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DETERMINATION OF THE RELATIONSHIP BETWEEN RETENTION INDEX AND COLUMN TEMPERATURE IN GAS CHROMATOGRAPHY THROUGH THE TEMPERATURE-DEPENDENCE OF THE NET RETENTION VOLUME

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SUMMARY

By working with one of the most characteristic fundamentals of gas chromatography, *viz.* the net retention volume, we have shown that the temperature-dependence of the retention index may be generally determined by an equation of Antoine-type:

$$I_{\text{substance}}^{\text{stationary phase}}(T) = A + \frac{B}{T + C}$$

The three constants of the equation depend only on the material quality of the substance and of the stationary phase and can easily be determined from experimental results. In this work we also describe the relationships necessary for the definition in question. Furthermore, we were able to show that in spite of the fact that the graphic image of the Antoine-type equation is a hyperbola, in the temperature-interval used in gas chromatography this plot has a linear section. Finally we present some practical examples for the application of the equation.

INTRODUCTION

In qualitative analytical gas chromatography the identification of the individual peaks of a chromatogram is generally effected by means of pure standard substances. However, we only have limited quantities of these at our disposal, therefore for a complete qualitative analysis we need other methods as well. A very suitable method for this purpose is the retention index system of KOVÁTS[1], the application of which makes qualitative analysis possible without requiring any standard substances. In practice, however, there is a serious problem because the retention index depends not only on the quality of the material but also on the column temperature. This latter question has been investigated by a number of workers[2–13], but in spite of their remarkable findings they could not agree about the solution of this question. While engaged in studies on the applicability of the retention index we obtained results[14] from programmed flow gas chromatography which made it clear that the question must be approached in the first place by mathematical methods. By this means, with the help of specific retention volumes, we were able to show[15] that the temperature-dependence of the retention index may generally be determined by an Antoine-type equation.

Seeing however that this evidence is based on specific retention volumes, in spite of the latter being incontestable in principle, from practical considerations it seemed more convenient to base the demonstration on a more characteristic constant of gas chromatography, *viz.* the net retention volume, as this value can be precisely determined experimentally whereas the specific retention volume is uncertain on account of the doubt concerning the effective mass of the stationary phase.

THEORY

In an earlier paper[16] we demonstrated that the temperature-dependence of the net retention volume can generally be represented by the following equation:

$$V_N = T \cdot 10^{m \cdot \frac{1}{T} + b} \tag{1}$$

where

V_N = net retention volume (ml carrier gas)
T = column temperature (°K)
m = slope of the straight line[13]
b = axial section Y of the straight line[13]

Now taking the logarithm of both sides of eqn. (1) we get:

$$\log V_N = \log T + m \cdot \frac{1}{T} + b \tag{2}$$

Next, let us write the definition of the retention index in terms of the net retention volumes[4]

$$I_T^{\text{stationary phase}}(x) = 100 \left[\frac{\log V_N(x) - \log V_N(nP_z)}{\log V_N(nP_{z+1}) - \log V_N(nP_z)} + z\right] \tag{3}$$

stipulating that:

$$V_N(nP_z) \leqq V_N(x) \leqq V_N(nP_{z+1}) \tag{4}$$

where

I = the symbol for the retention index
x = the symbol for the unknown substance
(nP_z) = the symbol for a normal paraffin hydrocarbon of carbon number "z"
(nP_{z+1}) = the symbol for a normal paraffin hydrocarbon of carbon number "$z + 1$"
z = the carbon number

Then, substituting the terms from eqn. (2) into eqn. (3):

$$I_T^{\text{st.ph.}}(x) = 100 \left[\frac{\log T + m_x \cdot \frac{1}{T} + b_x - \log T - m_{(nP_z)} \cdot \frac{1}{T} - b_{(nP_z)}}{\log T + m_{(nP_{z+1})} \cdot \frac{1}{T} + b_{(nP_{z+1})} - \log T - m_{(nP_z)} \cdot \frac{1}{T} - b_{(nP_z)}} + z \right] \quad (5)$$

where st.ph. is the symbol for the stationary phase. As T is constant, eqn. (5) can be simplified to the following form:

$$I_T^{\text{st.ph.}}(x) = 100 \left[\frac{(m_x - m_{(nP_z)}) \cdot \frac{1}{T} + (b_x - b_{(nP_z)})}{(m_{(nP_{z+1})} - m_{(nP_z)}) \cdot \frac{1}{T} + (b_{(nP_{z+1})} - b_{(nP_z)})} + z \right] \quad (6)$$

or:

$$I_T^{\text{st.ph.}}(x) = 100 \left[\frac{(b_x - b_{(nP_z)}) \cdot T + (m_x - m_{(nP_z)})}{(b_{(nP_{z+1})} - b_{(nP_z)}) \cdot T + (m_{(nP_{z+1})} - m_{(nP_z)})} + z \right] \quad (7)$$

On introducing the following symbols

$$B_x = 100(b_x - b_{(nP_z)}) \quad (8)$$

$$M_x = 100(m_x - m_{(nP_z)}) \quad (9)$$

$$B_1 = (b_{nP_{z+1})} - b_{(nP_z)}) \quad (10)$$

$$M_1 = [m_{(nP_{z+1})} - m_{(nP_z)}) \quad (11)$$

eqn. (7) may then be written as follows:

$$I_T^{\text{st.ph.}}(x) = 100z + \frac{B_xT + M_x}{B_1T + M_1} \quad (12)$$

With a common denominator for the right hand side of the eqn. (12) we get:

$$I_T^{\text{st.ph.}}(x) = \frac{B_xT + M_x + 100zB_1T + 100zM_1}{B_1T + M_1} \quad (13)$$

which can be contracted to:

$$I_T^{\text{st.ph.}}(x) = \frac{(B_x + 100zB_1) \cdot T + (M_x + 100zM_1)}{B_1T + M_1} \quad (14)$$

When the following symbols are introduced:

$$a = (B_x + 100zB_1) \quad (15)$$

$$c = (M_x + 100zM_1) \quad (16)$$

eqn. (14) may be written as follows:

$$I_T^{\text{st.ph.}}(x) = \frac{aT + c}{B_1T + M_1} \quad (17)$$

Eqn. (17) can be given in another form:

$$I_T^{\text{st.ph.}}(x) = \frac{a}{B_1} \cdot \frac{T + \frac{c}{a}}{T + \frac{M_1}{B_1}} \quad (18)$$

On adding and subtracting the term M_1/B_1 to the second factor on the right side of eqn. (18), we get:

$$I_T^{\mathrm{st.ph.}}(x) = \left(\frac{a}{B_1}\right) \cdot \left[\frac{T + \frac{c}{a} + \frac{M_1}{B_1} - \frac{M_1}{B_1}}{T + \frac{M_1}{B_1}}\right] \tag{19}$$

Eqn. (19) can be rewritten as:

$$I_T^{\mathrm{st.ph.}}(x) = \left(\frac{a}{B_1}\right) \cdot \left[\frac{T + \left(\frac{M_1}{B_1}\right)}{T + \left(\frac{M_1}{B_1}\right)} + \frac{\left(\frac{c}{a}\right) - \left(\frac{M_1}{B_1}\right)}{T + \left(\frac{M_1}{B_1}\right)}\right] \tag{20}$$

which after dividing by $(T + M_1/B_1)$ and multiplying out gives:

$$I_T^{\mathrm{st.ph.}}(x) = \left(\frac{a}{B_1}\right) + \frac{\dfrac{B_1c - M_1a}{B_1^2}}{T + \left(\frac{M_1}{B_1}\right)} \tag{21}$$

On introducing the following symbols:

$$A = \left(\frac{a}{B_1}\right) \tag{22}$$

$$B = \left(\frac{B_1c - M_1a}{B_1^2}\right) \tag{23}$$

$$C = \left(\frac{M_1}{B_1}\right) \tag{24}$$

eqn. (21) will now take the form:

$$I_T^{\mathrm{st.ph.}}(x) = A + \frac{B}{T + C} \tag{25}$$

which can be seen to be an equation of the Antoine-type.

Because the determination of the retention index depends on the column temperature, the manner of denoting the retention index used up to now is altered and takes the following form:

$$I_{\mathrm{substance}}^{\mathrm{st.ph.}}(T) = A + \frac{B}{T + C} \tag{26}$$

Three equations are needed for the determination of the value of the three constants occurring in eqn. (26); these three equations can be written:

$$I_1 = A + \frac{B}{T_1 + C} = \frac{AT_1 + AC + B}{T_1 + C} \tag{27}$$

$$I_2 = A + \frac{B}{T_2 + C} = \frac{AT_2 + AC + B}{T_2 + C} \tag{28}$$

$$I_3 = A + \frac{B}{T_3 + C} = \frac{AT_3 + AC + B}{T_3 + C} \tag{29}$$

Multiplying eqns. (27) and (28) by their denominators, we get:

$$I_1T_1 + I_1C = AT_1 + AC + B \qquad (30)$$

$$I_2T_2 + I_2C = AT_2 + AC + B \qquad (31)$$

On subtracting eqn. (30) from eqn. (31):

$$I_2T_2 - I_1T_1 + C(I_2 - I_1) = A(T_2 - T_1) \qquad (32)$$

As eqn. (32) still contains two unknown quantities (A, C) eqn. (29) is also multiplied by its denominator to give:

$$I_3T_3 + I_3C = AT_3 + AC + B \qquad (33)$$

which after subtracting eqn. (30) from it is:

$$I_3T_3 - I_1T_1 + C(I_3 - I_1) = A(T_3 - T_1) \qquad (34)$$

"A" from eqn. (32) is now substituted into eqn. (34):

$$I_3T_3 - I_1T_1 + C(I_3 - I_1) = \left[\frac{I_2T_2 - I_1T_1 + C(I_2 - I_1)}{(T_2 - T_1)}\right](T_3 - T_1) \qquad (35)$$

Thus, eqn. (35) contains only one unknown quantity (C), and this may be expressed as:

$$C = \frac{(T_2 - T_1)(I_3T_3 - I_1T_1) + (T_3 - T_1)(I_1T_1 - I_2T_2)}{(T_3 - T_1)(I_2 - I_1) - (T_2 - T_1)(I_3 - I_1)} \qquad (36)$$

If the value determined for "C" is introduced into eqn. (34), "A" is determined from:

$$A = \frac{I_3T_3 - I_1T_1 + C(I_3 - I_1)}{(T_3 - T_1)} \qquad (37)$$

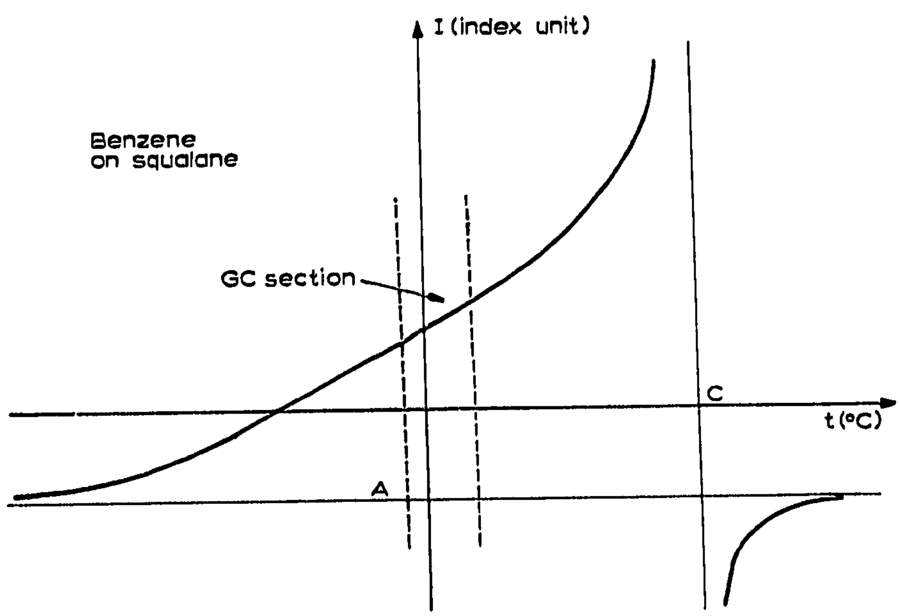

Fig. 1. The general plot of the equation describing the temperature dependence of the retention index in the case of an apolar (squalane) stationary phase.

Knowing "A" and "C", "B" may be calculated by means of eqn. (33):

$$B = I_3T_3 + I_3C - A(T_3 + C) \tag{38}$$

Thus, as we know all three constants of the equation describing the dependence of the retention index on the column temperature, the retention index on a given stationary phase is available for all column temperatures.

The general plot of the Antoine-type equation describing the temperature dependence of the retention index is a hyperbola, as shown in Figs. 1 and 2.

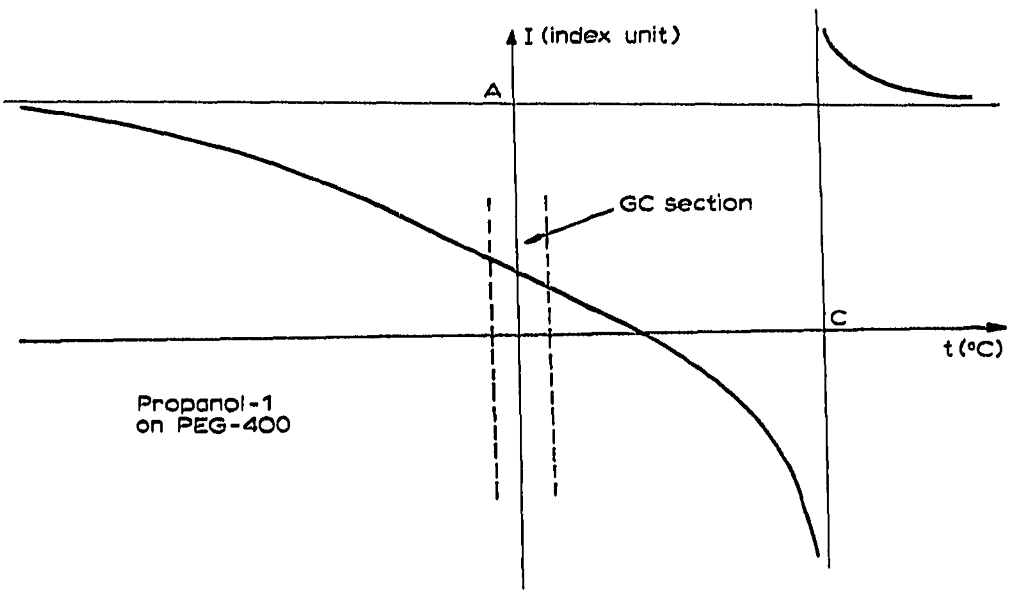

Fig. 2. The general plot of the equation describing the temperature dependence of the retention index in the case of a polar (PEG-400) stationary phase.

It is clearly visible from the plots shown in Figs. 1 and 2 that they have a linear section in the temperature interval used in practice in gas chromatography. Thus as a first approximation, the procedure used up to now, which assumed a linear relationship between column temperature and retention index, is acceptable. However, we must mention that disregard of eqn. (25) may in some cases result in considerable errors, chiefly when columns with a polar stationary phase are used.

Before proceeding to the experimental part we should like to point out that it could so happen that the denominator of eqn. (36) is zero. In this case:

$$(T_3 - T_1)\,(I_2 - I_1) = (T_2 - T_1)\,(I_3 - I_1) \tag{39}$$

Re-arranging this equation:

$$T_3(I_2 - I_1) + T_1(I_3 - I_2) = T_2(I_3 - I_1) \tag{40}$$

Eqn. (40) makes it possible for us to prevent the denominator of eqn. (36) eventually becoming zero without considerably influencing the determination of the dependence of the retention index on the column temperature. For, if we become aware that eqn. (40) is valid, we then add 0.1 to the value of $(I_3 - I_1)$. In the experimental part we shall come back to this case in connection with a concrete example.

EXPERIMENTAL

As indicated in the theoretical part, to calculate the retention index–temperature dependence, we need to know the constants of the Antoine-type equation. The determination of these is done by measuring the index-values (I_1, I_2 and I_3) at three different temperatures (T_1, T_2 and T_3), and then calculating the constants from eqns. (36), (37) and (38).

As an example, the calculation of the constants of the equation describing the temperature dependence of the retention index of limonene is presented. The measurements were done on an Apiezon L stationary phase and gave the results summarized in Table I.

The partial results necessary for the calculation are given in Table II.

TABLE I

TEMPERATURE AND INDEX-VALUES DETERMINED ON APIEZON L

Serial number of measurement	*Temperature*		*Measured index (index units)*
	(°C)	*(°K)*	
1	130	403	1061
2	150	423	1066
3	170	443	1073

TABLE II

PARTIAL RESULTS NECESSARY FOR THE CALCULATION OF THE CONSTANTS A, B AND C

$(T_2 - T_1)$	20
$(T_3 - T_1)$	40
I_1T_1	427 583
I_2T_2	450 918
I_3T_3	475 339
$(I_2 - I_1)$	5
$(I_3 - I_1)$	12

Substituting the respective values from Table II into eqn. (36) we get:

$$C = \frac{20(475339-427583) + 40(427583-450918)}{40\cdot5-20\cdot12} = \frac{955120-933400}{(-40)} =$$

$$= -\frac{21720}{40} = -543 \qquad (41)$$

Similarly the value of constant "A" is given by eqn. (37):

$$A = \frac{475339-427583-543\cdot12}{40} = \frac{47756-6516}{40} = \frac{41240}{40} = 1031 \qquad (42)$$

Finally the value of constant "B" is determined from eqn. (38):

$$B = 475339 - 543\cdot1073 - 1031(443 - 543) = 475339 - 582639 +$$
$$+ 103100 = -4200 \qquad (43)$$

After this the temperature dependence of the retention index of limonene on Apiezon L stationary phase may be expressed:

$$I_{\text{Limonene}}^{\text{Apiezon L}}(T) = 1031 - \frac{4200}{T-543} \tag{44}$$

As we had at our disposal an index value observed at another temperature as well as corresponding literature data[3] it was possible to compare the measured index value with those calculated by eqn. (26). The data used in the course of the comparison as well as the results obtained are given in Table III.

TABLE III

COMPARISON OF RETENTION INDEX DATA

Temperature (°K)	*Retention index (index units)*				
	Experimental	*Literature data*[3]	*Average of experimental values*	*Calculated by eqn. (26)*	*Divergence from the average experimental values*
403	1061	1060	1060.5	1061.0	+0.5
423	1066	1067	1066.5	1066.0	−0.5
443	1073	1074	1073.5	1073.0	−0.5
463	1084	1081	1082.5	1083.5	+1.0

The relationship between the retention index of limonene and column temperature on an Apiezon L stationary phase is shown in Fig. 3.

In Figs. 1, 2 and 3, it is clearly visible that the relationship between the retention index and column temperature over the temperature interval usual in gas chromatography may have shorter or longer linear sections.

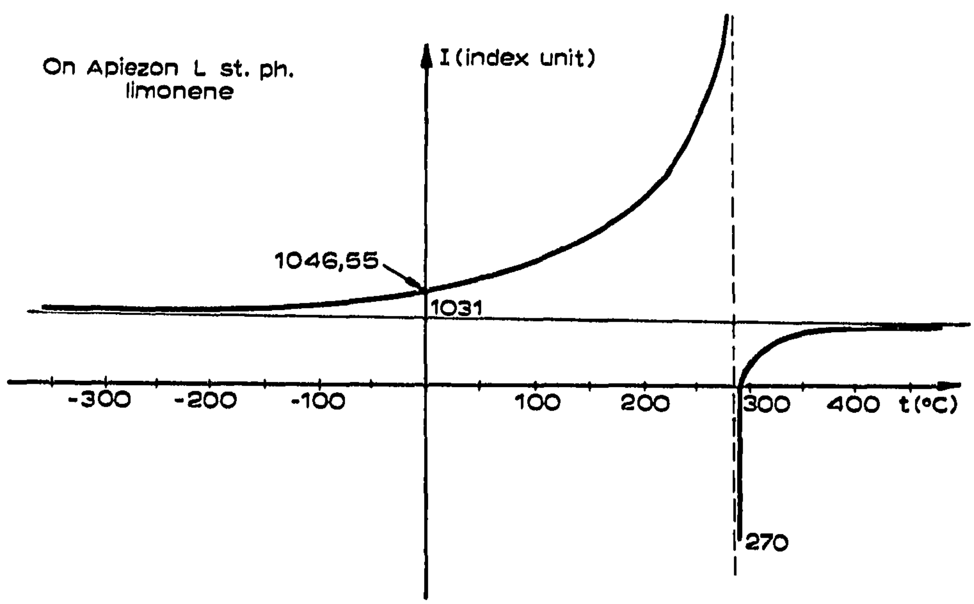

Fig. 3. Change of the retention index of limonene with respect to the column temperature, on an Apiezon L stationary phase.

Finally, we return to the case mentioned in the theoretical part, where the denominator of eqn. (36) becomes zero. Such a case actually happened, among others, while we were examining the temperature relationship of the retention index of hexanol-1 on a PEG-400 stationary phase; the data are summarized in Table IV.

TABLE IV

TEMPERATURE RELATIONSHIP OF THE RETENTION INDEX OF HEXANOL-1 ON A PEG-400 STATIONARY PHASE

Temperature (°K)	*Retention index (index units)*
$T_1 = 373$	$I_1 = 1076$
$T_2 = 393$	$I_2 = 1072$
$T_3 = 413$	$I_3 = 1068$
$(T_2 - T_1) = 20$	
$(T_3 - T_1) = 40$	
$I_1T_1 = 401\,348$	
$I_2T_2 = 421\,296$	
$I_3T_3 = 441\,084$	
$(I_2 - I_1) = (-4)$	
$(I_3 - I_1) = (-8)$	
$(I_3 - I_2) = (-4)$	

Substituting in eqn. (40):

$$413 \cdot (-4) + 373 \cdot (-4) = 393 \cdot (-8) \tag{45}$$

i.e.

$$-3144 = -3144 \tag{46}$$

the equality of the equation (40) was valid. In order to solve this anomaly (the denominator of the fraction must not be zero) we resorted to the step of adding 0.1 to the difference $(I_3 - I_1)$. This solution to the problem led to the equation as given below:

$$I^{\text{PEG-400}}_{\text{hexanol-1}}(T) = 1317.4 + \frac{296197.8}{T - 1600} \tag{47}$$

To demonstrate that the above step has not essentially influenced the reliability of the data obtained by eqn. (47), giving the temperature dependence of the hexanol-1 retention index on a PEG-400 stationary phase, we compared the literature data[16] with that calculated by eqn. (47). The results are shown in Table V.

TABLE V

COMPARISON OF RETENTION INDEX DATA

Temperature (°K)	*Literature data[13] (index units)*	*Calculated values (index units)*
373	1076	1076.0
393	1072	1072.0
413	1068	1067.9

It should be mentioned that the calculations may also be done by a computer. We must not forget, however, when programming the computer, that the denominator of eqn. (36) must not become zero, and therefore the method advised for the solution of this problem must also be programmed.

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SYMBOLS

I	= retention index
st.ph.	= stationary phase
T	= column temperature
A, B, and C	= constants of Antoine-type equation
V_N	= net retention volume
m	= slope of the straight line
b	= axial section Y of the straight line
x	= the symbol for the unknown substance
$(n\mathrm{P}_z)$	= the symbol for normal paraffin hydrocarbon of carbon number "z"
$(n\mathrm{P}_{z+1})$	= the symbol for normal paraffin hydrocarbon of carbon number "$z + 1$"
z	= carbon number
B_x	$= 100(b_x - b_{(n\mathrm{P}_z)})$
M_x	$= 100(m_x - m_{(n\mathrm{P}_z)})$
B_1	$= (b_{(n\mathrm{P}_{z+1})} - b_{(n\mathrm{P}_z)})$
M_1	$= (m_{(n\mathrm{P}_{z+1})} - m_{(n\mathrm{P}_z)})$
a	$= B_x + 100zB_1$
c	$= M_x + 100zM_1$
PEG-400	= polyethyleneglycol-400

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