

CHROM. 21 981

PROGRAMMED-TEMPERATURE RETENTION INDICES

A SURVEY OF CALCULATION METHODS

E. FERNÁNDEZ-SÁNCHEZ, J. A. GARCÍA-DOMÍNGUEZ*, V. MENÉNDEZ and J. M. SANTIUSTE

Instituto de Química Física "Rocasolano", CSIC, Serrano 119, 28006 Madrid (Spain)

(First received April 28th, 1989; revised manuscript received September 8th, 1989)

SUMMARY

Retention temperatures of various solutes were measured on an OV-105 column under different heating rates. The experimental results agree with those evaluated by means of the equation of Curvers *et al.* Several methods of assigning programmed-temperature retention indices to each solute were tested. Comparison of the results does not allow a clear choice of any of the methods, although a procedure based on an interpolation through the use of cubic splines polynomials is preferred. The sensitivity of the various procedures towards small changes in the input data is reported.

INTRODUCTION

A number of workers have attempted to report retention data in a systematic way in order to identify compounds and characterize stationary phases. In 1958 Kováts¹ formulated his well known isothermal retention index. A generalization of the Kováts definition to the field of programmed-temperature chromatography was made by van den Doole and Kratz² by the use of the retention temperature (T_R) as the parameter that characterizes each solute, and with the assumption that the retention temperatures of the n -alkanes are linearly dependent on their retention index as defined by Kováts.

Van den Doole and Kratz's equation is written as

$$PTRI = 100Z + 100 \cdot \frac{T_{RX} - T_{RZ}}{T_{RZ+1} - T_{RZ}} \quad (1)$$

where $PTRI$ represents the programmed-temperature retention index, and $T_{RZ} < T_{RX} < T_{RZ+1}$ are the retention temperatures of the n -alkane with Z carbon atoms, the solute and the n -alkane with $Z+1$ carbon atoms, respectively.

The use of programmed-temperature gas chromatography has increased enormously as it is a valuable tool in many fields, such as pharmaceutical drugs, petroleum, foods, spirits, flavours and cosmetics, where complex mixtures occur.

TABLE I
 EXPERIMENTAL RETENTION TEMPERATURES (°C) AND VALUES OBTAINED ACCORDING TO EQN. 2
 r (°C/min) is the heating rate $T_0 = 80^\circ\text{C}$.

Solute	$r = 1$		$r = 2$		$r = 3$		$r = 5$		$r = 6$		$r = 8$	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
<i>n</i> -Hexane	83.4	83.7	86.7	87.1	89.9	90.4	95.3	96.3	98.6	99.2	104.5	104.6
<i>n</i> -Heptane	85.8	85.9	91.2	91.2	96.0	96.0	104.1	104.3	108.8	108.2	116.6	115.2
<i>n</i> -Octane	90.3	90.4	98.6	98.6	105.7	105.5	116.7	116.8	122.5	121.5	132.2	130.0
<i>n</i> -Nonane	97.6	97.7	109.2	109.3	118.4	118.1	132.1	131.6	138.7	137.1	150.0	146.5
<i>n</i> -Decane	107.1	107.7	121.3	122.3	132.6	132.6	148.8	147.6	155.6	153.5	168.3	163.3
<i>n</i> -Undecane	119.3	120.3	135.8	136.8	148.3	148.0	165.5	163.5	172.7	169.6		
<i>n</i> -Dodecane	132.3	133.6	150.7	151.2	163.4	162.6						
Benzene	85.1	85.3	89.2	90.2	94.1	94.6			106.4	106.3		
1-Butanol	85.8	85.8	90.4	90.0	95.4	95.6			108.1	107.6		
2-Pentanone	86.0	86.5	91.5	92.2	96.9	97.3			110.4	110.2		
1-Nitropropane	88.8	89.4	96.3	97.0	103.2	103.5			119.8	119.1		
Pyridine	89.1	89.2	95.7	96.8	102.6	103.3			119.5	119.1		
2-Methyl-2-pentanol	88.3	88.3	95.3	95.2	101.5	101.2			117.2	115.7		
1-Iodobutane	92.4	92.5	102.1	102.0	110.1	109.8			129.4	127.7		
2-Octyne	95.2	95.6	105.1	106.4	114.5	114.8			134.5	133.1		
1,4-Dioxane	86.6	86.8	91.8	92.8	97.6	98.1			111.9	111.5		
<i>cis</i> -Hydrindane	107.2	107.6	122.5	122.8	133.8	133.7			158.5	155.9		

Therefore, the definition of a retention index similar to that of Kováts is required. Several equations have been reported³⁻¹³; however, none of them has gained universal recognition as in isothermal gas chromatography. This paper shows again the ability of the equation of Curvers *et al.*¹⁴, based on the work of Grant and Hollis³, to evaluate the retention temperature of a solute. The calculation of a *PTRI* according to the definition of van den Doole and Kratz is considered to be impractical in some instances, and retention indices calculated according to different procedures are reported here in an attempt to establish a method of choice.

EXPERIMENTAL

C₆-C₁₂ *n*-alkanes and the ten McReynolds' probes¹⁵ were used as solutes. Chromatograms were obtained on a Perkin-Elmer Sigma 2 gas chromatograph with a 2 m × 1/8 in. O.D. stainless-steel column packed with OV-105 on Chromosorb W and a flame ionization detector was used. The oven temperature was monitored to within ±0.2°C with the aid of a thermocouple. Nitrogen was used as the carrier gas, regulated at 10 ml/min with a mass flow regulator. Calculations were carried out in a CYBER 855 computer. IMSL routines were used when required.

RESULTS AND DISCUSSION

Retention temperatures in programmed-temperature gas chromatography

An interesting problem that has attracted the attention of many workers is to find of a method for evaluating programmed-temperature parameters from readily available isothermal data. Habgood and Harris¹⁶ found the retention temperature by means of the dependence between isothermal and temperature-programmed retention volumes. A modified equation was offered by Grant and Hollis³. According to Curvers *et al.*¹⁴, the equation may be written as

$$\int_{T_0}^{T_R} \frac{dT}{t_m(T) \left[1 + \frac{a}{\beta} \exp(\Delta H/RT) \right]} = r \quad (2)$$

where the 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. Other symbols have their usual meanings.

Table I shows the retention temperatures found experimentally and those calculated by eqn. 2 for several heating rates. The reported values are the averages of at least three independent runs. The agreement observed gives support to the use of eqn. 2 for the calculation of retention temperatures in programmed-temperature gas chromatography. At the higher heating rates there is a discrepancy between the experimental and calculated values of T_R probably because the temperatures reported are oven temperatures and the column is colder. Most experiments considered in this paper correspond to an initial column temperature of 80°C. We have carried out experiments at $T_0 = 50^\circ\text{C}$ and also at higher flow-rates using hydrogen as the carrier gas. The results were similar to those reported.

Retention indices in programmed-temperature gas chromatography

The *PTRI* of a solute is closely related to its retention temperature under given experimental conditions. The first step in establishing a retention index is therefore to determine the retention temperature. The different procedures discussed here used to calculate *PTRI* values follow two different approaches: in the first, the procedures are really methods of calculation of the retention temperatures of the different solutes of the mixture from isothermal data, leaving the determination of the *PTRI* to the application of an equation such as that of van den Doole and Kratz. Sometimes the methods find "equivalent temperatures", which are then used in the *PTRI* calculation. In the second group of procedures, the methods use values of T_R calculated or measured experimentally and apply equations that are different from the linear interpolation mentioned.

Giddings⁴ defined an equivalent retention temperature as 0.92 times the experimental T_R . Guiochon⁵ proposed for the same purpose subtracting 20°C from the experimental value of T_R . These empirical approaches have been shown to be acceptable. They are not considered in this discussion, however.

Lee and Taylor⁶ used as an equivalent temperature (T_{eq}) the harmonic mean of the experimental T_R and the starting temperature of the heating programme T_0 . That is,

$$T_{eq} = 2 T_0 T_R / (T_0 + T_R) \quad (3)$$

Krupčík *et al.*⁷ avoided the numerical evaluation of an integral. Their equation thus appears to be more suited to manual calculations:

$$T_{RX} = \frac{[I(T_1) - 100 Z - T_1(dI/dT)](T_{RZ+1} - T_{RZ}) + 100 T_{RZ}}{100 - (dI/dT)(T_{RZ+1} - T_{RZ})} \quad (4)$$

where T_{RX} is the retention temperature of compound X , $I(T_1)$ is the isothermal retention index at temperature T_1 , not necessarily the initial temperature, dI/dT is the rate of change of the isothermal retention index of the compound *versus* temperature and the other symbols have their usual meanings.

The indices of the ten McReynolds' standards found by the linear interpolation procedure (eqn. 1), using both experimental and calculated retention temperatures, are given in Table II. Values of *PTRI* found with equivalent temperatures obtained by eqn. 3 do not differ from those obtained by the direct use of the experimental T_R , or that calculated with eqn. 2. Values of *PTRI* evaluated using the retention temperatures deduced with the help of eqn. 4 tend to be higher.

As mentioned earlier, other methods do not calculate values of T_R . They are procedures of finding the *PTRI* of a solute under temperature-programmed conditions. Golovnya and Uraletz⁸ propose a simple equation:

$$PTRI = I(T_0) + 0.5 r t_R (dI/dT) \quad (5)$$

where $I(T_0)$ is the Kováts' retention index of the solute at the programme starting temperature (T_0) and r is the constant heating rate.

The approach of Erdey *et al.*⁹ avoids data related to the n -alkanes, as does eqn. 5,

TABLE II

PTRI OF VARIOUS SUBSTANCES OBTAINED BY EQN. 1 USING EXPERIMENTAL AND CALCULATED VALUES OF T_R

Heating rate 3°C/min. $T_0 = 80^\circ\text{C}$.

<i>Solute</i>	<i>Exp.</i>	<i>Calc.</i> ^a	<i>Eqn. 3</i>		<i>Eqn. 4</i>	
			<i>Exp.</i> ^b	<i>Calc.</i> ^c	<i>Exp.</i> ^b	<i>Calc.</i> ^c
Benzene	672	673	669	674	682	685
1-Butanol	689	693	690	693	693	695
2-Pentanone	708	714	709	714	714	717
1-Nitropropane	775	779	776	780	784	785
Pyridine	768	777	767	777	785	785
2-Methyl-2-pentanol	756	755	758	755	760	760
1-Iodobutane	835	834	836	835	843	844
2-Octyne	869	874	870	874	875	875
1,4-Dioxane	717	722	718	723	728	728
<i>cis</i> -Hydrindane	1008	1007	1009	1008	1018	1018

^a T_R values found by eqn. 2.

^b T_{eq} or T_{RX} calculated with experimental values of T_R .

^c T_{eq} or T_{RX} calculated with values of T_R obtained by eqn. 2.

and assumes that the temperature dependence of the isothermal retention index is given by an expression such as

$$I(T) = A + \frac{B}{T + C} \quad (6)$$

The coefficients A , B and C are evaluated by obtaining isothermal experimental data at three temperatures (100, 120 and 140°C in our case), and the use of the following expressions:

$$C = \frac{(T_2 - T_1)(I_3T_3 - I_1T_1) + (T_3 - T_1)(I_1T_1 - I_2T_2)}{(T_3 - T_1)(I_2 - I_1) - (T_2 - T_1)(I_3 - I_1)} \quad (7)$$

$$A = \frac{I_3T_3 - I_1T_1 + C(I_3 - I_1)}{(T_3 - T_1)} \quad (8)$$

$$B = I_3T_3 + I_3C - A(T_3 + C) \quad (9)$$

where I_i is the isothermal retention index at the temperature T_i .

The *PTRI* of a solute eluting with a retention temperature T_R in a programme starting at T_0 is calculated as

$$PTRI = A + \frac{B \ln\left(\frac{T_R + C}{T_0 + C}\right)}{T_R - T_0} \quad (10)$$

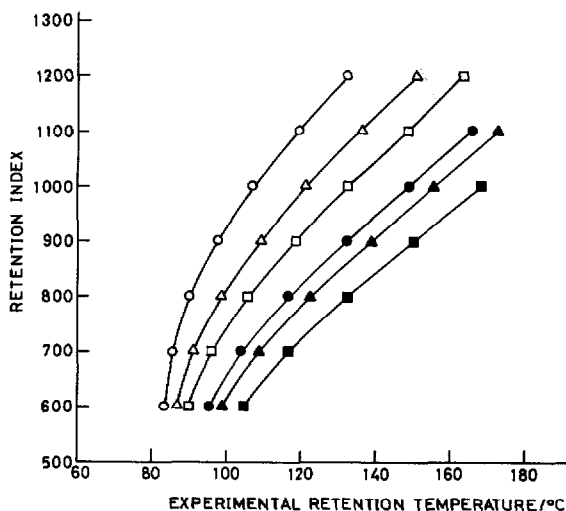


Fig. 1. Plot of retention indices *versus* retention temperatures for various *n*-alkanes at different heating rates (\circ , 1.0; \triangle , 2.0; \square , 3.0; \bullet , 5.0; \blacktriangle , 6.0; \blacksquare , 8.0°C/min. Column, OV-105 on Chromosorb W (2 m \times $\frac{1}{8}$ in. O.D.). Carrier gas, nitrogen at 10 ml/min. $T_0 = 80^\circ\text{C}$.

Fig. 1 shows a plot of the Kováts retention indices of various *n*-alkanes *versus* the experimental value of T_R obtained at six different heating rates. A clear curvature may be observed at the low values of T_R . As mentioned earlier, the same shapes have been found for plots drawn using values obtained at lower initial column temperatures and also at higher flow-rates, for this and other columns. We used a mass flow regulator for the carrier gas in our experiments. The use of a pressure regulator (capillary gas chromatography) would result in a more pronounced curvature. Other workers^{7,8,13,17-20} have reported the same type of curvatures under different chromatographic conditions, or the curves may be deduced from their results. The question now being posed is how the curve joining the points must be drawn. The mathematical answer is that an interpolation procedure should be used. Following these lines, various equations have been proposed.

Zenkevich and Ioffe^{10,11} performed a linear logarithmic interpolation between *n*-alkanes of Z and $Z + K$ carbon atoms. The "generalized retention index" (GI_X) of a solute X with a retention time of t'_{RX} is given by

$$GI_X = 100Z + 100K \frac{(t'_{RX} + q \log t'_{RX}) - (t'_{RZ} + q \log t'_{RZ})}{(t'_{RZ+K} + q \log t'_{RZ+K}) - (t'_{RZ} + q \log t'_{RZ})} \quad (11)$$

with

$$q = \frac{(n_2 - n_1)t'_{R1} + (n_3 - n_2)t'_{R3} - (n_3 - n_1)t'_{R2}}{\log(t'_{R2}^2/t'_{R1}t'_{R3})} \quad (12)$$

Where n_1 , n_2 and n_3 are the number of carbon atoms of *n*-alkanes 1, 2 and 3 eluting under the same experimental conditions.

TABLE III

RETENTION INDICES OBTAINED BY EQNS. 5⁸, 10⁹, 11¹¹ AND 13¹² AND BY THE CUBIC SPLINES METHOD¹³

Temperature programmed from 80 to 180°C at 3°C/min. Retention temperature used were calculated by eqn. 2.

Solute	Eqn. 5	Eqn. 10	Eqn. 11	Eqn. 13	Cubic splines
Benzene	681	682	680	680	678
1-Butanol	696	701	694	694	694
2-Pentanone	715	715	717	715	719
1-Nitropropane	783	783	783	780	783
Pyridine	781	783	780	778	782
2-Methyl-2-pentanol	760	759	759	761	763
1-Iodobutane	839	837	837	841	835
2-Octyne	877	877	876	874	875
1,4-Dioxane	726	726	727	727	729
cis-Hidriindane	1003	1004	1007	1000	1007

Wang and Sun¹² modified the expression for GI_x :

$$GI_x = 100N + 100 \cdot \frac{(q \ln Y_x + Y_x^B) - (q \ln Y_z + Y_z^B)}{(q \ln Y_{z+1} + Y_{z+1}^B) - (q \ln Y_z + Y_z^B)} \quad (13)$$

with $B > 1$; q is calculated according to eqn. 12. Y_i represents a retention parameter which may be volume or time.

The procedure of Halang *et al.*¹³ for assigning the *PTRI* of a solute is based on a direct interpolation through the T_R values of the n -alkanes. The interpolation polynomials chosen are cubic splines. A short description of the numerical properties of this kind of polynomial and a computer program were given by Press *et al.*²¹, and a broader mathematical treatment of the subject was given by de Boor²².

Results obtained with eqns. 5, 10, 11 and 13 and the cubic splines method, using the values of T_R deduced with the help of eqn. 2 applied to our experimental isothermal data, are presented in Table III. The differences observed among the various values of the *PTRI* of a substance are now smaller than those which can be deduced from Table II.

Fig. 1 shows that the plots of the retention indices of n -alkanes *versus* their T_R are curves for low values of the difference $T_R - T_0$. It seems clear that any deduction of the *PTRI* of a substance eluting between two n -alkanes in this region must be carried out bearing in mind the existence of this curvature, and not using the linear interpolation method proposed by van den Doole and Kratz. It is therefore reasonable to consider that the value obtained using the cubic splines procedure is closer to the real *PTRI* of the compound. Unfortunately, unlike the situation with T_R , where calculated values can be compared with experimental results, the *PTRI* of a substance cannot be compared with any standard value. Therefore, direct comparison of the different methods of deducing a *PTRI* is not possible. However, if we accept that the method of Halang *et al.*¹³ is a good choice for calculating a *PTRI*, a comparison of the various

TABLE IV

SENSITIVITY TEST: CHANGE IN RETENTION INDEX UNITS PER MINUTE CHANGE IN RETENTION TIME

Temperature programmed from 50 to 180°C at 2°C/min.

<i>Eqn.</i>	<i>Low-temperature value</i>	<i>High-temperature value</i>
1	20	12
10	0.06	0.1
11	42	5.6
13	55	0.6
Cubic splines	28	13

columns in Table III indicates that the differences are sufficiently small to consider all five methods to be approximately correct. Experimental errors in the determination of Kováts retention indices are frequently as large as those found among the various values corresponding to the same substance in Table III.

From the experimental point of view, those methods which do not require the injection of the *n*-alkanes seem to offer certain advantages. Reality is different however. The methods of Golovnya and Uraletz⁸ and Erdey *et al.*⁹ do not require the injection of *n*-alkanes with the sample but they are not useful for finding the *PTRI* of an unknown peak in a chromatogram (isothermal retention indices of the substance are needed). The increasing availability of personal computers and microprocessor-controlled chromatographs makes the cubic splines interpolation a useful procedure, as it takes into account automatically the fact that the points defined by the retention indices of the *n*-alkanes do not lie on a straight line.

Sensitivity of the various methods

In order to compare further the different methods discussed, a sensitivity analysis was carried out so that the robustness of the procedures towards small changes in the retention input data could be established. Derivatives of the different equations were evaluated numerically for a temperature programme from 50 to 180°C at 2°C/min. With the equation of Erdey *et al.*⁹, benzene was the solute used in the sensitivity test.

Table IV gives the results obtained, presented in the form of the change in retention index units per minute. The sensitivity of an equation based on a linear interpolation is, of course, the slope of the straight line obtained by a least-squares method. It is clear that in this instance the sensitivity remains constant. Fig. 1, however, shows that interpolation between two consecutive *n*-alkanes means that the straight line that should be used depends on the region where the value of T_R lies. The values in Table IV are the two extreme values corresponding to the low- and high-temperature ends of the plot. In all other instances the sensitivity changes more smoothly with retention time. The sensitivity of the cubic splines interpolation becomes close to that of the linear interpolation procedure when retention times increase, in agreement with the fact that the curvature decreases. Van den Doole and Kratz's equation becomes sound for solutes eluting with long retention times.

ACKNOWLEDGEMENTS

The computing facilities provided by the Centro de Cálculo of the Consejo Superior de Investigaciones Científicas are gratefully acknowledged. This work was carried out under Project number PB87-0393 of the Dirección General de Ciencia y Tecnología (DGICYT).

REFERENCES

- 1 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 2 H. van den Doole and P. D. Kratz, *J. Chromatogr.*, 11 (1963) 463.
- 3 D. W. Grant and M. G. Hollis, *J. Chromatogr.*, 158 (1978) 3.
- 4 J. C. Giddings, in N. Brenner, J. E. Callen and M. D. Weiss (Editors), *Gas Chromatography*, Academic Press, New York, 1962, p. 57.
- 5 G. Guiochon, *Anal. Chem.*, 36 (1964) 661.
- 6 J. Lee and D. R. Taylor, *Chromatographia*, 16 (1982) 286.
- 7 J. Krupčík, P. Cellar, D. Repka, J. Garaj and G. Guiochon, *J. Chromatogr.*, 351 (1986) 111.
- 8 R. V. Golovnya and V. P. Uraletz, *J. Chromatogr.*, 36 (1968) 276.
- 9 L. Erdey, J. Takács and E. Szalánczy, *J. Chromatogr.*, 46 (1970) 29.
- 10 I. G. Zenkevich, *Zh. Anal. Khim.*, 39 (1984) 1297.
- 11 I. G. Zenkevich and B. V. Ioffe, *J. Chromatogr.*, 439 (1988) 185.
- 12 T. Wang and Y. Sun, *J. Chromatogr.*, 390 (1987) 261.
- 13 W. A. Halang, R. Langlais and E. Kugler, *Anal. Chem.*, 50 (1978) 1829.
- 14 J. Curvers, J. Rijks, C. Cramers, K. Knaus and P. Larson, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 607.
- 15 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
- 16 H. W. Habgood and W. E. Harris, *Anal. Chem.*, 32 (1960) 450.
- 17 G. Janssens, *Anal. Chim. Acta*, 95 (1977) 153.
- 18 P. Kusz and W. Czelakowski, *Int. Lab.*, (1987) 92.
- 19 J. Krupčík, D. Repka, E. Benická, T. Hevesi, J. Nolte, B. Paschold and H. Mayer, *J. Chromatogr.*, 448 (1988) 203.
- 20 E. E. Akporhonor, S. Le Vent and D. R. Taylor, *J. Chromatogr.*, 463 (1989) 271.
- 21 W. H. Press, B. P. Flannery, S. A. Tenkolsky and W. T. Vetterling, *Numerical Recipes*, Cambridge University Press, Cambridge, 1986, p. 77.
- 22 C. de Boor, *A Practical Guide to Splines*, Springer, New York, Heidelberg, Berlin, 1978.