Journal of Chromatography, 88 (1974) 311–321

CHROM. 7077

GAS CHROMATOGRAPHIC INVESTIGATION OF ORGANOMETALLIC COMPOUNDS AND THEIR CARBON ANALOGUES

II. IMPROVED METHOD FOR CALCULATING RETENTION INDICES OF TETRAALKOXYSILANES

I.-B. PEETRE

Department of Technical Analytical Chemistry, Chemical Center, Lund (Sweden)

(Received September 6th, 1973)

SUMMARY

A modified equation for the calculation of retention indices of mixed tetraalkoxysilanes from retention indices of the symmetrical counterparts is given. This equation is compared with the corresponding equation reported in a previous paper, and found to be more accurate. It is shown that the temperature dependence of retention indices of mixed tetraalkoxysilanes can be derived from those of the symmetrical counterparts with fair accuracy. A comparison is made between retention indices obtained on different stationary phases and different types of columns. It is inferred that the equations derived are valid for any column.

INTRODUCTION

In the previous paper[1], it was shown that retention indices of mixed tetraalkoxysilanes can be calculated with fair accuracy by using eqn. 1:

$$I(\mathrm{RO})_4\mathrm{Si} = \Sigma I(\mathrm{RO})\mathrm{Si} + \Sigma(n \cdot d \cdot k)_{\mathrm{RO-RO}} \quad (1)$$

where

RO denotes a normal alkoxy group;
$I(\mathrm{RO})\mathrm{Si}$ = group retention index;
n = combination number;
d = difference in carbon numbers between combined alkoxy groups;
k = constant dependent on the smallest alkoxy group in a combination*.

It was also shown that the retention indices of homologous series of mixed tetraalkoxysilanes were linear functions of the retention indices of the symmetrical counterparts (see eqn. 2). The way in which this fact can be utilized for calculating

* For further explanation, see ref. 1.

retention indices of mixed tetraalkoxysilanes is the main subject of this paper. In addition, the temperature dependence of the retention indices of tetraalkoxysilanes is discussed and a comparison made between retention indices measured on packed and capillary columns.

EXPERIMENTAL

The experimental details are given in ref. 1. The main difference between this and the previous investigation was that capillary columns were chiefly used in the present work. Thus, the retention indices in Table I were measured using Perkin-Elmer capillary steel columns (50 m × 0.25 mm) containing Apiezon L and cyanosilicone XE-60 as stationary phases. For comparison, some measurements were also made using packed steel columns (2 m × 1/8 in. O.D.) with Apiezon L and a loading of 4 and 10% (w/w). These values are listed in Table VII.

For the determination of accurate retention indices, a computer method, recently described[2] by the author, was utilized.

RESULTS AND DISCUSSION

Improved method for calculating retention indices of mixed tetraalkoxysilanes

It was previously shown[1] that a linear relationship according to eqn. 2 holds for retention indices of homologous series $(RO)_xSi(OR')_{4-x}$:

$$I(RO)_xSi(OR')_{4-x} = p_x I(R'O)_4Si + q_x \quad (2)$$

where

$R' \geqslant R$;
$x = 1$, 2 or 3;
$(RO)_x$ = the fixed part of the mixed tetraalkoxysilane;
$(R'O)_{4-x}$ = the changing part of the mixed tetraalkoxysilane, *i.e.*, R'O = MeO, EtO, *n*-PrO, etc.;
p_x and q_x are constants.

Experimental and calculated retention indices of six homologous series measured on Apiezon L and XE-60 capillary columns are given in Tables I and II. Table III gives the values of p_x and q_x in eqn. 2 and the correlation coefficient r for these retention indices. It can be seen that a very good linear relationship exists, especially for the Apiezon L retention indices. In order to calculate retention indices of compounds that belong to the three series $(RO)_xSi(OR')_{4-x}$ ($x = 1$–3) from the retention indices of compounds $Si(OR')_4$, three p_x constants and three q_x constants are needed. However, it can be shown that the p_x values for the three series are related and that the same is true for the q_x values. This reduces the number of constants necessary for calculating the linear relationship in eqn. 2.

If the group retention indices* were additive, the following relationship should hold:

$$I(RO)_xSi(OR')_{4-x} = [(4-x)/4]I(R'O)_4Si + [x/4]I(RO)_4Si \quad (3)$$

* The group retention indices, $I(RO)Si$, are obtained from the retention indices of symmetrical tetraalkoxysilanes, $I(RO)_4Si$, by division by four.

TABLE I

COMPARISON OF EXPERIMENTAL AND CALCULATED RETENTION INDICES OF TETRAALKOXYSILANES

Apiezon L capillary column.

Compound	I_{160}^{ApL*}				
	Exptl.	*Calcd. eqn. 1***	*Diff.*	*Calcd. eqn. 7*	*Diff.*
$(MeO)_4Si$	668.2				
$(EtO)_4Si$	851.5				
$(PrO)_4Si$	1162.3				
$(BuO)_4Si$	1483.2				
$(MeO)_3SiOEt$	720.9	723.0	+2.1	720.7	−0.2
$(MeO)_2Si(OEt)_2$	769.5	772.0	+2.5	768.8	−0.7
$MeOSi(OEt)_3$	812.1	814.7	+2.6	812.4	+0.3
$(MeO)_3SiOPr$	808.2	809.7	+1.5	809.2	+1.0
$(MeO)_2Si(OPr)_2$	938.2	939.2	+1.0	938.5	+0.3
$MeOSi(OPr)_3$	1056.2	1056.8	+0.6	1056.2	0.0
$(MeO)_3SiOBu$	900.7	899.0	−1.7	900.5	−0.2
$(MeO)_2Si(OBu)_2$	1113.7	1111.7	−2.0	1113.7	0.0
$MeOSi(OBu)_3$	1308.1	1306.5	−1.6	1308.0	−0.1
$(EtO)_3SiOPr$	931.9	932.8	+0.9	932.8	+0.9
$(EtO)_2Si(OPr)_2$	1010.5	1011.7	+1.2	1011.7	+1.2
$EtOSi(OPr)_3$	1087.7	1088.2	+0.5	1088.2	+0.5
$(EtO)_3SiOBu$	1016.6	1016.6	0.0	1016.8	+0.2
$(EtO)_2Si(OBu)_2$	1177.5	1177.0	−0.5	1177.2	−0.3
$EtOSi(OBu)_3$	1333.5	1332.5	−1.0	1332.7	−0.8
$(PrO)_3SiOBu$	1243.0	1242.5	−0.5	1242.5	−0.5
$(PrO)_2Si(OBu)_2$	1323.0	1322.8	−0.2	1322.8	−0.2
$PrOSi(OBu)_3$	1402.0	1403.0	+1.0	1403.0	+1.0
$(MeO)_2Si(OPr)OBu$	1025.9	1025.5	−0.4	1026.1***	+0.2
$MeOSi(OPr)_2OBu$	1141.1	1140.0	−1.1	1140.2***	−0.9
$MeOSi(OPr)(OBu)_2$	1224.5	1223.3	−1.2	1224.1***	−0.4

* The slope of the linear part of the plot of log t'_r *versus* carbon number for *n*-alkanes at 160° was 0.226.

** The k values are 3.0, 1.2 and 0 for MeO EtO and PrO, respectively.

*** Eqn. 8 was used.

As $x = 1$, 2 or 3, $(4-x)/4$ will become 0.75, 0.50 or 0.25 and $x/4$ will become 0.25, 0.50 or 0.75. The former values correspond to p_x in eqn. 2. Comparison with, for example, the Apiezon L p_x values of $(MeO)_xSi(OR)_{4-x}$ in Table III shows that the group retention indices are non-additive. We can write

$$(x = 1) \quad p_x = 0.7852 = 0.75 + 0.0352 = 0.75 + 3 \cdot 0.0117$$
$$(x = 2) \quad p_x = 0.5449 = 0.50 + 0.0449 = 0.50 + 4 \cdot 0.0112$$
$$(x = 3) \quad p_x = 0.2846 = 0.25 + 0.0346 = 0.25 + 3 \cdot 0.0115$$

Accordingly the general equation for calculating p_x will become

$$p_x = p_t + n \cdot k' \tag{4}$$

where

p_t = the theoretical p value $(4-x)/4$ $(x = 1\text{–}3)$;

n = the combination number[1] $= x(4-x)$, *i.e.*, 3 or 4;

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED RETENTION INDICES OF TETRAALKOXYSILANES; EXPERIMENTAL ΔI VALUES

XE-60 capillary column.

Compound	I_{160}^{XE*}					ΔI_{160}^{XE-ApL}
	Exptl.	*Calcd. eqn. 1***	*Diff.*	*Calcd. eqn. 7*	*Diff.*	*Exptl.*
$(MeO)_4Si$	909.2					241
$(EtO)_4Si$	1011.0					159.5
$(PrO)_4Si$	1295.1					132.8
$(BuO)_4Si$	1601.8					118.6
$(MeO)_3SiOEt$	944.2	944.3	+0.1	943.5	−0.7	223.3
$(MeO)_2Si(OEt)_2$	972.3	972.9	+0.6	971.8	−0.5	202.8
$MeOSi(OEt)_3$	993.5	995.2	+1.7	994.3	+0.8	181.4
$(MeO)_3SiOPr$	1023.9	1024.9	+1.0	1024.6	+0.7	215.7
$(MeO)_2Si(OPr)_2$	1126.7	1127.8	+1.1	1127.4	+0.7	188.5
$MeOSi(OPr)_3$	1217.3	1217.8	+0.5	1217.6	+0.3	161.1
$(MeO)_3SiOBu$	1112.8	1111.2	−1.6	1112.3	−0.5	212.1
$(MeO)_2Si(OBu)_2$	1295.4	1293.9	−1.5	1295.3	−0.1	181.7
$MeOSi(OBu)_3$	1458.3	1457.5	−0.8	1458.5	+0.2	149.9
$(EtO)_3SiOPr$	1083.6	1086.3	+2.7	1085.3	+1.7	151.7
$(EtO)_2Si(OPr)_2$	1155.0	1158.6	+3.6	1157.5	+2.5	144.5
$EtOSi(OPr)_3$	1226.4	1228.3	+1.9	1227.4	+1.0	138.7
$(EtO)_3SiOBu$	1166.6	1167.1	+0.5	1166.5	−0.1	150.0
$(EtO)_2Si(OBu)_2$	1317.5	1317.6	+0.1	1316.8	−0.7	140.0
$EtOSi(OBu)_3$	1463.2	1462.5	−0.7	1461.9	−1.3	129.7

* As the XE-60 stationary phase has a recommended maximum temperature of 150°, the I_{160}^{XE} values were obtained by extrapolation. The slope of the linear part of the plot of log t'_r *versus* carbon number for *n*-alkanes at 150° was 0.199.

** The k values are 3.2 and 1.2 for MeO and EtO, respectively.

TABLE III

VALUES OF p_x AND q_x IN EQN. 2 AND OF THE CORRESPONDING CORRELATION COEFFICIENT, r

RO	x	*Apiezon L capillary column*			*XE-60 capillary column*		
		p_x	q_x	r	p_x	q_x	r
MeO	3	0.2846	478.1	0.99997	0.2854	655.1	0.99996
	2	0.5449	305.3	1.00000	0.5469	419.0	0.99999
	1	0.7852	143.5	1.00000	0.7862	198.8	1.00000
EtO	3	0.2609	629.1	0.99999	0.2634	743.9	0.9998
	2	0.5161	411.5	0.99999	0.5189	485.2	0.99992
	1	0.7630	201.5	0.99999	0.7655	236.4	0.9998

k' = constant dependent on the kind of RO group, *i.e.*, the smallest group present.

q_x can be treated in a similar manner. Thus, we can write

$$q_x = q'_x I(RO)_4Si \qquad (5)$$

Inserting the Apiezon L q_x values of $(MeO)_xSi(OR)_{4-x}$ from Table III and the value of $I(RO)_4Si = I^{ApL}_{160}(MeO)_4Si$ from Table I in eqn. 5 gives the following q'_x values:

$(x = 1)$ $q'_x = 0.2148 = 0.25 - 0.0352 = 0.25 - 3 \cdot 0.0117$
$(x = 2)$ $q'_x = 0.4569 = 0.50 - 0.0431 = 0.50 - 4 \cdot 0.0108$
$(x = 3)$ $q'_x = 0.7155 = 0.75 - 0.0345 = 0.75 - 3 \cdot 0.0115$

and the general equation for calculating q'_x will become

$$q'_x = q'_t - n \cdot k'' \quad (6)$$

where q'_t = the theoretical q' value $x/4$ $(x = 1\text{–}3)$, and n and k'' have the same meaning as n and k' in eqn. 4.

By combining eqns. 2, 4, 5 and 6, we obtain eqn. 7 for calculating the retention indices of mixed tetraalkoxysilanes with two dissimilar alkoxy groups:

$$I(RO)_xSi(OR')_{4-x} = [(4-x)/4]I(R'O)_4Si + [x/4]I(RO)_4Si + n[k'I(R'O)_4Si - k''I(RO)_4Si] \quad (7)$$

The values of k' and k'', calculated from the retention indices given in Tables I and II, for RO = MeO and EtO, respectively, are presented in Table IV. As shown, the values of k' and k'' are identical for RO = EtO, nearly identical for RO = MeO on Apiezon L, but different for RO = MeO on XE-60. The number of constants needed to calculate retention indices of mixed tetraalkoxysilanes that belong to the three homologous series $(RO)_xSi(OR')_{4-x}$ $(x = 1\text{–}3)$ has thus been reduced from six to one for RO = EtO and from six to two for RO = MeO for each stationary phase.

TABLE IV

VALUES OF k' AND k'' IN EQNS. 7 AND 8 FOR CAPILLARY COLUMNS

No corrections are necessary for RO = PrO.

RO	*Apiezon L, 160°*		*XE-60, 160°*	
	k'	k''	k'	k''
MeO	0.0115	0.0113	0.0119	0.0100
EtO	0.0039	0.0039	0.0040	0.0040

The last term in eqn. 7 may be regarded as a correction term that accounts for the deviation from additivity of the group retention indices. A corresponding correction term is included in eqn. 1. As n is the same in the two equations, $k \cdot d$ in eqn. 1 must have approximately the same value as $[k'I(R'O)_4Si - k''I(RO)_4Si]$ or, when $k' = k''$, it may be expressed as $k'[I(R'O)_4Si - I(RO)_4Si]$. Accordingly, in the last case the difference in the retention indices of the two symmetrical tetraalkoxysilanes, the groups of which appear in the mixed tetraalkoxysilane, has been substituted for the difference in carbon numbers, d, in eqn. 1.

That this manner of calculating the retention indices of mixed tetraalkoxysilanes is superior to that used in eqn. 1 is evident from a comparison between the experimental and calculated values in Tables I and II. The mean deviation between

the calculated and experimental values for the Apiezon L stationary phase is 0.5 index units using eqn. 7 and 1.2 index units using eqn. 1. The corresponding mean deviations for the XE-60 stationary phase are 0.8 and 1.2 index units, respectively.

Eqn. 1 was used previously[1] for calculating the retention indices of a large number of mixed tetraalkoxysilanes with fair accuracy. The advantage of this equation is its simplicity, as only one constant is needed for each pair of alkoxy groups in a combination. Using eqn. 7, one constant is also sufficient in certain instances, but in others, two are necessary. This makes eqn. 7 more laborious to apply, but more accurate values are obtained.

In the foregoing, only mixed tetraalkoxysilanes $(RO)_xSi(OR')_{4-x}$ with RO = MeO and EtO have been considered. A more general equation for calculating the retention indices of mixed tetraalkoxysilanes is

$$I(R_xO)_4Si = \Sigma I(R_xO)Si + \Sigma n[k'I(R_{x'}O)_4Si - k''I(R_{x''}O)_4Si] \quad (8)$$

where

$R_x = R_{x'}$, $R_{x''}$, etc., up to four different groups;
$OR_{x'}$ and $OR_{x''}$ = alkoxy groups in a combination ($R_{x'} > R_{x''}$);
$I(R_xO)Si$ = group retention indices, obtained from retention indices of symmetrical tetraalkoxysilanes by division by four;
k' and k'' for different combinations are taken from Tables IV and V.

Eqn. 7 is a special case of eqn. 8. In order to test eqn. 8 on a larger number of mixed tetraalkoxysilanes, k' and k'' for different combinations were calculated from the experimental data obtained in the previous investigation, in which packed columns with Apiezon M and XE-60 were utilized[1]. The values of k' and k'' are collected in Table V, and should be usable for calculating retention indices of all types of mixed tetraalkoxysilanes with normal alkoxy groups. The group retention indices and indices of symmetrical tetraalkoxysilanes needed are taken from Tables IV and V of the previous paper[1].

TABLE V

VALUES OF k' AND k'' IN EQN. 8 FOR PACKED COLUMNS

RO	*Apiezon M, 160°*		*XE-60, 160°*	
	k'	k''	k'	k''
MeO	0.0094	0.0071	0.0099	0.0070
EtO	0.0049	0.0056	0.0050	0.0052
PrO	0.0028	0.0031	0.0032	0.0036
BuO	0.0015	0.0015	0.0015	0.0016

Temperature dependence of retention indices, its calculation and use for identification purposes

It was previously reported[1] that the temperature dependence of retention indices of mixed tetraalkoxysilanes could be calculated from the increments of the symmetrical counterparts by using eqn. 9:

$$10[dI/dT](R_xO)_4Si = \Sigma\{10[dI/dT](R_xO)Si\} \quad (9)$$

where R_x = R,R', etc. (up to four different groups), and the right-hand expression

denotes group increments, obtained from the temperature increments of retention indices of symmetrical tetraalkoxysilanes by division by four.

The agreement between experimental and calculated values in Table VI is satisfactory considering the crude method of calculation used. Eqn. 9 makes it possible to calculate approximate retention indices within the measuring range and also somewhat outside it.

TABLE VI

COMPARISON OF EXPERIMENTAL AND CALCULATED TEMPERATURE INCREMENTS OF RETENTION INDICES OF TETRAALKOXYSILANES

Compound	$10\frac{dI}{dT}$					
	Apiezon L capillary column			*XE-60 capillary column*		
	Temp. range (°C)	*Exptl.*	*Calcd.*	*Temp. range (°C)*	*Exptl.*	*Calcd.*
$(MeO)_4Si$	80–160	−3.3		100–150	−1.0	
$(EtO)_4Si$	100–160	−4.8		100–150	−4.4	
$(PrO)_4Si$	100–180	−5.5		100–160	−5.3	
$(BuO)_4Si$	140–180	−5.8		140–150	−5.8	
$(MeO)_3SiOEt$	100–160	−3.6	−3.7	100–140	−1.5	−1.9
$(MeO)_2Si(OEt)_2$	100–160	−3.8	−4.1	100–140	−2.3	−2.7
$MeOSi(OEt)_3$	100–160	−4.4	−4.4	100–140	−3.5	−3.6
$(MeO)_3SiOPr$	100–180	−3.6	−3.9	120–140	−1.9	−2.1
$(MeO)_2Si(OPr)_2$	100–180	−4.1	−4.4	120–140	−2.8	−3.2
$MeOSi(OPr)_3$	100–180	−4.5	−5.0	120–140	−3.7	−4.2
$(MeO)_3SiOBu$	140–180	−3.5	−3.9	140–150	−1.8	−2.2
$(MeO)_2Si(OBu)_2$	140–180	−4.3	−4.5	120–160	−3.0	−3.4
$MeOSi(OBu)_3$	140–180	−5.6	−5.2	140–150	−4.3	−4.6
$(EtO)_3SiOPr$	120–160	−5.0	−5.0	120–140	−4.7	−4.6
$(EtO)_2Si(OPr)_2$	120–160	−5.2	−5.2	120–140	−5.0	−4.9
$EtOSi(OPr)_3$	120–160	−5.2	−5.3	120–140	−5.1	−5.1
$(EtO)_3SiOBu$	140–180	−5.5	−5.1	140–150	−4.6	−4.7
$(EtO)_2Si(OBu)_2$	140–180	−5.6	−5.3	140–150	−5.2	−5.1
$EtOSi(OBu)_3$	140–180	−5.8	−5.6	140–150	−5.5	−5.5

Eqn. 9 will also be useful for determining the best column temperature to be used in difficult separations. For example, the two tetraalkoxysilanes $(PrO)_4Si$ and $(MeO)_2Si(OBu)_2$ have nearly the same retention indices at 160° on the XE-60 stationary phase and, accordingly, they cannot be separated at this temperature. However, Fig. 1 demonstrates that a separation can be achieved at 120°, for example, as a consequence of the different values of $10\,dI/dT$ for the two compounds. That this is so is shown by the chromatogram in Fig. 2.

The considerable variation in the magnitude of the temperature increment with structure makes it useful for identification purposes. However, for this purpose, so-called two-temperature plots are even more valuable. It has been shown by Walraven[3] that if retention indices of, for example, hydrocarbons belonging to the same structure group and measured at two different temperatures on the same stationary

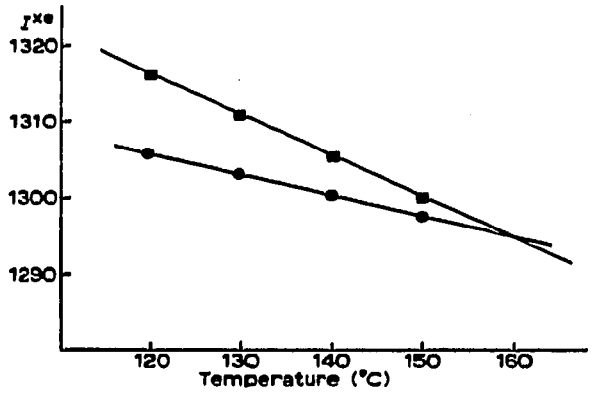

Fig. 1. Dependence of retention indices on column temperature. ●, $(PrO)_4Si$; ■, $(MeO)_2Si(OBu)_2$. XE-60, capillary column.

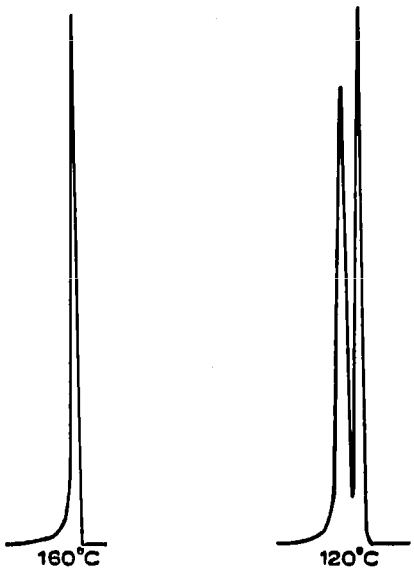

Fig. 2. Chromatograms showing the separation of $(PrO)_4Si$ and $(MeO)_2Si(OBu)_2$ at 160° and 120°. XE-60, capillary column.

phase, are plotted against each other, the points align themselves along imbricated straight lines. The same has been found to be the case for tetraalkoxysilanes (see Fig. 3).

These lines are equivalent to the structure lines previously discovered in the I_{160}^{APM} *versus* I_{160}^{XE} two-phase plots[1]. All compounds on the same structure line in Fig. 3 have the same number of CH_3, CH_2, CH and C groups. The structure code is written *a–b–d–e* where *a* indicates the number of CH_3 groups, etc., and *d* and *e* are always zero as the tetraalkoxysilanes studied contain only normal alkoxy groups. Two structure lines are shown in Fig. 3, along which the tetraalkoxysilanes are arranged by

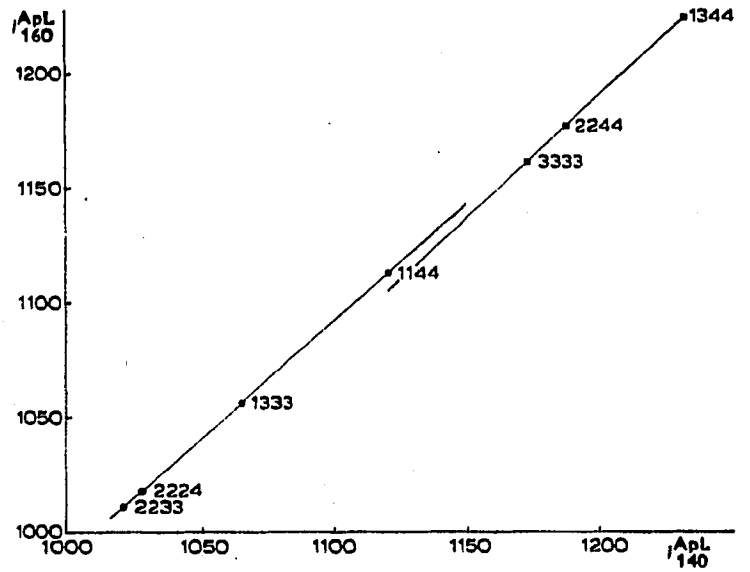

Fig. 3. Two-temperature plot, I_{160}^{ApL} *versus* I_{140}^{ApL}, capillary column. Structure code: ●, 4–6–0–0 and ■, 4–8–0–0.

decreasing formula code*, just as was found to be the case for the structure lines in the two-phase plot. In fact, the structure lines in Fig. 3 seem to exhibit all the characteristics of the structure lines in the two-phase plot. It therefore appears that for identification purposes the two-temperature plot in Fig. 3 may be substituted for the two-phase plot.

Comparison between retention indices measured on different stationary phases and different types of columns

It is well-known that one of the major difficulties in gas chromatography is to obtain reproducible retention values, not only between different laboratories but also within one laboratory. This difficulty arises because retentions change very easily when some column parameter is altered, *e.g.*, the batch of carrier or batch of stationary phase, especially when the latter is polymeric. However, even when care is taken to use the same batch of carrier and stationary phase, difficulties may arise, for example because of the variable thickness of the stationary phase or a change in the method of its application to the carrier. It might also be expected to be difficult to reproduce the retention values measured on a packed column, on a capillary column with the same stationary phase.

In order to study these problems in some detail, some comparative measurements of retention indices on Apiezon L and Apiezon M were made, using both packed and capillary columns, and the results are given in Table VII. It was found that retention indices measured on a commercial Apiezon L capillary column slowly increased until, after about 200 h, they attained constant values. It is plausible to assume

* The formula code denotes the alkoxy groups bonded to the central silicon atom: 1 = MeO, 2 = EtO, 3 = PrO, etc.

TABLE VII

COMPARISON BETWEEN RETENTION INDICES MEASURED ON DIFFERENT STATIONARY PHASES AND DIFFERENT TYPES OF COLUMNS

Carriers: 10% Apiezon L, Chromosorb G, AW-HMDS, 80–100 mesh; 4% Apiezon L and 4% Apiezon M, Chromosorb G, AW-DMCS, 80–100 mesh. Calculation: eqn. 7 with the k values from Table IV was used in the case of Apiezon L and the same equation with the k values from Table V in the case of Apiezon M.

Compound	*Apiezon L (new capillary column)*			*Apiezon L (aged capillary column)*			*10% Apiezon L (Perkin-Elmer)*			*4% Apiezon L*			*4% Apiezon M*		
	Exptl.	*Calcd.*	*Diff.*	*Exptl.*	*Calcd.*	*Diff.*	*Exptl.*	*Calcd.*	*Diff.*	*Exptl.*	*Calcd.*	*Diff.*	*Exptl.*	*Calcd.*	*Diff.*
$(MeO)_4Si$	660			668.2			665			656			658		
$(EtO)_4Si$	847			851.5			851			844			850		
$(PrO)_4Si$	1160			1162.3			1163			1158			1163		
$(BuO)_4Si$				1483.2			1480			1480			1488		
$(MeO)_3SiOEt$	713	713	0	720.9	720.7	−0.2	718	718	0	708	709	+1	716	716	0
$(MeO)_2Si(OEt)_2$	761	762	+1	769.5	768.8	−0.7	766	767	+1	758	759	+1	766	767	+1
$MeOSi(OEt)_3$	807	807	0	812.1	812.4	+0.3	811	811	0	803	804	+1	812	812	0
$(MeO)_3SiOPr$				808.2	809.2	+1.0	807	807	0	798	799	+1	803	803	0
$(MeO)_2Si(OPr)_2$				938.2	938.5	+0.3	937	937	0	929	930	+1	934	935	+1
$MeOSi(OPr)_3$				1056.2	1056.2	0	1056	1056	0	1050	1050	0	1056	1055	−1
$(MeO)_3SiOBu$				900.7	900.5	−0.2				890	891	+1	894	893	−1
$(MeO)_2Si(OBu)_2$				1113.7	1113.7	0				1106	1106	0	1110	1110	0
$MeOSi(OBu)_3$				1308.1	1308.0	−0.1				1303	1303	0	1306	1308	+2
$(EtO)_3SiOPr$	929	929	0	931.9	932.8	+0.9	931	932	+1	924	926	+2	930	932	+2
$(EtO)_2Si(OPr)_2$	1006	1008	+2	1010.5	1011.7	+1.2	1010	1012	+2	1004	1006	+2	1010	1011	+1
$EtOSi(OPr)_3$	1085	1085	0	1087.7	1088.2	+0.5	1089	1089	0	1083	1083	0	1088	1088	0
$(EtO)_3SiOBu$				1016.6	1016.8	+0.2				1010	1010	0	1018	1018	0
$(EtO)_2Si(OBu)_2$				1177.5	1177.2	−0.3				1173	1172	−1	1179	1180	+1
$EtOSi(OBu)_3$				1333.5	1332.7	−0.8				1330	1328	−2	1339	1337	−2

that this change in retention is caused by the slow evaporation of the stationary phase during the early life of the column.

Two packed columns containing 4 and 10% (w/w) Apiezon L were compared. It can be seen in Table VII that there is a considerable difference between the two sets of retention indices, those from the 10% column being the highest. This difference could be caused by a decrease in the retention times of the reference *n*-alkanes on the 10% column and/or an increase in the retention times of the tetraalkoxysilanes. However, there is no obvious explanation for either change.

Comparison between the various sets of retention indices shows that there is a distinct similarity between the values from the aged Apiezon L capillary column and from the packed column with 10% Apiezon L. Both of these materials were obtained from Perkin-Elmer (Norwalk, Conn., U.S.A.). A peculiarity is the fact that the two packed columns with 4% Apiezon L and 4% Apiezon M gave more dissimilar retention indices than the latter column and that with 10% Apiezon L.

These results verify the above-mentioned difficulty of reproducing retention values. However, it should be pointed out that in the previous work[1] numerous columns containing 4% Apiezon M, from one batch, and applied on carriers from one batch, gave reproducible retention indices within the limits of experimental error. It therefore appears that reproducible columns may be prepared if suitable precautions are taken. The percentage of stationary phase should be kept constant and care should be exercised when using capillary columns so as to ensure that the retention indices do not change with time.

An important result of the present investigation is that although the retention indices obtained may differ from one column to another, the equations previously derived for the calculation of retention indices can always be applied. Only the set of group retention indices to be used changes while the same k values can be employed for all the Apiezon L columns in Table VII. It therefore appears that although the set of group retention indices deduced from the experimental data, obtained on a certain column, is primarily useful for calculating and comparing retention indices obtained on the same or a closely similar column, the k values have a more extensive use and can be applied to data from different columns containing the same stationary phase.

ACKNOWLEDGEMENT

The co-operation of Mrs. Kerstin Svensson in the experimental work is gratefully acknowledged.

REFERENCES

1 G. Ellrén, I.-B. Peetre and B. E. F. Smith, *J. Chromatogr.*, 88 (1974) 295.
2 I.-B. Peetre, *Chromatographia*, 6 (1973) 257.
3 J. J. Walraven, *Dissertation*, Eindhoven University of Technology, Eindhoven, 1968.