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## ITERATIVE METHOD FOR THE CALCULATION OF THE GAS HOLD-UP TIME ON THE BASIS OF NON-ADJUSTED RETENTION TIMES OF CONSECUTIVE HOMOLOGUES IN GAS CHROMATOGRAPHY

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### SUMMARY

This paper presents an iterative method for the calculation of the gas hold-up time ( $t_M$ ) on the basis of non-adjusted retention times of consecutive homologues. The values of  $t_M$  were determined by an iterative algorithm. A comparison of the  $t_M$  values, calculated by the iterative method and other methods for homologues of *n*-alkanes and fatty acid methyl esters, was made.

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### INTRODUCTION

Much work has been done on obtaining an accurate estimate of the gas hold-up time ( $t_M$ ) in gas chromatography (GC), which has considerable practical and theoretical significances. Gas hold-up times can be determined by experimental and mathematical methods.

This paper introduces a new iterative method (IM) for the determination of  $t_M$ , which assumes a linear relationship between the logarithm of the adjusted retention time and the number of carbon atoms. When the IM is repeated  $p$  times, the  $t_M$  value is approximately constant. Other mathematical methods for determination of the  $t_M$  value have been described by other authors<sup>1-15</sup>.

### EXPERIMENTAL

#### *Columns and packings*

Anisotropic and isotropic stationary phases were used. The first group includes two nematic liquid-crystalline stationary phases: 4-nitrobenzoate-4-hydroxy-4-ethylazoxybenzene (I) and 4-methylbenzoate-4-hydroxy-4-ethylazobenzene (II). The characteristics of these liquid-crystalline stationary phases were described earlier<sup>16</sup>. Squa-

lane was used as the isotropic stationary phase. The column packings were precoated with 6% (w/w) of each of the liquid crystals and 20% (w/w) of squalane on Gas-Chrom Q, 80–100 mesh (Applied Science, State College, PA, U.S.A.) as the support. The supports with the deposited anisotropic and isotropic stationary phases were packed into glass columns (3.6 m × 2 mm I.D.). All glass columns were treated with a solution of dimethyldichlorosilane in toluene before packing<sup>17</sup>.

### Chromatographic procedure

A Varian Model 2100 gas chromatograph (Varian, Palo Alto, CA, U.S.A.) equipped with a flame-ionization detector was used, with argon as the carrier gas at different flow-rates for each column. The flow-rates chosen were somewhat greater than required for the minimum height equivalent to a theoretical plate (HETP). The temperatures of the columns, injector, and detector were different for every stationary phase. The applicable flow-rates and temperatures are given in Table I.

TABLE I  
SEPARATION CONDITIONS

Column No.	Flow-rate (ml/min)	Temperature (K)		
		Column	Detector	Injector
I	15	413	443	443
II	13	433	443	443
III	20	373	383	383

Mixtures of *n*-alkanes and fatty acid methyl esters (FAME), were dissolved in diethyl ether at a concentration of *ca.* 10 µg/ml. Diethyl ether solutions (0.2 µl) of the compounds were injected with a 1-µl microsyringe (SGE, Ringwood, Australia), supplied by Pierce (Oud-Beijerland, Holland).

Retention times were measured with an electronic integrator (Varian CDS 111) with an accuracy of ±0.01 min.

### CALCULATIONS

The IM assumes that

$$\log(t_{R_i} - t_M) = an_i + b \quad (1)$$

where  $t_{R_i}$  is the non-adjusted retention time of the homologue  $i$ ,  $t_M$  is the gas hold-up time or the retention time of a non-retarded substance,  $a$  is the slope,  $b$  is the intercept and  $n_i$  is the number of carbons in a molecule of  $i$ .

For the mathematical determination of the values of  $t_M$ ,  $a$ , and  $b$ , it is necessary to work out a system of  $k$  equations:

$$\log(t_{R_i} - t_M) = an_i + b \quad \text{for } i = 1, 2, \dots, k \quad (2)$$

At the beginning of this algorithm it will be supposed that  $t_M = t_{M(0)} = 0$ , where  $t_{M(0)}$  is the  $t_M$  value after  $p$  iterative steps, for  $p = 0$ . The successive natural numbers in brackets are iterative steps and the system of equations is solved by:

$$\log t_{R_i} = a_{(0)}n_i + b_{(0)} \quad \text{for } i = 1, 2, \dots, k \quad (3)$$

for  $a_{(0)}$  and  $b_{(0)}$ . The values of the gas hold-up times for individual homologues and the arithmetic mean are calculated from

$$t_{M_i(0)} = t_{R_i} - 10^{a_{(0)}n_i + b_{(0)}} \quad (4)$$

and

$$\overline{t_{M(1)}} = \frac{1}{k} \sum_{i=1}^{i=k} t_{M_i(0)} \quad (5)$$

where  $t_{M_i(0)}$  is the value of the gas hold-up time for the homologue  $i$ , where  $\log(t_{R_i} - t_{M_i}) = a_{(0)}n_i + b_{(0)}$ ;  $k$ , as in eqn. 2, is the number of homologues;  $\overline{t_{M(1)}}$  is the arithmetic mean for all consecutive homologues. The  $\overline{t_{M(1)}}$  value is applied in the next iterative step, for  $p = 1$ , to solve the following system of  $k$  equations:

$$\log(t_{R_i} - \overline{t_{M(1)}}) = a_{(1)}n_i + b_{(1)} \quad \text{for } i = 1, 2, \dots, k \quad (6)$$

For  $a_{(1)}$  and  $b_{(1)}$ , the values  $t_{M_i(1)}$  and  $\overline{t_{M(2)}}$  are computed as follows

$$t_{M_i(1)} = t_{R_i} - 10^{a_{(1)}n_i + b_{(1)}} \quad (7)$$

and

$$\overline{t_{M(2)}} = \frac{1}{k} \sum_{i=1}^{i=k} t_{M_i(1)} \quad (8)$$

Finally the equation

$$\log(t_{R_i} - \overline{t_{M(2)}}) = a_{(2)}n_i + b_{(2)} \quad \text{for } i = 1, 2, \dots, k \quad (9)$$

is solved, and the values of  $a_{(2)}$ ,  $b_{(2)}$ ,  $\overline{t_{M(3)}}$  are calculated. This algorithm is repeated  $p$  times, until  $\overline{t_{M(p)}} = t_M = \text{constant}$ , when the accuracy of the numerical value  $t_M$  is established to 0.01 min.

The calculated values of  $t_M$  by the IM and other methods were compared for such homologues as  $n$ -alkanes and FAME esters. Comparable results were obtained. All results were calculated by the computer Odra 1300. The program was written in FORTRAN.

## RESULTS AND DISCUSSION

*Retention data*

The chromatographic data are given in Tables II–IV. For six replicate samples the Nalimov test<sup>18</sup> was used to eliminate doubtful data. Such data were excluded.

TABLE II

RETENTION MEASUREMENTS FOR *n*-ALKANES AND FAME ON THE LIQUID-CRYSTALLINE STATIONARY PHASE I

Run	Non-adjusted retention times for <i>n</i> -alkanes (min)							Non-adjusted retention time for FAME (min)				
	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>15</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>
1	1.84	2.06	2.44	3.05	4.06	5.70	8.33	4.64	6.71	10.15	15.81	24.99
2	1.83	2.06	2.43	3.03	4.03	5.66	8.33	4.63	6.70	10.14	15.78	24.87
3	1.81	2.04	2.42	3.03	4.05	5.71	8.43	4.67*	6.75*	10.18	15.73	24.80
4	1.84	2.06	2.43	3.05	4.05	5.70	8.40	4.63	6.69	10.08	15.60	24.50
5	1.82	2.05	2.42	3.04	4.05	5.71	8.42	4.64	6.67	10.08	15.57	24.54
6	1.81	2.04	2.41	3.03	4.03	5.68	8.38	4.64	6.67	10.03	15.52	24.40

\* Results which are performing the Nalimov test for 99%, the other values for 95%.

TABLE III

RETENTION MEASUREMENTS FOR *n*-ALKANES AND FAME ON THE LIQUID-CRYSTALLINE STATIONARY PHASE II

Run	Non-adjusted retention time for <i>n</i> -alkanes (min)							Non-adjusted retention time for FAME (min)				
	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>15</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>
1	2.18	2.60	3.29	4.42	6.26	9.25	14.07	5.25	7.61	11.49	17.76	28.00
2	2.19	2.62	3.32	4.45	6.32	9.34	14.19	5.24	7.60	11.50	17.84	28.09
3	2.18	2.61	3.31	4.44	6.28	9.30	14.15	5.25	7.63	11.52	17.79	28.17
4	2.19	2.62	3.31	4.45	6.29	9.29	14.12	5.20*	7.55	11.42	17.68	27.80
5	2.18	2.61	3.29	4.43	6.27	9.26	14.09	5.24	7.59	11.48	17.78	28.00
6	2.16	2.58	3.27	4.41	6.23	9.24	14.06	5.23	7.57	11.44	17.68	27.87

\* Results which are performing the Nalimov test for 99%, the other values for 95%.

TABLE IV

RETENTION MEASUREMENTS FOR *n*-ALKANES ON SQUALANE

Run	Non-adjusted retention time (min)				
	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>
1	4.95	9.95	20.67	43.50	91.78
2	4.95	9.95	20.70	43.50	92.00
3	4.94	9.91	20.58	43.39	91.62
4	4.94	9.00	20.59	43.23	91.36
5	4.93	9.91	20.56	43.23	91.46
6	4.94	9.91	20.60	43.27	91.34

TABLE V  
COMPARISON OF THE METHODS FOR DETERMINATION OF THE GAS HOLD-UP TIME VALUES FOR ALKANES ON COLUMN I

Run	Gas hold-up time (min)										Mean $\pm$ S.D.	Grobler-Balazs method	Iterative method
	Peterson-Hirsch method					C <sub>9</sub> -C <sub>15</sub>							
	C <sub>9</sub> -C <sub>11</sub>	C <sub>10</sub> -C <sub>12</sub>	C <sub>11</sub> -C <sub>13</sub>	C <sub>12</sub> -C <sub>14</sub>	C <sub>13</sub> -C <sub>15</sub>						C <sub>9</sub> -C <sub>15</sub>	C <sub>9</sub> -C <sub>15</sub>	
1	1.54	1.43	1.51	1.43	1.50	1.48 $\pm$ 0.02	1.50	1.48 $\pm$ 0.02	1.50	1.48 $\pm$ 0.02	1.50	1.49	1.49
2	1.45	1.46	1.53	1.44	1.48	1.47 $\pm$ 0.02	1.48	1.47 $\pm$ 0.02	1.47	1.47 $\pm$ 0.02	1.47	1.47	1.47
3	1.46	1.41	1.51	1.40	1.45	1.45 $\pm$ 0.02	1.45	1.45 $\pm$ 0.02	1.45	1.45 $\pm$ 0.02	1.45	1.45	1.45
4	1.52	1.51	1.42	1.51	1.46	1.48 $\pm$ 0.02	1.46	1.48 $\pm$ 0.02	1.50	1.48 $\pm$ 0.02	1.50	1.49	1.49
5	1.44	1.50	1.43	1.47	1.43	1.45 $\pm$ 0.01	1.43	1.45 $\pm$ 0.01	1.46	1.45 $\pm$ 0.01	1.46	1.42	1.42
6	1.43	1.49	1.40	1.49	1.44	1.45 $\pm$ 0.02	1.44	1.45 $\pm$ 0.02	1.45	1.45 $\pm$ 0.02	1.45	1.45	1.45
Mean	$\pm$ S.D.					1.46 $\pm$ 0.01		1.46 $\pm$ 0.01		1.47 $\pm$ 0.01		1.47 $\pm$ 0.01	1.47 $\pm$ 0.01
<i>Mean squares <math>\cdot 10^{-7}</math></i>													
1						50						40	
2						20						50	
3						5						20	
4						40						60	
5						6						50	
6						6						40	
Mean						21						52	

### Comparison of methods

Tables V–IX permit a comparison of the methods for the determination of  $t_M$  values with regard to reproducibility and to satisfying the conditions of the linear relation between  $\log(t_R - t_M)/n$  and linearity. The criterion of reproducibility was the standard deviation (S.D.) of the arithmetic mean of  $t_M$ . For the Peterson–Hirsch method<sup>1</sup> the weighted average and the S.D.s of the weighted average were calculated, treating every repetition as a separate series of results. The criterion of linearity was the mean squares representing the deviation of experimental points from the straight line  $\log(t_R - t_M) = an + b$ .

TABLE VI

COMPARISON OF THE METHODS FOR DETERMINATION OF THE GAS HOLD-UP TIME VALUES FOR FAME ON COLUMN I

Run	Gas hold-up time (min)					
	Peterson–Hirsch method				Grobler–Balizs method	Iterative method
	$C_8-C_{10}$	$C_8-C_{11}$	$C_{10}-C_{12}$	Mean $\pm$ S.D.	$C_8-C_{12}$	$C_8-C_{12}$
1	1.51	1.38	1.05	1.31 $\pm$ 0.14	1.27	1.40
2	1.50	1.25	1.17	1.31 $\pm$ 0.10	1.22	1.36
3	1.47	1.20	1.43	1.37 $\pm$ 0.08	1.28	1.36
4	1.44	1.29	1.07	1.27 $\pm$ 0.11	1.22	1.33
5	1.65	1.08	1.42	1.38 $\pm$ 0.17	1.20	1.41
6	1.54	1.37	1.14	1.35 $\pm$ 0.12	1.29	1.42
Mean $\pm$ S.D.				1.33 $\pm$ 0.05	1.25 $\pm$ 0.02	1.38 $\pm$ 0.01
					Mean squares $\cdot 10^{-7}$	
1					5	5
2					5	4
3					2	2
4					4	4
5					10	11
6					5	5
Mean					5	5

Tables V–IX show that for *n*-alkanes and for FAME the reproducibility of the  $t_M$  values is better according to the IM than the reproducibility of the  $t_M$  values according to the Grobler–Balizs method<sup>4</sup> and still better than according to the Peterson–Hirsch method. The linearity is better satisfied by the Grobler–Balizs method, than by the IM, but it is necessary to add that in the Grobler–Balizs method  $t_M$  values to ten decimal places were used, whereas in the IM  $t_M$  values to two decimal places were used, in accordance with the assumption of this method, that the precision of the calculated  $t_M$  values is equal to the precision of the measured values  $t_R$ . In spite of this, the differences in linearity are not large.

TABLE VII  
COMPARISON OF THE METHODS FOR DETERMINATION OF THE GAS HOLD-UP TIME VALUES FOR ALKANES ON COLUMN II

Run	Gas hold-up time (min)										Mean $\pm$ S.D.	Grobler-Balitz method	Iterative method
	Peterson-Hirsch method					Grobler-Balitz method							
	C <sub>9</sub> -C <sub>11</sub>	C <sub>10</sub> -C <sub>12</sub>	C <sub>11</sub> -C <sub>13</sub>	C <sub>12</sub> -C <sub>14</sub>	C <sub>13</sub> -C <sub>15</sub>	C <sub>9</sub> -C <sub>14</sub>	C <sub>9</sub> -C <sub>15</sub>	C <sub>9</sub> -C <sub>14</sub>	C <sub>9</sub> -C <sub>15</sub>	C <sub>9</sub> -C <sub>15</sub>			
1	1.53	1.52	1.49	1.48	1.37	1.48 $\pm$ 0.03	1.52	1.51	1.51	1.51			
2	1.51	1.48	1.59	1.41	1.34	1.47 $\pm$ 0.04	1.51	1.51	1.50	1.50			
3	1.56	1.47	1.51	1.57	1.30	1.48 $\pm$ 0.05	1.52	1.51	1.51	1.51			
4	1.48	1.56	1.45	1.53	1.37	1.48 $\pm$ 0.03	1.51	1.51	1.50	1.50			
5	1.44	1.60	1.43	1.49	1.41	1.47 $\pm$ 0.03	1.50	1.50	1.50	1.50			
6	1.51	1.52	1.36	1.63	1.22	1.45 $\pm$ 0.07	1.50	1.50	1.49	1.49			
Mean $\pm$ S.D.						1.47 $\pm$ 0.02	1.51 $\pm$ 0.00	1.51 $\pm$ 0.00	1.50 $\pm$ 0.00	1.50 $\pm$ 0.00			
Mean squares $\cdot 10^{-7}$													
1											2	9	
2											3	16	
3											7	2	
4											3	16	
5											10	20	
6											8	12	
Mean											6	12	

TABLE VIII

COMPARISON OF THE METHODS FOR DETERMINATION OF THE GAS HOLD-UP TIME VALUES FOR FAME ON COLUMN II

Run	Gas hold-up time (min)					
	Peterson-Hirsch method				Grobler-Balitz method	Iterative method
	$C_8-C_{10}$	$C_9-C_{11}$	$C_{10}-C_{12}$	Mean $\pm$ S.D.	$C_8-C_{12}$	$C_8-C_{12}$
1	1.59	1.31	1.59	1.50 $\pm$ 0.09	1.49	1.48
2	1.62	1.37	1.22	1.40 $\pm$ 0.12	1.48	1.47
3	1.50	1.27	1.95	1.57 $\pm$ 0.20	1.49	1.48
4	1.57	1.28	1.27	1.37 $\pm$ 0.10	1.43	1.42
5	1.65	1.31	1.36	1.44 $\pm$ 0.11	1.50	1.48
6	1.65	1.25	1.58	1.49 $\pm$ 0.12	1.51	1.49
Mean $\pm$ S.D.				1.46 $\pm$ 0.02	1.48 $\pm$ 0.01	1.47 $\pm$ 0.01
					Mean squares $\cdot 10^{-7}$	
1					1	1
2					4	4
3					3	4
4					3	3
5					4	4
6					3	3
Mean					3	3

TABLE IX

COMPARISON OF THE METHODS FOR DETERMINATION OF THE GAS HOLD-UP TIME VALUES FOR ALKANES ON COLUMN III

Run	Gas hold-up time (min)					
	Peterson-Hirsch method				Grobler-Balitz method	Iterative method
	$C_6-C_8$	$C_7-C_9$	$C_8-C_{10}$	Mean $\pm$ S.D.	$C_6-C_{10}$	$C_6-C_{10}$
1	0.58	0.46	0.19	0.41 $\pm$ 0.12	0.53	0.50
2	0.60	0.36	0.47	0.48 $\pm$ 0.07	0.53	0.51
3	0.61	0.53	0.11	0.42 $\pm$ 0.16	0.57	0.54
4	0.65	0.35	0.45	0.48 $\pm$ 0.09	0.56	0.53
5	0.56	0.47	0.45	0.49 $\pm$ 0.03	0.53	0.52
6	0.62	0.37	0.37	0.45 $\pm$ 0.08	0.55	0.51
Mean $\pm$ S.D.				0.46 $\pm$ 0.04	0.54 $\pm$ 0.01	0.52 $\pm$ 0.01
					Mean squares $\cdot 10^{-7}$	
1					5	4
2					4	3
3					6	4
4					7	5
5					1	1
6					6	5
Mean					5	4



## CONCLUSION

It has been established that the IM gives reproducible results for  $t_M$  equivalent to the Grobler-Balitz method and more reproducible results than the Peterson-Hirsch method.

The decrease in linearity together with the increase of the chain of homologues and the regular change of  $t_M$  values with increasing number of carbons in homologues permits the assumption that the relationship of the logarithm of the adjusted retention times to the number of carbon atoms is only approximately linear, even in theory.

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