

CHROM. 17 948

## Note

### A problem with Kováts' retention index equation

R. J. SMITH, J. K. HAKEN\* and M. S. WAINWRIGHT

*Departments of Industrial Chemistry and Polymer Science, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)*

(First received April 15th, 1985; revised manuscript received June 7th, 1985)

Our recent review on the estimation of dead time and the calculation of Kováts indices<sup>1</sup> revealed two problems with the standard linear relationship between the logarithm of the adjusted retention time and the carbon number of a substance.

$$\ln(t_{Rz} - t_M) = bz + c \quad (I = 100z) \quad (1)$$

where  $t_M$  is the dead time,  $t_{Rz}$  is the gross retention time of a homologue with a carbon number of  $z$ ,  $b$  and  $c$  are constants, and  $I$  is Kováts retention index.

The first anomaly results from the consideration of the gross retention time of a theoretically unretained substance. The retention time of such a substance is by definition the column dead time. Substituting this into eqn. 1 gives

$$\ln(t_M - t_M) = bz + c$$

$$\text{That is } \ln(0) = bz + c \quad (2)$$

Eqn. 2 is, however, undefined and this means that at least one point on the curve is undefined.

Secondly, a relationship involving the ratio of differences between the retention times of successive homologues can be derived from eqn. 1 as follows:

$$t_{Rz} - t_M = e^{bz} \cdot e^c \quad (3)$$

A similar relationship exists for homologues  $z+1$  and  $z-1$  as follows

$$\ln(t_{Rz+1} - t_M) = b(z+1) + c$$

and

$$t_{Rz+1} - t_M = e^{bz} \cdot e^b \cdot e^c \quad (4)$$

also

$$\ln(t_{Rz-1} - t_M) = b(z-1) + c$$

and

$$t_{Rz-1} - t_M = e^{bz} \cdot e^{-b} \cdot e^c \quad (5)$$

Subtracting eqn. 3 from eqn. 4 gives

$$(t_{Rz+1} - t_M) - (t_{Rz} - t_M) = e^{bz} \cdot e^b \cdot e^c - e^{bz} \cdot e^c$$

Thus

$$t_{Rz-1} - t_{Rz} = e^{bz} \cdot e^c \cdot (e^b - 1) \quad (6)$$

Subtracting eqn. 5 from eqn. 3 gives

$$(t_{Rz} - t_M) - (t_{Rz-1} - t_M) = e^{bz} \cdot e^c - e^{bz} \cdot e^{-b} \cdot e^c$$

$$t_{Rz} - t_{Rz-1} = e^{bz} \cdot e^c \cdot (1 - e^{-b}) \quad (7)$$

Dividing eqn. 6 by eqn. 7 gives

$$\begin{aligned} \frac{t_{Rz+1} - t_{Rz}}{t_{Rz} - t_{Rz-1}} &= \frac{e^{bz} \cdot e^c \cdot (e^b - 1)}{e^{bz} \cdot e^c \cdot (1 - e^{-b})} \\ &= \frac{e^b - 1}{1 - e^{-b}} \\ &= \frac{e^b \cdot (e^b - 1)}{(e^b - 1)} \\ &= A \end{aligned}$$

where  $A$ , which is a constant, equals  $e^b$ .

In their 1978 paper, Ševčík and Löwentap<sup>2</sup> started with this relationship (which they had found from experimental evidence) and went on to derive a relationship for relative retention.

Defining the difference between consecutive gross retention times as  $\Delta$  gives

$$\Delta_z = t_{Rz} - t_{R(z-1)} \quad (9)$$

Therefore the adjusted retention of a homologue can be expressed as

$$t'_{Rz} = \Delta_1 + \Delta_2 + \Delta_3 + \dots + \Delta_{z-1} + \Delta_z \quad (10)$$

where  $\Delta_1$  is the time difference between the elution of a substance with  $I = 0$  and one with  $I = 100$ , etc. In the case of  $\Delta_1$  this actually equals the adjusted retention time of a homologue with a carbon number of one (*i.e.*  $\Delta_1 = t'_{R1}$ ).

Thus eqn. 8 becomes

$$\Delta_z = A^{-1} \Delta_{z+1} \tag{11}$$

Thus

$$\Delta_{z-1} = A^{-1} \Delta_z$$

Therefore eqn. 10 can be written as

$$\begin{aligned} t'_{Rz} &= \Delta_z + \Delta_{z-1} + \Delta_{z-2} + \dots + \Delta_2 + \Delta_1 \\ &= \Delta_z + A^{-1} \Delta_z + A^{-2} \Delta_z + \dots + A^{2-z} \Delta_z + A^{1-z} \Delta_z \\ &= \Delta_z (1 + A^{-1} + A^{-2} + \dots + A^{2-z} + A^{1-z}) \end{aligned} \tag{12}$$

This is a geometric series and can be summed as follows

$$t'_{Rz} = \Delta_z \cdot \frac{[1 - (1/A)^z]}{[1 - (1/A)]} = \Delta_z \cdot \frac{(A^z + 1 - A)}{(A^z + 1 - A^2)} \tag{13}$$

By a similar process eqn. 14 can be derived

$$t'_{Rz+1} = \Delta_z \cdot \frac{(A^z + 2 - A)}{(A^z + 1 - A^2)} \tag{14}$$

Dividing eqn. 14 by eqn. 13 gives

$$\begin{aligned} \frac{t'_{Rz+1}}{t'_{Rz}} &= \Delta_z \cdot \frac{(A^z + 2 - A)}{(A^z + 1 - A^2)} \cdot \frac{1}{\Delta_z} \cdot \frac{(A^z + 1 - A^2)}{(A^z + 1 - A)} \\ &= \frac{(A^z + 2 - A)}{(A^z + 1 - A)} \end{aligned} \tag{15}$$

Eqn. 15 can be rearranged to give

$$\frac{t'_{Rz+1}}{t'_{Rz}} = \frac{[A - (1/A^z)]}{[1 - (1/A^z)]} \tag{16}$$

From this expression it can be seen that as  $z \rightarrow \infty$  then  $t'_{Rz+1}/t'_{Rz} \rightarrow A$ . Thus the method predicts that relative retention will only be constant at high values of  $z$ , but for smaller values of  $z$  this will not be the case.

It is also possible to derive an expression for relative retention directly from the standard relationship by dividing eqn. 4 by eqn. 3 to give

$$\frac{t_{Rz+1} - t_M}{t_{Rz} - t_M} = \frac{e^b \cdot e^{bz} \cdot e^c}{e^{bz} \cdot e^c}$$

thus

$$\frac{t'_{Rz} + 1}{t'_{Rz}} = e^b = A \quad (17)$$

Unfortunately this equation is in conflict with the one derived by Ševčík and Löwentap (eqn. 16) because while their relationship predicts that relative retention is dependent on carbon number, eqn. 17 requires it to be independent of carbon number. Thus a second anomaly exists.

Although there are many ways to overcome these anomalies, including the rejection of eqn. 1, we will discuss two alternatives.

#### *Alternative I*

First, assume that the parameter in the logarithm in eqn. 1 is not a direct measure of the column dead time but some mathematical function of the dead time. We will therefore refer to this term as the mathematical dead time as opposed to the "real" column dead time. As the simplest function is a constant we propose that the mathematical dead time equals the column dead time minus a constant,  $d$ . Thus

$$\ln \{t_{Rz} - (t_M - d)\} = bz + c \quad (18)$$

Now by substituting the retention time of an unretained compound into eqn. 18 the following relationship is obtained.

$$\ln (t_M - t_M + d) = bz + c$$

$$\ln (d) = bz + c$$

$$d = e^{bz} \cdot e^c \quad (19)$$

As  $d$  has been defined as a constant, this equation is only valid if  $z = 0$ . That is, a theoretical alkane with a carbon number of zero is unretained. Hence  $d = e^c$  and we now have an expression for  $d$  which can be substituted into eqn. 18 giving

$$\ln (t_{Rz} - t_M + e^c) = bz + c \quad (20)$$

This equation can now be used to derive a relationship for relative retention.

$$t_{Rz} - t_M + e^c = e^{bz} \cdot e^c$$

$$t'_{Rz} = e^{bz} \cdot e^c - e^c = e^c \cdot (e^{bz} - 1) \quad (21)$$

Similarly

$$t'_{Rz} + 1 = e^{bz} \cdot e^b \cdot e^c - e^c = e^c \cdot (e^{bz} \cdot e^b - 1) \quad (22)$$

Dividing eqn. 22 by eqn. 21 gives

$$\begin{aligned} \frac{t'_{Rz+1}}{t'_{Rz}} &= \frac{e^c \cdot (e^{bz} \cdot e^b - 1)}{e^c \cdot (e^{bz} - 1)} \\ &= \frac{e^{b(z+1)} - 1}{e^{bz} - 1} \\ &= \frac{A^{z+1} - 1}{A^z - 1} \end{aligned} \tag{23}$$

Rearranging eqn. 23 gives

$$\frac{t'_{Rz+1}}{t'_{Rz}} = \frac{[A - (1/A^z)]}{[1 - (1/A^z)]} \tag{24}$$

which is identical to Ševčík and Löwentap's equation (eqn. 16). Therefore, by this simple modification, all anomalies have been removed and the expression of Ševčík and Löwentap confirmed.

ALTERNATIVE II

Assume that the net retention time of a theoretical alkane having a carbon number of zero is  $e^c$ . Substituting this into eqn. 1 gives

$$\ln(e^c) = b \cdot 0 + c \tag{25}$$

which yields a valid expression.

Because, with this alternative explanation, eqn. 17 is now valid, it is necessary to review the Ševčík-Löwentap derivation. This derivation (eqn. 12) assumes that  $t'_{R1}$  is  $\Delta_1$  which is the time difference between between the elution of a substance with  $I = 0$  and one with  $I = 100$ . However, this alternative assumes that  $t'_{R0} = e^c$  and thus  $t'_{R1} = e^c + \Delta_1$ . Eqn. 12 can therefore be rewritten as

$$t'_{Rz} = e^c + \Delta_z(1 + A^{-1} + A^{-2} + \dots + A^{2-z} + A^{1-z}) \tag{26}$$

As before, this is a geometric series and can be summed as follows

$$\begin{aligned} t'_{Rz} &= e^c + \Delta_z \cdot \frac{(A^{z+1} - A)}{(A^{z+1} - A^z)} \\ &= \frac{e^c \cdot (A^{z+1} - A^z) + \Delta_z \cdot (A^{z+1} - A)}{(A^{z+1} - A^z)} \end{aligned} \tag{27}$$

Similarly

$$t'_{Rz+1} = \frac{e^c \cdot (A^{z+1} - A^z) + \Delta_z \cdot (A^{z+2} - A)}{(A^{z+1} - A^z)} \quad (28)$$

Dividing eqn. 28 by eqn. 27 gives

$$\frac{t'_{Rz+1}}{t'_{Rz}} = \frac{e^c \cdot (A^{z+1} - A^z) + \Delta_z \cdot (A^{z+2} - A)}{e^c \cdot (A^{z+1} - A^z) + \Delta_z \cdot (A^{z+1} - A)} \quad (29)$$

Now

$$\Delta_z = A^{z-1} \cdot \Delta_1$$

Also

$$\begin{aligned} \Delta_1 &= t_{R1} - t_{R0} \\ &= e^b \cdot e^c - e^c \\ &= e^c \cdot (A - 1) \end{aligned}$$

Thus

$$\Delta_z = A^{z-1} \cdot e^c \cdot (A - 1) \quad (30)$$

Substituting eqn. 30 into eqn. 29 gives

$$\frac{t'_{Rz+1}}{t'_{Rz}} = \frac{A^{2z+2} - A^{2z+1}}{A^{2z+1} - A^{2z}} \quad (31)$$

Rearranging produces

$$\begin{aligned} \frac{t'_{Rz+1}}{t'_{Rz}} &= \frac{A^2 - A}{A - 1} \\ &= A \quad (A \neq 1) \end{aligned} \quad (32)$$

which is the required equation.

Therefore this alternative resolves the conflict between the Ševčík-Löwentap derivation and eqn. 17. One other point to be made with this method is that it predicts that the retention index of an unretained substance is undefined. This occurs when  $t_{R(\text{unretained})} = t_M$  is substituted into eqn. 1 leading to  $\ln(0)$  which is undefined.

Finally, some comment should be made on the consequences of these two alternative explanations. The most important point to note is that the calculation of retention indices is not effected by either method. For the first alternative, the constant  $e^c$  can be combined with  $t_M$  and thought of as a single entity, say  $t'_M$  (the mathematical dead time). Therefore all statistical and iterative methods of calculating Kováts indices will operate without modification.

However, with this first alternative it is obvious that the calculation of dead

time, when carried out for purposes other than as an intermediate step in the calculation of other parameters, will be effected. In fact, it can be seen from eqn. 20 that the column dead time will vary from the mathematical dead time by an amount that is dependent on the stationary phase and temperature, since it is equal to  $e^c$ , which is dependent on the system conditions. We believe that this may explain the difficulty in the literature in equating the mathematical dead time to the retention time of an "unretained" substance.

Also eqn. 24 shows that, with this alternative, relative retention is not constant, but varies with carbon number. It does, however, rapidly approach a constant value with increasing carbon number and for realistic values of  $A$ , is not significantly different above a carbon number of four or five.

It should also be noted that this alternative provides an explanation for the very large variations in mathematical dead time reported by us in a recent paper<sup>3</sup>, when fitting higher degree polynomials. In these cases the constant  $d$  is no longer  $e^c$  but is itself, the solution of a higher order equation. It can thus take on a wide range of values, which will differ depending on the degree of the polynomial that is being fitted to the raw retention data.

On the other hand, the second alternative equates the mathematical dead time to the actual column dead time and supports the view that relative retention is constant, even at low carbon numbers. With this alternative, the variation of dead time when higher degree polynomials are fitted must be put down to extrapolation errors. This alternative also predicts that the carbon number of an unretained substance is undefined, whereas the first alternative predicts a value of 0.

As our purpose in writing this paper was to stimulate thought on the matter, we will conclude with Table I which is a summary of the major differences between the two alternative explanations. We believe that further discussion on the matter is necessary before a decision can be made as to the most satisfactory explanation for the points which we have raised.

TABLE I

COMPARISON OF MAJOR DIFFERENCES BETWEEN TWO ALTERNATIVE EXPLANATIONS OF ANOMALIES WITH KOVÁTS' RETENTION INDEX EQUATION

<i>Alternative I</i>	<i>Alternative II</i>
$t_{RO} = 0$	$t_{RO} = e^c$
$t_{R(\text{unretained})} = 0$	$t_{R(\text{unretained})} = \text{undefined}$
$t_{M(\text{calc.})} = t_{M(\text{actual})} - e^c$	$t_{M(\text{calc.})} = t_{M(\text{actual})}$
$\frac{t'_{Rz+1}}{t'_{Rz}} = \frac{[A - (1/A^z)]}{[1 - (1/A^z)]}$	$\frac{t'_{Rz+1}}{t'_{Rz}} = A$

## REFERENCES

- 1 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 334 (1985) 95.
- 2 J. Ševčík and M. S. Löwentap, *J. Chromatogr.*, 147 (1978) 75.
- 3 R. J. Smith, J. K. Haken, M. S. Wainwright and B. G. Madden, *J. Chromatogr.*, 328 (1985) 11.