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DEFINITIONS AND METHODS OF CALCULATION OF THE TEMPERATURE-PROGRAMMED RETENTION INDEX, I_{TP}

II. COMPARISON OF I_{TP} VALUES CALCULATED ACCORDING TO DIFFERENT DEFINITIONS

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SUMMARY

Temperature-programmed retention indices, I_{TP}, calculated according to three different definitions are compared. The advantages and shortcomings of these definitions are discussed in terms of their theoretical background, accuracy, ease of calculation and applicability. The Generalized Retention Index (GI) seems to be the best definition of I_{TP}, while Van den Dool's definition and the Extended Kováts Definition are approximate and can be applied only to simple temperature programme.

INTRODUCTION

In the previous paper[1], three definitions of temperature-programmed retention indices, I_{TP}, were considered: that of Van den Dool and Kratz (see Part I, eqn. 2a and b) (I_D); the Extended Kováts Definition (having the same form as eqn. 1) (I_E); the Generalized Retention Index (GI) (see eqn. 6). The first and the third definitions are different in principle, the second seems to be inexact.

In fact, eqn. 2b is not an independent definition of I_{TP}, being only a transformation of eqn. 2a, and cannot be used for temperature programmes containing isothermal steps. Nevertheless, some chromatographers have used it for such programs for convenience. In this paper, eqn. 2b is taken as a method of I_{TP} calculation for isothermal steps and compared with other methods.

EXPERIMENTAL

The equipment and techniques used were similar to those described in the previous paper[1].

The dead time at the initial column temperature was calculated according to Tóth and Zala's iterative method[2] using n-alkanes, C_6–C_{10} for an OV-101 column and C_9–C_{13} for a PEG-20M column.

RESULTS AND DISCUSSION

In our opinion, an ideal definition of I_{TP} should be in accord with theory, applicable to any temperature programme, easy to calculate and accurate compared with the experimental precision.

Generalized Retention Index (GI)

The GI has a close theoretical relationship to Kováts definition which has been studied in detail and used widely, therefore, it is expected to be suitable for correlation between I_{TP} and I_i (isothermal retention index) or thermodynamic parameters, etc. From the previous paper[1] it is seen that GI is applicable to any temperature programme, and its accuracy is excellent. So, in the present study, we regard it as the standard value of I_{TP}.

The shortcoming of GI is that all the constants needed have to be redetermined when the temperature programme is varied, and the calculation procedure is tedious.

Van den Dool's definition

In this definition, the application of a linear interpolation yields an approximation to the relationship between I_{TP} and T_R or t_R for n-alkanes as is shown in Fig. 1. The differences between I_D (I_{TP} calculated by eqn. 2b) and GI are given in Tables I and II. It is seen that during the early stage of a heating step as well as the final isothermal step, I_D is 1–7 i.u. smaller than GI, while during the later stage of a heating step, I_D is 0.4–0.6 i.u. larger than GI, except for a complex temperature programme
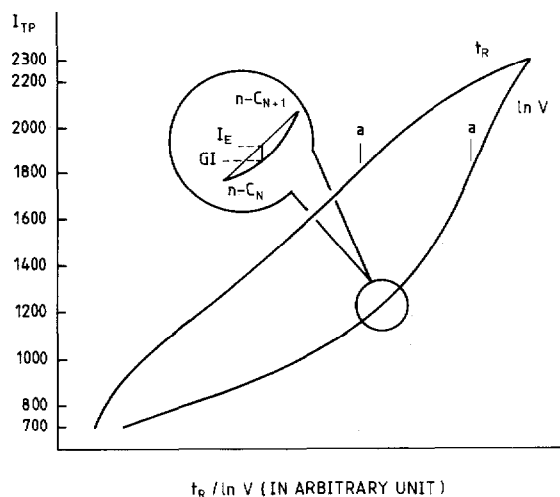

t_R / ln V (IN ARBITRARY UNIT)

Fig. 1. Experimental curves of I_{TP} *versus* t_R/ln V for n-alkanes on an OV-101 column, from 80 to 240°C at 6°C/min. For GI and I_E see the text. At a (I_{TP} = 1800 i.u.) the column temperature reaches the final isothermal stage.

TABLE I

COMPARISON OF I_{TP} CALCULATED BY DIFFERENT DEFINITIONS

OV-101 column, 80 to 240°C at 6°C/min.

Hypothetical compound	Program step	$I_D{}^\star$	$I_E{}^\star$	GI	$I_D - GI$	$I_E - GI$	$I_D - I_E$
A	Heating at	750.5	757.9	756.9	−6.4	1.0	−7.4
B	6°C/min	849.7	856.3	854.3	−4.6	2.0	−6.6
C		950.0	955.6	952.7	−2.7	2.9	−5.6
D		1050.2	1054.7	1051.4	−1.2	3.3	−4.5
E		1150.2	1153.7	1150.6	−0.4	3.1	−3.5
F		1250.0	1252.8	1250.0	0.0	2.8	−2.8
G		1350.0	1352.3	1349.5	0.5	2.8	−2.3
H		1450.0	1451.9	1449.4	0.6	2.5	−1.9
I		1550.0	1551.6	1549.4	0.6	2.2	−1.6
J		1650.0	1651.4	1649.5	0.5	1.9	−1.4
K		1750.3	1751.5	1749.8	0.5	1.7	−1.2
L	Isothermal	1850.3	1851.2	1852.0	−1.7	−0.8	−0.9
M		1950.2	1951.2	1952.1	−1.9	−0.9	−1.0
N		2050.2	2051.2	2052.4	−2.2	−1.2	−1.0
O		2150.2	2151.3	2152.9	−2.7	−1.6	−1.1
P		2250.0	2251.3	2253.6	−3.6	−2.3	−1.3

$\star$ I_D = I_{TP} calculated according to Van den Dool's definition; I_E = I_{TP} calculated according to the Extended Kováts Definition.

TABLE II

COMPARISON OF I_{TP} CALCULATED BY DIFFERENT DEFINITIONS

OV-101 column, 80°C for 5 min, then to 136°C at 2°/min, and to 240°C at 9°C/min.

Hypothetical compound	Program step	I_D	I_E	GI	$I_D - GI$	$I_E - GI$	$I_D - I_E$
A	Isothermal	750.0	758.7	—	—	—	−8.7
B	Heating at	850.2	858.6	857.2	−7.0	1.4	−8.4
C	2°C/min	950.0	957.3	954.6	−4.6	2.7	−7.3
D		1050.1	1055.9	1052.3	−2.2	3.6	−5.8
E		1150.1	1154.5	1150.9	−0.8	3.6	−4.4
F		1250.0	1253.4	1250.2	−0.2	3.2	−3.4
G	9°/min	1350.1	1352.8	1340.6	9.5	12.2	−2.7
H		1450.0	1451.4	1445.6	4.4	5.8	−1.4
I		1550.0	1551.0	1547.1	2.9	3.9	−1.0
J		1650.3	1651.1	1648.1	2.2	3.0	−0.8
L	Isothermal	1850.3	1850.7	1852.1	−1.8	−1.4	−0.4
M		1950.0	1950.5	1952.1	−2.1	−1.6	−0.5
N		2050.2	2050.8	2052.6	−2.4	−1.8	−0.6
O		2150.2	2150.8	2153.1	−2.9	−2.3	−0.6
P		2250.1	2250.9	2253.7	−3.6	−2.8	−0.8

(see Table II). The larger differences usually occur in smaller values of I_{TP} and this becomes a serious obstacle to a correlation of I_{TP} and I_i.

In previous work[3] on the correlation of I_{TP} and I_i we found some anomalous results: the I_{TP} values of some compounds having a positive $\Delta I/\Delta T$ value were smaller than their I_i values at the initial column temperature. This can be explained by an unsuitable choice of calculation methods. When Van den Dool's definition is used for calculating I_{TP}, the anomalies occur, while use of the Extended Kováts Definition or GI results in no anomalies.

For a complex temperature programme (see Table II), when the heating rate is changed from a smaller to a large value, the difference $I_D - GI$ becomes considerably larger (9.5 i.u.), so eqn. 2b seems not to be applicable in such a situation.

The advantage of Van den Dool's definition is the ease of calculation.

Extended Kováts Definition

This definition is only approximate. From Fig. 1 it is evident that the relationship between I_{TP} and ln V for n-alkanes is non-linear. For the definition to be applicable in such a case, the curve has to be visualized as a set of successive straight lines. The error thus introduced has been studied experimentally and the results are given in Tables I and II.

It is seen that I_E (calculated by eqn. 1) is always larger than GI during a heating step because the I_{TP} *vs.* ln V curve at this stage is concave downwards (see Fig. 1), while I_E is always smaller than GI during the final isothermal step because the curve is then convex upwards. For simple temperature programme (Table I) the absolute differences $I_E - GI$ are mainly in the range 1–3 i.u. and do not change greatly with variation of the heating rate. However, for complex temperature programmes (see Table II), when the heating rate is changed from a lower to a higher value, the difference $I_E - GI$ becomes considerably larger, up to 12.2 i.u. Therefore, the Extended Kováts Definition seems not to be universally applicable.

It should be emphasized that the data in Tables I and II represent almost the maximum differences between two consecutive n-alkanes. When the t_R or V values of hypothetical compounds are chosen to be similar to those of n-alkanes, $I_{TP} \rightarrow (100N)$i.u., the differences become smaller and smaller and finally approach zero.

The results obtained on a PEG-20M column were similar to those on an OV-101 column.

CONCLUSIONS

(1) GI seems to be the best definition of I_{TP} except as regards the complexity of calculation. When accurate I_{TP} values are needed, GI should be used.

(2) Van den Dool's definition and the Extended Kováts Definition are approximate methods for calculating I_{TP} and can be applied only to simple temperature programme. Either equation has its merits and shortcomings.

(3) Van den Dool's definition is not closely related to GI and I_i. At the early stage of a simple temperature programme without an initial isothermal step, the I_{TP} values calculated by eqn. 2a or b may be 7 i.u. smaller than GI and may give rise to anomalous results in the correlation between I_{TP} and I_i.

(4) The extended Kováts Definition is an approximate method of calculating

I_{TP} and is applicable only to simple temperature programmes without or with shorter initial isothermal steps. In these cases, the difference $I_E - GI$ is about 1–3 i.u.

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