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Note

Accurate calculation of adjusted retention time. I

J. ŠEVČÍK

Packard-Becker BV, P.O. Box 519, Delft (The Netherlands)

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The calculation of adjusted retention times, t_s , has previously been based on the determination of the dead time, t_m . To determine the latter, different procedures are used, either experimental¹ with measurement of the gross retention time of a non-sorbent substance (for example methane, air or helium) or by calculation^{2,3} using the fitness of equations, for example

$$\frac{\log \left(\frac{t_{ms3} - t_m}{t_{ms1} - t_m} \right)}{\log \left(\frac{t_{ms2} - t_m}{t_{ms1} - t_m} \right)} = \frac{I_3 - I_1}{I_2 - I_1} = \text{constant}$$

where t_{ms} and I are gross retention time and value of Kováts indices, respectively. However, in the above examples the imprecision of the time of sample injection and consequent imprecision of the gross retention time lead to erroneous results.

The gross retention time as measured represents the sum of the following contributions. (1) duration of syringe introduction; (2) diffusion from syringe; (3) duration of injection; (4) path through injector volume and injector-column connection; (5) path through column volume; (6) path through volume of column-detector connection, (7) detector time constant; and (8) recorder time constant. Of these contributions, the importance of the indefinite gross retention time, which is related to the marking procedure, is clear, and it varies between periods 1-3. When the read-out of gross retention time is changed owing to the shift in marking, the dead time, t_m , either measured or calculated, is also changed, in spite of the GC system remaining unchanged.

To overcome these disadvantages, the concept of calculation of adjusted retention time is proposed.

THEORETICAL

The proposed concept of calculation of adjusted retention time is based on the fact that the adjusted retention time is related only to time period 5 in above list, when the substances in a chromatographic column are retarded and separated. Hence, those substances have Kováts retention indices (I) greater than zero, while substances which take no part in the separation process have $I = 0$. Thus the adjusted retention time is related to a substance with $I = 0$.

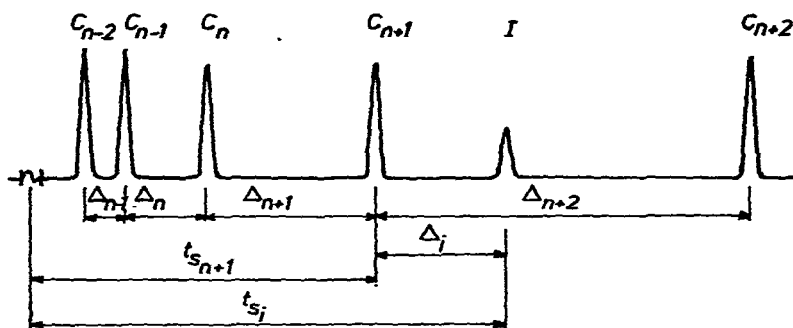


Fig. 1. Schematic chromatogram. t_s = adjusted retention time; Δ_n = time difference between the n -alkanes in row; Δ_i = time difference between the peaks not in row.

The adjusted retention time of any peak in a chromatogram can be expressed as the sum of the time differences between neighbouring peaks. Let assume that $t_{s_{n+1}}$, t_{s_n} , $t_{s_{n-1}}$ and $t_{ms_{n+1}}$, t_{ms_n} , $t_{ms_{n-1}}$ are the adjusted retention times and gross retention times of n -alkanes with known numbers of carbon atom $n + 1$, n and $n - 1$, respectively. Then,

$$\Delta_{n+1} = t_{s_{n+1}} - t_{s_n} = t_{ms_{n+1}} - t_{ms_n} \quad (1)$$

$$\Delta_n = t_{s_n} - t_{s_{n-1}} = t_{ms_n} - t_{ms_{n-1}} \quad (2)$$

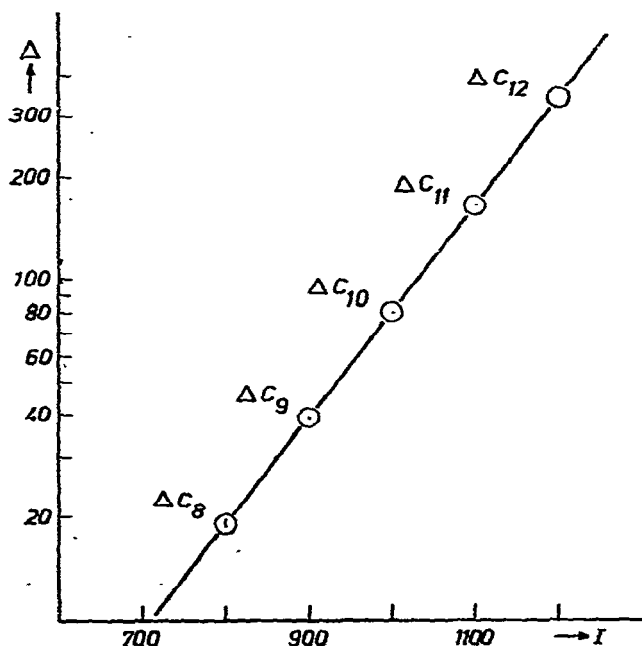


Fig. 2. Dependence of $\log \Delta$ on I .

The adjusted retention time, $t_{s_{n+1}}$, can be expressed by the following equation (see Fig. 1):

$$t_{s_{n+1}} = \Delta_1 + \Delta_2 + \cdots + \Delta_n + \Delta_{n+1} \quad (3)$$

where Δ_1 is time difference between the elution of a substance with $I = 0$ and one with $I = 100$, etc. From eqn. 3, it follows that the adjusted retention time can be calculated if the sum of all time differences is known. Then,

$$t_{s_i} = \sum_0^I \Delta_x \quad (4)$$

It was found that the ratio of neighbouring time differences, $\Delta_{n \pm x}$, in a homologous series is constant:

$$\Delta_{n+x} = A \Delta_{n+x-1} \quad (5)$$

Hence the dependance of logarithm of the time difference $\log \Delta_x$ versus I_x is a straight line (Fig. 2). On the basis of the validity of eqn. 5, we can calculate the time differences, Δ_x , between all peaks until we reach the start of separation, i.e. $I = 0$. From eqns. 1, 2 and 5 it follows that

$$\Delta_1 = \Delta_n A^{-(n-1)} \quad (6)$$

$$\Delta_2 = \Delta_n A^{-(n-2)} \quad (7)$$

$$\Delta_3 = \Delta_n A^{-(n-3)} \quad (8)$$

$$\vdots \quad \vdots$$

$$\vdots \quad \vdots$$

$$\Delta_n = \Delta_n A^{-(n-n)} = \Delta_n \quad (9)$$

$$\Delta_{n+1} = \Delta_n A^{-[n-(n+1)]} = \Delta_n A \quad (10)$$

$$\Delta_{n+2} = \Delta_n A^2 \quad (11)$$

$$\vdots \quad \vdots$$

$$\vdots \quad \vdots$$

$$\Delta_{n+x} = \Delta_n A^x \quad (12)$$

In this way, the calculation of any time difference is possible and, by their summation, the calculation of adjusted retention time is achieved (see eqns. 3 and 4). The resulting equation for the adjusted retention time of a peak with n carbon atoms in the molecule is

$$t_{s_n} = \Delta_n [A^{-(n-1)} + A^{-(n-2)} + \cdots + 1] \quad (13)$$

or

$$t_{s_n} = \Delta_n \frac{A^{n+1} - A}{A^{n+1} - A^n} \quad (14)$$

DISCUSSION

Based on the proposed theory, the calculation of the adjusted retention time of any peak in a chromatogram is possible. This concept allowed us to divide the time axis of a chromatogram into time intervals corresponding to the elution of *n*-alkanes. In this way, the identification of substances is much more easy as the position of all $I = n \cdot 100$ values is known directly from one measurement. The accuracy of calculation is very high as the results are not biased due to marking the start, errors during injection, etc.

Calculation of adjusted retention time

A method for the calculation of adjusted retention time without respect to the dead time is now proposed. The precise measured time differences between at least three *n*-alkanes in a homologous series are used. The differences, Δ , between the peaks are measured (see Fig. 1), stored (see Table I) and their ratio, A , is calculated according to eqn. 5. If more than three *n*-alkanes in a homologous series are considered, the ratio

TABLE I

CALCULATION OF ADJUSTED RETENTION TIME USING A MIXTURE OF *n*-ALKANES
0.1 μ l of an *n*-C₇₋₁₂ alkane mixture injected, separation at 85° with 1.7 bar pressure gap, chart speed 30 mm/min.

C_n	I	Δ	A^*	$\log \Delta$	$\log A^{**}$	t_s
12	1200					656.78
		336.5		2.5270		
11	1100		2.0644		0.3148	320.10
		163.0		2.2122		
10	1000		2.0375		0.3091	155.95
		80.0		1.9031		
9	900		2.0513		0.3120	75.95
		39.0		1.5911		
8	800		2.0526		0.3123	36.95
		19.0		1.2788		
7	700					17.95
		9.26		0.96675		
6	600					8.69
		4.52		0.65470		
5	500					4.17
		2.20		0.34265		
4	400					1.97
		1.07		0.03060		
3	300					0.89
		0.52		-0.28145		
2	200					0.37
		0.25		-0.59350		
1	100					0.12
		0.12		-0.90555		
0	0					0

* $\bar{A} = 2.0514$.

** $\log \bar{A} = 0.31205$.

A is calculated for all neighbouring pairs of differences (see Table I) and the arithmetic mean is used for further calculation. The adjusted retention time is then calculated according to eqn. 13 or 14, respectively, for a chosen value of n .

Calculation of adjusted retention time of non-alkanes

The adjusted retention times of n -alkanes are calculated by the above procedure. As the calculation is related to the value $I = 0$, the calculated adjusted retention times serve as fixed points on the time axis of the chromatogram. In relation to these points, the difference, Δ_i , can be measured and the adjusted retention time of any substance can thus be calculated (see Fig. 1).

Calibration of time axis of chromatogram

A method for the calculation of the adjusted retention time of any n -alkane is now proposed on the basis of measured time differences between three n -alkanes in a homologous series. By this calculation, the positions of the indices $I = n \cdot 100$ are known for the whole chromatogram and the identification of substances is thus possible.

Accuracy of method

The proposed method requires at least three n -alkanes in a homologous series in order to measure two differences and to calculate the ratio A . When using this method, the delay and shift in marking have no effect and the resulting data are unbiased. This method permits an accurate evaluation to be made without respect to the gross retention time and dead time, without a knowledge of the start of injection etc.

Table II indicates the shift in calculated adjusted retention times, which may be due to imprecise read-out of the gross retention times in published data.

To increase the precision of the proposed method, more n -alkanes in a homologous series can be used, as the number of ratios A , N_A , is related to the number of n -alkanes, N_{C_n} , used, by the equation

$$N_A = N_{C_n} - 2 \quad (15)$$

TABLE II

COMPARISON OF CALCULATED AND PUBLISHED³ DATA OF ADJUSTED RETENTION TIME

Substance	I	Δ	A^*	t_s	
				Calculated	Published
n -Tridecane	1300			545.77	544.5
		317.0			
n -Dodecane	1200		2.3835	228.77	227.5
		133.0			
n -Undecane	1100		2.3878	95.89	94.5
		55.7			
n -Decane	1000			40.2	38.8

* $\bar{A} = 2.38563$.

The precision of the time differences is not determined by the proposed method, but by the precision of the time of distance measurement. If more *n*-alkanes are used, the precision of the calculation increases when a linear regression for the logarithms of the differences is applied.

REFERENCES

- 1 R. Kaiser, *Chromatographia*, 2 (1969) 215.
- 2 H. Groenendijk and A. W. C. van Kemenade, *Chromatographia*, 1 (1968) 472.
- 3 R. E. Kaiser, *Chromatographia*, 9 (1976) 337.