	732.9	725.6	−0.1	727.0	0.0
Ethylcyclopentane	733.8	737.5	727.0	0.3	728.9	0.2
2,3-Dimethylhexane	760.1	761.5	753.1	0.2	754.9	0.3
3,4-Dimethylhexane	770.6	772.6	764.6	0.1	766.4	0.0
1-cis, 3-Dimethylcyclohexane	785.0	789.8	781.5	0.3	783.8	0.4
1-trans, 2-Dimethylcyclohexane	801.8	807.5	802.0	0.3	803.5	0.4
1-trans, 3-Dimethylcyclohexane	805.6	810.8	805.3	0.4	806.8	0.4
Ethylbenzene	834.6	839.8	832.4	0.4	835.1	0.5
Isopropylcyclopentane	812.1	817.0	811.1	0.3	812.9	0.4
1,4-Dimethylbenzene	849.1	854.0	847.0	0.3	849.9	0.5

Component	Isothermal (°C)		Programming rate (°C/min)					
	50.0	70.0	1.0		2.0		3.0	
			$I_{calc.}$[a]	ΔI[a]	$I_{calc.}$[a]	ΔI[a]	$I_{calc.}$[a]	ΔI[a]
2-Methyl-2-butene	514.3	514.4	508.9	−0.1	509.1	−0.1	509.2	−0.2
4-Methyl-1-pentene	549.4	550.4	536.8	0.0	537.5	0.0	538.0	−0.1
2,3-Dimethylbutane	567.3	568.8	555.2	−0.1	556.0	0.0	556.6	−0.1
2-Methyl-1-pentene	580.1	580.5	571.3	−0.1	571.8	−0.1	572.3	−0.1
Methylcyclopentane	627.9	630.9	618.7	0.2	619.9	0.3	620.8	0.3
2,4-Dimethylpentane	629.8	630.5	620.9	−0.1	621.9	−0.1	622.6	−0.1
Benzene	637.2	641.8	625.9	−0.4	627.5	−0.3	628.7	−0.3
Cyclohexane	662.7	667.1	650.6	0.3	652.6	0.4	654.2	0.5
2-Methylhexane	666.6	666.9	656.4	−0.1	657.7	−0.1	658.7	0.0
1-Heptene	681.8	682.3	674.6	−0.2	675.7	−0.1	676.4	−0.1

[a] In all tables, ΔI = LTPRI(calculated) − LTPRI(measured).

Kováts retention indices measured on both columns (cf., Tables III and V) is within 0.3 i.u. for the test sample, although the columns have a different film thickness or phase ratio and are from different manufacturers.

The ratio β(column 2)/β(column 4) was found to be 2.3 from the specification of

TABLE III

COMPARISON OF CALCULATED AND MEASURED LTPRI VALUES ON COLUMN 2

$T_0 = 40.0°C$; $P_i = 0.600$ kg/cm²; $u = 34$ cm/s. Flow-rates measured at 60°C here and in all following tables.

Component	Isothermal (°C)				Programming rate (°C/min)						Elution temperature (°C)
	45.0	60.0	65.0	75.0	2.0		4.0		8.0		
					$I_{calc.}$	ΔI	$I_{calc.}$	ΔI	$I_{calc.}$	ΔI	
2-Methyl-2-butene	520.0		519.8		513.6	-0.1	513.8	0.0	514.2	-0.1	
4-Methyl-1-pentene	556.7		557.1		545.6	0.1	546.2	0.1	547.0	0.0	
3-Dimethylbutane	566.3		567.7		555.8	0.1	556.4	0.1	557.3	-0.2	
2-Methyl-1-pentene	588.0		588.0		582.7	-0.2	583.0	-0.2	583.5	-0.1	
2,2-Dimethylpentane	624.8		628.1		617.6	-0.1	618.3	-0.1	619.4	0.0	
Methylcyclopentane	628.2		631.1		620.1	-0.1	621.1	-0.1	622.6	-0.4	
2,4-Dimethylpentane	630.5		631.3		622.2	0.0	623.0	-0.2	624.2	0.1	
Benzene	651.4		655.8		640.7	-0.2	642.3	-0.1	644.5	-0.1	
3,3-Dimethylpentane	656.2		659.0		645.8	-0.1	647.2	0.0	649.2	0.0	
Cyclohexane	660.6		665.6		650.1	-0.2	651.9	-0.1	654.4	-0.1	
2-Methylhexane	667.6		668.1		658.4	-0.1	659.5	-0.1	660.9	-0.1	
2,3-Dimethylpentane	669.9		672.0		660.8	0.0	662.0	0.0	663.9	0.2	
1,1-Dimethylcyclopentane	673.3		677.4		664.5	-0.1	666.0	0.0	668.3	0.1	
1-cis, 3-Dimethylcyclopentane	683.3		687.5		676.8	-0.2	678.2	0.0	680.3	0.4	

Compound									
3-Ethylpentane	686.4	687.5	681.2	0.0	682.0	0.1	683.1	0.1	
1-Heptene	688.6	688.7	684.2	−0.1	684.7	−0.1	685.4	−0.2	
1-cis, 2-Dimethylcyclopentane	719.5	723.8	714.4	−0.1	715.8	−0.1			
2,2-Dimethylhexane	722.1	723.8	716.6	−0.1	717.8	0.0			
3,3-Dimethylhexane	741.2	744.0	733.2	−0.1	735.2	−0.1	737.8	0.2	
Toluene	753.6	758.4	745.3	−0.1	747.9	−0.2	751.3	0.1	
2,3-Dimethylhexane	760.3	762.2	752.3	0.0	754.4	−0.1	756.9	0.2	
3,4-Dimethylhexane	769.0	771.1	761.9	0.0	764.0	−0.1	766.7	0.2	
1-cis, 3-Dimethylcyclohexane	774.9	780.3	768.7	0.0	771.4	−0.1	774.9	0.2	
1-cis, 2-Dimethylcyclohexane	822.2	828.8	819.0	−0.1	822.0	−0.1	825.8	0.3	
n-Propylcyclopentane	827.2	831.6	823.3	−0.1	825.9	−0.1	829.0	0.2	
Ethylbenzene	844.6	849.7	840.0	−0.1	843.4	−0.1	847.2	0.2	
1,4-Dimethylbenzene	854.2	859.0	849.6	−0.2	853.1	0.0	856.9	0.3	
1,2-Dimethylbenzene	874.0	879.6	871.4	−0.1	874.9	−0.1	879.0	0.3	
Dichloromethane	516.9	516.5	511.6	0.1	511.7	0.0	512.0	0.2	52.62
1-Butanol	646.8	643.9	639.9	−0.7	640.4	−0.5	641.1	−0.3	58.83
Toluene	756.6	759.9	745.3	0.0	747.8	0.0	751.0	0.0	69.10
n-Hexyl chloride	842.9	844.6	836.3	−0.1	838.7	0.0	841.2	0.1	81.12
3-Heptanone	866.2	866.5	861.2	−0.2	863.1	0.1	864.6	0.0	84.67
p-Chlorotoluene	936.3	941.3	932.0	0.1	935.9	0.2	940.6	0.2	96.69
1-Heptanol	954.9	952.8	952.9	−0.1	953.1	0.1	952.4	−0.2	98.62
1,2,4-Trimethylbenzene	976.2	980.5	973.7	0.1	977.5	0.3	981.6	0.3	103.41

TABLE IV

COMPARISON OF CALCULATED AND MEASURED LTPRI VALUES ON COLUMN 3 (SE-54)

$T_0 = 40.0°C$; $P_i = 0.600$ kg/cm^2; $u = 36$ cm/s.

Component	Isothermal (°C)				Programming rate (°C/min)						Elution temperature (°C)
	45.0	60.0	65.0	75.0	2.0 $I_{calc.}$	ΔI	4.0 $I_{calc.}$	ΔI	8.0 $I_{calc.}$	ΔI	
2-Methyl-2-butene	522.9		523.0		515.5	0.0	515.7	0.0	516.2	0.1	
4-Methyl-1-pentene	558.7		559.2		547.4	0.0	547.8	−0.1	548.7	−0.2	
2,3-Dimethylbutane	566.2		567.8		555.3	−0.1	555.9	−0.2	556.9	−0.3	
2-Methyl-1-pentene	590.7		591.2		586.3	−0.2	586.6	−0.2	587.0	−0.2	
2,4-Dimethylpentane	629.3		629.8		621.1	−0.1	621.8	−0.1	622.8	−0.3	
Methylcyclopentane	632.3		635.8		623.3	0.0	624.2	−0.2	625.8	−0.1	
Benzene	666.5		667.4		656.3	−0.1	657.8	−0.2	660.1	0.0	
1-Heptene	691.8		691.8		688.3	−0.1	688.7	−0.1	689.2	−0.1	
Dichloromethane		537.8		537.9	527.5	0.0	527.8	0.0	528.4	0.1	52.36
1-Butanol		661.9		659.6	654.6	−1.2	655.2	0.8	655.9	−0.6	58.50
Toluene		771.9		775.4	760.9	0.0	763.4	0.0	766.6	0.0	68.98
n-Hexyl chloride		858.2		859.7	851.4	−0.1	853.9	0.1	856.3	0.0	81.14
3-Heptanone		887.5		887.4	885.1	−0.2	885.9	0.0	886.5	0.0	85.65
p-Chlorotoluene		956.4		961.7	951.9	0.1	956.3	0.3	961.3	0.3	97.69
1-Heptanol		971.1		969.2	969.2	−0.1	969.4	0.2	968.8	−0.2	98.90
1,2,4-Trimethylbenzene		991.9		996.6	990.6	0.0	994.0	0.2	998.1	0.2	103.71

TABLE V

COMPARISON OF CALCULATED AND MEASURED LTPRI VALUES ON COLUMN 4

$T_0 = 40.0°C$.

| Component | Isothermal (°C) | | Programming rate (°C/min) | | | | | |
| | 45.0 | 65.0 | 2.0 | | 4.0 | | 8.0 | |
			$I_{calc.}$	ΔI	$I_{calc.}$	ΔI	$I_{calc.}$	ΔI
2-Methyl-2-butene	520.0	519.8	513.7	0.0	514.1	0.1	514.7	0.1
4-Methyl-1-pentene	556.7	557.1	546.0	0.2	546.9	0.3	548.2	0.4
2,3-Dimethylbutane	566.3	567.7	556.2	0.2	557.1	0.2	558.6	0.3
2-Methyl-1-pentene	588.0	588.0	583.0	0.1	583.5	−0.1	584.1	0.0
MethylCyclopentane	628.2	631.3	620.9	0.1	622.3	0.1		
2,4-Dimethylpentane	630.4	631.3	623.0	0.0	624.2	0.0		
Benzene	651.3	655.4	642.0	0.2	644.2	0.5	647.2	0.6
Cyclohexane	660.6	665.6	651.6	0.2	654.0	0.4	657.3	0.6
2-Methylhexane	667.6	667.7	659.5	0.1	661.0	0.0	662.8	0.0
1-Heptene	688.6	688.7	684.7	0.0	685.5	0.0	686.4	0.0

the columns. However, the ratio of the entropy terms of a component $[(\alpha/\beta)$ (column 4]/[(α/β) (column 2)] between the two columns is larger than 4 (cf., Table VI). The deviation from theory could be the result of inaccurate values of the phase ratio or the strong surface effect on the stationary phase. The latter causes the properties of a coated stationary phase to deviate from that of the bulk system, and the entropy and enthalpy of a component to depend on the film thickness. In either instance, it is possible to correct this ratio based on the entropy terms of a known component measured on both columns, without the need to know the absolute values of the phase ratios or the degree of the surface effect. With this correction, the Curvers et al. concept[1,2] is still valid if the enthalpy terms are constant.

TABLE VI

CALCULATED ENTROPY AND ENTHALPY TERMS ON COLUMNS 2 and 4

| Component | α/β ($\times 10^{-7}$) | | $-\Delta H/R$ (K) | |
	Column 2	Column 4	Column 2	Column 4
2-Methyl-2-butene	398.25	1624.4	2890.7	2753.8
4-Methyl-1-pentene	339.86	1377.4	3048.1	2913.6
2,3-Dimethylbutane	367.54	1487.4	3051.1	2917.2
2-Methyl-1-pentene	264.38	1065.3	3219.1	3086.8
n-Hexane	242.05	973.22	3282.3	3150.8
Methylcyclopentane	303.87	1231.8	3290.8	3156.5
Benzene	288.90	1179.1	3373.4	3236.8
Cyclohexane	305.44	1250.0	3382.3	3244.8
2-Methylhexane	149.81	614.36	3629.1	3490.9
2,4-Dimethylpentane	219.03	888.52	3401.5	3267.0
1-Heptene	127.33	525.39	3741.1	3600.8
n-Heptane	115.96	480.10	3803.6	3662.2

The data in Table VI showed that the enthalpy terms on the two columns were not consistent. Their differences are about 4% on average, which alone could generate at least a 30 i.u. difference in calculated LTPRIs if the enthalpy terms are taken as the basic data. The film thickness dependence of the enthalpy term invalidates the attempt to transfer the entropy and enthalpy terms from one column to another as proposed by Curvers et al.[1].

The procedure described here corrects the variations in film thickness, phase ratio or the surface effect of the phase through measurements on n-alkanes under isothermal conditions, without the need to know them. The retention times of n-alkanes together with the Kováts retention indices are used to calculate the entropy and enthalpy terms of each component on the column to be used for analysis. It is as if all the components were measured on this column with this procedure, when the reproducibility of Kováts retention indices of different columns can be guaranteed. Note that some components, which have larger dI/dT values (e.g., benzene and cyclohexane; cf., Table V) show slightly larger deviations between the calculated and mean real LTPRIs at higher programming rates for column 4. The probable reason is that the average programming rate is smaller than expected, owing to bundling of the column coils. For all other columns the coils were regularly distributed in single layers on a light metal frame. The coils at the inner side of the bundle cannot follow the set programming rate. Obviously this deviation of the actual column temperature from the set value will have a larger effect on components with a high dI/dT.

Effect of variation of Kováts retention indices

As isothermal retention indices are used as the basic data for the calculation of LTPRIs, their variation between different columns will certainly have an influence on the LTPRIs. We studied this effect by varying the Kováts retention indices by ± 0.5 i.u., which is an acceptable simulation of the real situation. The results in Table VII show that the error of calculated LTPRIs and the deviation of the Kováts retention indices used for the calculation are of the same order of magnitude or even less.

Effect of variation of column dead time

The column dead time reflects the integrated effects of column length and flow-rate. It has to be taken into account in the calculation of the elution temperature, T_r, in temperature-programmed gas chromatography (cf., eqn. 7).

The column dead time, t_0, is cancelled in the calculation of LTPRI when measured data are used. In the calculation of T_r, however, such a process is simulated, and the dead time $t_0(T)$ will certainly affect the T_r value. As the same dead time $t_0(T)$ is used for the calculation of the elution temperature of the components for a given programmed run, systematic errors in $t_0(T)$ can also be partly cancelled in the calculation of LTPRIs. From this point of view, some variation of $t_0(T)$ is acceptable. The t_0 values under isothermal conditions are involved in the calculation of the adjusted retention times or capacity ratios of n-alkanes, and have a direct influence on the values of the entropy and enthalpy terms.

In this study, methane was used as the dead-time marker, not because it can give the best accuracy in t_0 measurements, but because most of the published data were measured using the retention time of methane as t_0. The consistency in choosing the marker will improve the accuracy of the calculated LTPRIs, particularly for earlier

TABLE VII

EFFECT OF VARIATION OF ISOTHERMAL RETENTION INDEX ON LTPRI

Calculated for Column 2. $T_0 = 40.0°C$; $r = 8.0°C/min$.

Compound	Isothermal (°C)		$I_{calc.}$
	60.0	75.0	
Dichloromethane	516.90	516.50	512.0
Variation	−0.50	+0.50	−1.0
	−0.50	+0.0	+0.3
	+0.0	+0.50	−0.3
	+0.0	−0.50	+0.3
	+0.50	+0.0	+0.7
	+0.50	+0.50	+0.4
Toluene	756.62	759.90	751.0
Variation	−0.50	+0.50	−0.9
	−0.50	+0.0	−0.7
	+0.0	−0.50	+0.1
	+0.0	+0.50	+0.2
	+0.50	+0.0	+0.6
	+0.50	−0.50	+0.9
	+0.50	+0.50	+0.5
p-Chlorotoluene	936.25	941.30	940.6
Variation	−0.50	+0.50	+0.4
	−0.50	+0.0	−0.1
	+0.0	+0.50	+0.5
	+0.0	−0.5	−0.5
	+0.50	+0.0	+0.1
	+0.50	−0.50	−0.4

eluting components. This is illustrated in Table VIII, where LTPRIs were calculated using measured and extrapolated dead times on two different columns. For components having a retention index above 600 no significant differences were observed for the two methods.

Influence of carrier flow-rate or inlet pressure

For well deactivated columns and a sample amount far below the maximum capacity of the column, the entropy and enthalpy terms are expected to be independent of carrier gas flow-rate or inlet pressure under normal operating conditions, particularly when helium is used as the carrier gas and the inlet pressure is lower than 2 bar. For unknown reasons, the entropy and enthalpy terms are also affected by the flow-rate or pressure drop, as shown in Table IX. The data were calculated using measured Kováts retention indices and adjusted retention times of n-alkanes at corresponding isothermal temperatures at different inlet pressures. The effects of about a 1.5% variation in the entropy and enthalpy terms on the calculated LTPRI is shown in Table X. By comparison of these values with the results in Table IX, the error in the calculated LTPRIs caused only by the different flow-rate or inlet pressure can be calculated when the entropy and enthalpy terms are used as the basic data.

TABLE VIII

COMPARISON OF CALCULATED[8] AND MEASURED LTPRI VALUES ON COLUMNS 2 AND 3 USING DIFFERENT t_0 VALUES IN THE CALCULATION

$T_0 = 40.0°C$; $r = 8.0°C/min$.

Component	Column 2				Column 3			
	Calc. with				Calc. with			
	Measured t_0	ΔI	Calc. t_0	ΔI	Measured t_0	ΔI	Calc. t_0	ΔI
Dichloromethane	512.0	0.2	512.8	1.0	528.4	0.1	529.5	1.2
4-Methyl-1-pentene	547.0	0.0	548.0	1.0	548.7	−0.2	549.7	0.8
Methylcyclopentane	622.6	−0.4	622.9	−0.1	625.8	−0.3	626.2	0.1
1-Heptene	685.4	−0.2	685.6	0.0	689.2	−0.1	689.4	0.1
Toluene	751.0	0.0	751.2	0.2	766.6	0.0	766.8	0.2
n-Hexyl chloride	841.2	0.1	841.3	0.2	856.3	0.0	856.4	0.1
3-Heptanone	64.6	0.0	864.7	0.1	886.6	0.1	886.6	0.1
p-Chlorotoluene	940.6	0.2	940.7	0.3	961.3	0.3	961.4	0.4
1-Heptanol	952.4	−0.2	952.4	−0.2	968.8	−0.2	968.8	−0.2
1,2,4-Trimethylbenzene	981.6	0.3	981.7	0.4	998.1	0.2	998.1	0.2

These effects are avoided when using the procedure proposed in this paper. The results for both measured and calculated LTPRIs for two different columns at two different flow-rates or inlet pressures are given in Table XI and also Tables III and IV. The error was less than 0.4 i.u. for all the components tested, except the first

TABLE IX

VARIATION OF ENTROPY AND ENTHALPY TERMS WITH CARRIER FLOW-RATE OR INLET PRESSURE

Measured on column 2. $-\Delta H/R$ in Kelvin.

Component	Inlet pressure (kg/cm²)							
	0.300		0.450		0.600		0.800	
	$-\Delta H/R$	α/β^a	$-\Delta H/R$	α/β^a	$-\Delta H/R$	α/β^a	$-\Delta H/R$	α/β^a
2-Methyl-2-butene	2884.1	400.80	2867.3	424.96	2890.7	398.25	2923.6	353.52
4-Methyl-1-pentene	3041.9	341.88	3037.1	348.98	3048.1	339.86	3055.0	327.73
2,3-Dimethylbutane	3047.8	366.94	3049.3	366.98	3051.1	367.54	3069.3	342.25
2-Methyl-1-pentene	3212.9	266.55	3217.8	264.11	3219.1	264.38	3225.3	255.71
n-Hexane	3278.9	241.89	3283.4	239.85	3282.3	242.05	3289.8	233.26
Methylcyclopentane	3292.4	299.24	3294.6	298.68	3290.8	303.87	3299.1	292.28
2,4-Dimethylpentane	3400.1	217.56	3402.5	217.14	3401.5	219.03	3408.9	211.29
Benzene	3361.7	296.43	3363.3	296.48	3373.4	288.90	3371.0	287.23
Cyclohexane	3371.6	312.46	3376.4	309.32	3382.3	305.44	3382.7	301.13
2-Methylhexane	3630.5	147.48	3624.3	151.21	3629.1	149.81	3631.7	146.66
1-Heptene	3723.9	132.98	3729.3	131.40	3741.1	127.33	3740.4	125.98
n-Heptane	3788.0	120.41	3791.6	119.74	3803.6	115.96	3798.5	116.25

$^a \times 10^{-7}$.

TABLE X

EFFECT OF VARIATION OF ENTROPY AND ENTHALPY TERMS ON THE LTPRI VALUES

T_0 = 40.0°C; r = 8.0°C/min. Measured on column 2.

Isothermal (°C)		$-\Delta H/R$ (K)	α/β ($\times 10^{-7}$)	$I_{calc.}$
60.0	75.0			
756.62	759.90	3788.2	191.99	750.9
757.52	700.90	3787.0	194.11	751.9
800.00	800.00	4200.9	79.33	800.0
842.88	844.63	4321.9	78.13	840.5
954.92	952.77	5123.3	17.45	952.4
955.60	953.50	5123.9	17.51	953.1

component, 1-butanol. The reason for this close fit is that the entropy and enthalpy terms of each component were calculated based on the adjusted retention times of *n*-alkanes measured at the same inlet pressure condition to be used for the temperature-programmed run, and tabulated Kováts retention indices. This approach ensures the accuracy of the calculated LTPRI's, which is demonstrated further in Table XII for two different columns at different flow-rates for different structural types of substances.

CONCLUSION

For a given stationary phase and a given component at a given temperature, the entropy and enthalpy terms vary according to the film thickness or phase ratio, and

TABLE XI

COMPARISON OF CALCULATED AND MEASURED LTPRI VALUES ON COLUMNS 2 AND 3 AT P_i = 0.450 kg/cm²

T_0 = 40°C; r = 8.0°C/min. Flow-rate 26 cm/s.

Component	Column 2		Column 3	
	$I_{calc.}$	ΔI	$I_{calc.}$	ΔI
2-Methyl-2-butene	514.3	0.0	516.3	-0.1
4-Methyl-1-pentene	547.3	-0.1	549.1	-0.1
2,3-Dimethylbutane	557.8	-0.2	557.5	0.1
2-Methyl-1-pentene	583.8	0.0	587.3	0.0
Methylcyclopentane	Co-elute		626.6	-0.1
2,4-Dimethylpentane			623.3	-0.1
Benzene	645.6	-0.1	661.3	0.3
Cyclohexane	655.5	-0.1	Co-elutes with benzene	
2-Methylhexane	661.3	-0.2	Co-elutes with benzene	
1-Heptene	685.7	-0.1	689.5	0.0

TABLE XII

COMPARISON OF CALCULATED AND MEASURED LTPRI VALUES ON COLUMNS 5 AND 6 AT DIFFERENT FLOW-RATES

$T_0 = 35.0°C$; $r = 8.0°C/min$.

Component	Column 5						Column 6					
	Isothermal (°C)		LTPRI at flow-rate (cm/s)				Isothermal (°C)		LTPRI at flow-rate (cm/s)			
	60.0	80.0	38		26		60.0	80.0	38		26	
			$I_{calc.}$	ΔI	$I_{calc.}$	ΔI			$I_{calc.}$	ΔI	$I_{calc.}$	ΔI
Benzene	654.37	658.77	643.30	−0.2	645.07	−0.1	669.71	673.97	659.28	0.2	661.00	0.4
Isobutyl acetate	757.79	755.73	754.24	−0.5	754.82	−0.4	774.16	771.94	771.51	−0.1	771.80	−0.1
2-Methoxyethyl acetate	810.99	807.11	811.04	−0.4	810.33	−0.4	838.31	834.21	836.94	0.0	836.48	0.0
Cyclohexanone	860.93	867.57	859.15	−0.4	862.12	−0.3	894.47	900.00	895.34	0.1	897.22	−0.3
2-Ethoxyethyl acetate	882.41	878.15	880.94	−0.2	879.90	−0.3	909.22	904.54	908.02	0.1	906.51	0.0
2-(2-Methoxyethoxy)ethanol	906.07	906.00	905.97	−0.5	906.04	−0.8	934.85	934.77	934.56	−0.1	934.88	−0.2
2-(2-Ethoxyethoxy)ethanol	974.79	974.44	974.47	−0.2	974.62	−0.4						

even the carrier gas flow-rate or inlet pressure. The procedure proposed here utilizes the Kováts retention index, which represents the common properties of a given stationary phase for each component, and the adjusted retention time or capacity ratio of *n*-alkanes, which represents the characteristics of each column. When the reproducibility of the Kováts retention index can be guaranteed, combining these two features (using eqns. 5 and 6) is equivalent to measuring all the components on the particular column. This is why the calculated LTPRI fits the experimental results so well. This procedure can easily be used for interactive database compound identification in linear temperature programmed capillary gas chromatography.

REFERENCES

1 J. Curvers, J. Rijks and C. Cramers, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 607.
2 J. Curvers, *Thesis*, Eindhoven University of Technology, Eindhoven, 1985.
3 E. E. Akporhonor, S. Le Vent and D. R. Taylor, *J. Chromatogr.*, 405 (1987) 67.
4 J. Krupčik, P. Cellar, D. Repka, J. Garaj and G. Guiochon, *J. Chromatogr.*, 351 (1986) 111.
5 R. V. Golovnya and V. P. Uraletz, *J. Chromatogr.*, 36 (1968) 276.
6 L. Erdey, J. Takács and E. Szalánciy, *J. Chromatogr.*, 46 (1970) 29.
7 H. van den Dool and P. D. Kratz, *J. Chromatogr.*, 11 (1963) 463.
8 M. L. Peterson and J. Hirsch, *J. Lipid Res.*, 1 (1959) 132.