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## CALCULATION OF RETENTION INDICES IN TEMPERATURE-PROGRAMMED CAPILLARY GAS CHROMATOGRAPHY

AN ZHU

*Institute of Chemistry, Academia Sinica, Zhong Guan Cun, 100 080 Beijing (China)*

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### SUMMARY

Previously reported methods for calculating retention indices in temperature-programmed gas chromatography (TPGC) were restricted either to a simple linear temperature increase without a constant temperature stage, or to a complicated temperature programme operated at a constant mass flow-rate. The present method is applicable to complicated temperature programmes operated at constant pressure, which is the common practice in most applications of capillary GC.

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### INTRODUCTION

In the determination of retention indices, highly efficient (capillary) columns are always needed in order to obtain accurate and reliable data. If capillary gas chromatography (GC) is applied with temperature programming, difficulties arise in handling the results. Van den Dool and Kratz<sup>1</sup> used the retention temperature to calculate the retention index:

$$I = \frac{T_{R(x)} - T_{R(n)}}{T_{R(n+i)} - T_{R(n)}} \cdot 100i + 100n \quad (1)$$

which although simple, is restricted to a simple linear temperature increase without a constant temperature stage. The method proposed by Majlát *et al.*<sup>2</sup> is comprehensive, and is applicable to multi-ramp and multi-plateau temperature programmes. A prerequisite of their work is that a constant mass flow-rate of the carrier gas should be maintained throughout the GC determination, which can be met with nearly all conventional packed column gas chromatographs. In capillary GC, however, a pressure regulator with no mass flow controller downstream is fitted in most instances. The inlet pressure of the carrier gas is kept constant while the mass flow-rate decreases gradually as the column temperature increases. Apart from this, in calculations using Majlát *et al.*'s equation<sup>2</sup>, the inlet pressure during the emergence of a peak is required, which cannot be automatically recorded; also, Majlát *et al.* did not propose a method for its theoretical prediction.

A method of calculation suitable for constant-pressure operation is described

in this paper. Data obtained with this method for partially methylated glucitol and methyl glucosides have been reported elsewhere<sup>3</sup>. A comparison was made between Van den Dool and Kratz's and our method with a constant-temperature determination.

#### THEORETICAL

The volumetric flow of a gas through a capillary of circular cross-section is<sup>4</sup>

$$F = \frac{\pi r^4 (p_i^2 - p_0^2) j}{16 \eta L p_0} \quad (2)$$

$F$  is defined at the column temperature and under the average column pressure. On the right-hand side of eqn. 2 the only parameter that varies with temperature is the viscosity,  $\eta$ . A correlation between  $\eta$  and  $T$  has been described<sup>5</sup> as

$$\eta = \frac{T^{1/2}}{C_0 + \frac{C_1}{T} + \frac{C_2}{T^2} + \frac{C_3}{T^3} + \frac{C_4}{T^4}} \quad (3)$$

In the temperature range of interest to gas chromatographers, say 50–375°C, eqn. 3 can be approximated by

$$\eta = \frac{T^{1/2}}{A - BT} \quad (4)$$

where  $A$  and  $B$  are constants characteristic of the gas. With recently available data<sup>6</sup>, these constants were obtained by means of statistical regression and are given in Table I.

Combining eqns. 2 and 4, we have

$$F = K(AT^{-1/2} - BT^{1/2}) \quad (5)$$

where  $K$  is a function of pressure and the geometry of the column, and is independent of temperature.

The average flow-rate,  $\bar{F}$ , for a temperature change from  $T_1$  to  $T_2$  is

TABLE I  
CONSTANTS IN EQN. 4 CALCULATED BY STATISTICAL REGRESSION

Temperature range: 320–650°K.

Gas	$A$	$B$	Correlation coefficient	Number of data <sup>6</sup> regressed
Hydrogen	2.1351	$7.442 \cdot 10^{-4}$	-0.99378	14
Nitrogen	1.0548	$3.686 \cdot 10^{-4}$	-0.98116	14
Helium	0.9488	$3.073 \cdot 10^{-4}$	-0.99176	18

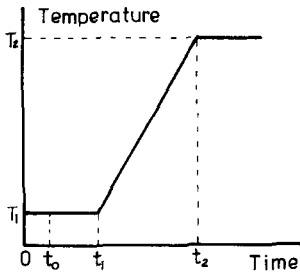


Fig. 1. Schematic diagram of the temperature programme.

$$\bar{F} = \frac{\int_{T_1}^{T_2} FdT}{T_2 - T_1} = K \left[ \frac{2A}{T_1^{1/2} + T_2^{1/2}} - \frac{2B}{3} \cdot \frac{(T_1 + T_2 + T_1^{1/2}T_2^{1/2})}{(T_1^{1/2} + T_2^{1/2})} \right] \quad (6)$$

For the temperature programme shown in Fig. 1, the retention volume can be calculated with one of the following equations according to the location of the peak on the time scale.

*Case I:*  $t_R \leq t_1$

The component elutes at the first temperature plateau.

$$V = K(AT_1^{-1/2} - BT_1^{1/2})(t_R - t_0) \quad (7)$$

*Case II:*  $t_1 < t_R \leq t_2$

The component elutes at the temperature rise stage.

$$V = K(AT_1^{-1/2} - BT_1^{1/2})(t_1 - t_0) + K \left[ \frac{2A}{T_1^{1/2} + T_R^{1/2}} - \frac{2B}{3} \cdot \frac{(T_1 + T_R + T_1^{1/2}T_R^{1/2})}{(T_1^{1/2} + T_R^{1/2})} \right] (t_R - t_1) \quad (8)$$

where  $T_R$  is the retention temperature of the component.

*Case III:*  $t_R > t_2$

The component elutes at the second temperature plateau.

$$V = K(AT_1^{-1/2} - BT_1^{1/2})(t_1 - t_0) + K \left[ \frac{2A}{T_1^{1/2} + T_2^{1/2}} - \frac{2B}{3} \cdot \frac{(T_1 + T_2 + T_1^{1/2}T_2^{1/2})}{(T_1^{1/2} + T_2^{1/2})} \right] (t_2 - t_1) + K(AT_2^{-1/2} - BT_2^{1/2})(t_R - t_2) \quad (9)$$

For more complex (multi-ramp and multi-plateau) temperature programmes, the retention volume can be calculated in a similar way. If, however, there is no first constant temperature stage, that is,  $t_1 = 0$ , the above equations must be modified as follows.

The dead volume,  $V_0$ , is

$$V_0 = Kt_0 \left[ \frac{2A}{T_1^{1/2} + (T_1 + st_0)^{1/2}} - \frac{2B}{3} \cdot \frac{2T_1 + st_0 + T_1^{1/2}(T_1 + st_0)^{1/2}}{T_1^{1/2} + (T_1 + st_0)^{1/2}} \right] \quad (10)$$

Case IV:  $t_1 = 0$ ,  $t_R \leq t_2$

The component elutes at the temperature rise stage.

$$V = Kt_R \left[ \frac{2A}{T_1^{1/2} + (T_1 + st_R)^{1/2}} - \frac{2B}{3} \cdot \frac{2T_1 + st_R + T_1^{1/2}(T_1 + st_R)^{1/2}}{T_1^{1/2} + (T_1 + st_R)^{1/2}} \right] - V_0 \quad (11)$$

Case V:  $t_1 = 0$ ,  $t_R > t_2$

The component elutes after the temperature rise has ended.

$$V = Kt_2 \left[ \frac{2A}{T_1^{1/2} + T_2^{1/2}} - \frac{2B}{3} \cdot \frac{(T_1 + T_2 + T_1^{1/2}T_2^{1/2})}{(T_1^{1/2} + T_2^{1/2})} \right] + K(AT_2^{-1/2} - BT_2^{1/2})(t_R - t_2) - V_0 \quad (12)$$

The retention index is

$$I = \frac{\log V_R - \log V_n}{\log V_{n+i} - \log V_n} \cdot 100i + 100n \quad (13)$$

where the retention volumes decrease in the order  $V_{n+i} > V_R > V_n$ .

## EXPERIMENTAL

### Instruments

A Carlo Erba (Milan, Italy) Model 4160 high-resolution gas chromatograph was used. The column was a Carlo Erba OV-1 bonded phase fused-silica capillary (15 m  $\times$  0.32 mm I.D.) with a flame-ionization detector. The carrier gas was hydrogen at an inlet pressure of 0.28 kg/cm<sup>2</sup> and a splitting ratio of 1:100; the hydrogen fuel gas and the nitrogen and air additives were all at a pressure of 1.0 kg/cm<sup>2</sup>. The injection block temperature was 260°C and the detector temperature was 220°C. The column temperature was increased from 150 to 180°C at a rate of 2°C/min.

*Reagents and chemicals*

The preparation of partially methylated methyl glucosides has been described previously<sup>7</sup>. Other chemicals were of analytical-reagent grade, purchased from Beijing Chemical Plant (Beijing, China).

## RESULTS AND DISCUSSION

The retention indices of more than twenty methylated methyl glucosides determined with different temperature programmes were obtained with differences of not more than 3 RI units for the same compound<sup>7</sup>. For comparison with the previously reported method, the data obtained with a linear temperature increase without a constant temperature stage were calculated by both Van den Dool and Kratz's and the present method and are given in Table II. As another reference, the retention indices determined at constant temperatures are also included in Table II.

Although the results of the two methods agree with those of the constant-temperature determination, the present method differs by less than 0.6%, whereas the Van den Dool and Kratz method may sometimes deviate by more than 1% from the isothermal data, especially with the early eluting components such as 2,3,4,6-tetra-O-methyl methyl- $\alpha$ - and  $\beta$ -glucosides.

## CONCLUSION

A method for the calculation of retention indices for complicated temperature programmes running at a constant column inlet pressure has been derived\*. Experimental results showed that there was good agreement between this method and isothermal determinations, which illustrates the validity of the derivation of the method. The proposed method should be useful for the identification of components in complex mixtures and in the collection of retention data of wide varieties of substances.

## LIST OF SYMBOLS

$A, B, C_0, C_1, C_2, C_3$ and $C_4$	Constants.
$F$	Volumetric flow-rate.
$\bar{F}$	Average flow-rate.
$I$	Retention index.
$j$	Martin and James pressure correction factor.
$K = \frac{\pi r^4 (p_i^2 - p_0^2)}{16Lp_0}$	
$L$	Length of the capillary column.
$n, n + i$	Number of carbon atoms of the $n$ -alkanes, $i = 1$ or $2$ .
$p_i$	Column inlet pressure.

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\* A Basic program for calculations with the present method can be obtained from the author on request.

TABLE II  
RETENTION INDICES OF METHYLATED METHYL GLUCOSIDES CALCULATED BY VAN DEN DOOL AND KRATZ'S AND THE PRESENT METHOD

Column temperature: increased from 150 to 180°C at 2°C/min.

Positions of methyl substitution*	Anomeric form**	<i>I</i>		Constant temperature detn. (170°C)	Difference A***	Relative deviation (%)	Difference B§	Relative deviation (%)
		Van den Dool and Kratz's method	This method					
2,3,4,6	$\beta$	1396	1418	1417	-21	-1.48	1	0.07
2,3,4,6	$\alpha$	1437	1454	1450	-13	-0.90	4	0.28
2,3,6	$\beta$	1553	1571	1566	-13	-0.83	5	0.32
3,4,6	$\beta$	1560	1578	-	-	-	-	-
2,4,6	$\beta$	1580	1599	1593	-13	-0.82	6	0.38
3,4,6	$\alpha$	1585	1605	-	-	-	-	-
2,3,4	$\alpha$	1592	1611	-	-	-	-	-
2,4	$\beta$	1636	1652	-	-	-	-	-
2,6	$\beta$	1657	1669	1663	-6	-0.36	6	0.36
4,6	$\beta$	1693	1696	1692	1	0.06	4	0.24
2,3	$\alpha$	1702	1700	1704§§	-2	-0.12	-4	-0.23
4,6	$\alpha$	1705	1706	-	-	-	-	-
2,6	$\alpha$	1712	1716	1706	6	0.35	10	0.59
2,4	$\alpha$	1732	1742	1735	-3	-0.17	7	0.40
3,4	?	1740	1751	1749§§	-9	-0.51	2	0.11
6	$\beta$	1771	1786	1777	-6	-0.34	9	0.51
2	$\beta$	1783	1799	1790	-7	-0.39	9	0.50
4	$\beta$	1830	1843	1834	-4	-0.22	9	0.49
2	$\alpha$	1839	1851	1843	-4	-0.22	8	0.43
4	$\alpha$	1849	1859	1852	-3	-0.16	7	0.38
3	$\beta$	1866	1874	1868	-2	-0.11	6	0.32

\* All the hydroxy groups not methylated are acetylated.

\*\* Tentative identification.

\*\*\* Difference A = *I* (Van den Dool and Kratz) - *I* (constant-temperature determination).

§ Difference B = *I* (this method) - *I* (constant-temperature determination).

§§ Determined at 160°C.

$p_0$	Column outlet pressure.
$r$	Inner radius of the capillary column.
$s$	Rate of increase of temperature, $s = (T_2 - T_1)/(t_2 - t_1)$ .
$t$	Time.
$T$	Temperature ( $^{\circ}\text{K}$ ).
$T_R$	Retention temperature = $s(t_R - t_1) + T_1$ .
$V$	Retention volume.
$\eta$	Viscosity.

### Subscripts

1	Initial state.
2	Final state.
R or x	Component to be determined.
0	Non-retarding component.

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