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GAS CHROMATOGRAPHIC INVESTIGATION OF ORGANOMETALLIC COMPOUNDS AND THEIR CARBON ANALOGUES

I. DETERMINATION, CALCULATION AND CORRELATION OF KOVÁTS' RETENTION INDICES FOR TETRAALKOXYSILANES

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SUMMARY

An equation is given for the accurate calculation of retention indices and ΔI values for mixed tetraalkoxysilanes on the basis of the corresponding values for the symmetrical counterparts. The linear relationships between retention index, and carbon number and molar refraction are discussed. A perfect linear relationship exists between retention indices of homologous series of mixed tetraalkoxysilanes and those of the symmetrical counterparts, which can be utilized for the calculation of retention indices of the former compounds. When retention indices of tetraalkoxysilanes on Apiezon M are plotted against the corresponding retention indices on XE-60, two main linear relationships are found.

INTRODUCTION

This paper is the first in a series devoted to the study of the relationship between structure and Kováts' retention index for organometallic compounds and their carbon analogues. Tetraalkoxysilanes, $(RO)_4Si$, were judged to be suitable for a first investigation of this type because of their four-fold functionality and the ease with which the structure around the silicon atom can be changed.

The main purpose of the investigation was to determine accurate retention indices for a number of symmetrical and mixed tetraalkoxysilanes with normal alkoxy groups and to establish whether indices of symmetrical compounds could be utilized for the calculation of indices of the mixed compounds. It was also our intention to study various interrelationships between retention indices, in addition to relationships between retention indices and certain physical constants. Another aim was to investigate the temperature dependence of retention indices.

Although gas chromatography has been applied to several types of organo-silicon compounds, tetraalkoxysilanes have received little attention; we are aware of only a few minor papers dealing with this type of compound. Thus, Thrash¹ measured the retention of tetraethoxysilane relative to toluene on three different

stationary phases, and Wurst² reported the specific retention volume of the same compound on a silicone oil. Subsequently, Wurst and Churáček³ measured a quantity called the silicon index (I_{Si}) for six symmetrical tetraalkoxysilanes. However, no data were given that permit the recalculation of the silicon index in the form of Kováts' retention index. Taylor⁴ studied the gas chromatographic separation of a number of symmetrical and mixed tetraalkoxysilanes present in a heat transfer liquid. The results were given only in the form of chromatograms. Garzó *et al.*⁵ reported retention indices of a considerable number of organosilicon compounds, but only two of the compounds were tetraalkoxysilanes, namely tetramethoxy- and tetraethoxysilane.

EXPERIMENTAL

Apparatus and columns

Most of the work was performed using a Varian Model 1400 gas chromatograph with a flame ionization detector. As the temperature scale on this instrument could not be read to better than $\pm 1^\circ$, an auxiliary thermocouple and temperature gauge were used, which enabled the temperature to be measured to $\pm 0.1^\circ$ (Mettler TM15).

Steel columns (0.3–6.0 m \times 1/8 in. O.D.) were packed with either Apiezon M (Apiezon, Great Britain) or cyanosilicone GE XE-60 (Applied Science Labs., State College, Pa., U.S.A.), 4 and 5% (w/w), respectively, on acid-washed and DMCS-treated Chromosorb G, 80–100 mesh. The column length was chosen to give a maximal retention time of about 1 h. The columns were conditioned for 12 h at 260° (Apiezon M) and 220° (XE-60) before use. The carrier gas was nitrogen at a flow-rate of about 30 ml/min.

Determination of retention indices

This work has been continuing over several years, and during that time the method of determining retention indices has undergone some changes. Originally, retention times were measured by means of a stop-watch or on recorder paper; later, an electronic HP 3370 A integrator was used (accuracy ± 0.01 min), and recently a slope detector was constructed that permitted the measurement of retention times to ± 0.1 sec. The last method was used in most instances.

The sample was mixed with an appropriate number of *n*-alkanes or, when overlapping prevented this method, the sample and mixture of *n*-alkanes were run alternately. A novel method of determining retention indices was recently described by one of the present authors⁶, involving the use of a computer for simulating the bracketing of each compound in the sample by two *n*-alkanes. However, this method has been used in the present work only to a minor extent.

The gas hold-up time was evaluated by injecting methane. The difference between the value thus obtained and the true gas hold-up time is insignificant in the present instance, as the lowest retention indices determined were as high as 650 on Apiezon M and 920 on XE-60. The amount of sample injected was less than 0.2 μ l so as to avoid deformation of the peaks with an accompanying inaccuracy in the retention time measurement. The standard temperature for measuring the retention indices was 160°. In addition, the retention indices of the symmetrical tetraalkoxy-

silanes and a few of the mixed compounds were measured over a 60° temperature range in order to establish the temperature increments. Retention indices were calculated according to the equation

$$I_x = 100n + \frac{\log t'_x - \log t'_n}{\log t'_{n+1} - \log t'_n} \cdot 100 \quad (1)$$

where I_x is the retention index of a compound X, the adjusted retention time of which is t'_x and t'_n and t'_{n+1} are the adjusted retention times of two consecutive n -alkanes with carbon numbers n and $n+1$, respectively, and which bracket the compound X. At 160°, the value of $\log t'_{n+1} - \log t'_n$ is 0.230 ($n > 8$) for Apiezon M and 0.178 ($n > 10$) for XE-60.

Materials

All compounds investigated were prepared in this laboratory. The symmetrical tetraalkoxysilanes were made either from silicon tetrachloride and alcohols or by alcoholysis of tetramethoxysilane. Mixed tetraalkoxysilanes were obtained either by alkoxy interchange between symmetrical tetraalkoxysilanes or by alcoholysis of the latter. Gaseous hydrogen chloride was used as the catalyst in the alkoxy interchange and alcoholysis reactions.

The syntheses of mixed tetraalkoxysilanes were generally performed on a small scale. No separations of the compounds formed were made, prior to the gas chromatographic investigation. The peaks in a chromatogram could be univocally assigned, as the various tetraalkoxysilanes resulting from the systematic exchange of one alkoxy group for another appeared in the order of increasing molecular weight on both of the stationary phases.

RESULTS AND DISCUSSION

Equations for the calculation of retention indices and ΔI values

Retention indices. Some attempts to calculate retention indices, relevant to the present work, have been made previously. Evans and Smith⁷ obtained relative retentions of unsymmetrical compounds R-X-R' from those of the symmetrical counterparts R-X-R and R'-X-R' by dividing the logarithms of the latter by two and summing so as to obtain the logarithm of the relative retention of R-X-R'. The nature of R, R' and X, in addition to the properties of the R-X and R'-X bonds, were found to influence the results. The agreement between observed and calculated values was good in certain instances but less good in others.

Semlyen and Phillips⁸ applied a similar method to the calculation of relative retentions of mixed tetraalkylsilanes from those of the symmetrical counterparts. From the results, they concluded that the more similar were the sizes of the alkyl groups in a mixed tetraalkylsilane, the better was the agreement between observed and calculated values. However, the average agreement is inadequate for this simple addition method to be useful for the accurate calculation of retentions of mixed tetraalkylsilanes*.

* The problem of calculating retention indices of tetraalkylsilanes will be dealt with in a forthcoming paper⁹.

TABLE I

RETENTION INDICES, TEMPERATURE DEPENDENCE AND ΔI VALUES OF SYMMETRICAL TETRAALKOXYSILANES

Compound	Temperature range (°C)	Apiezon M		XE-60		$\Delta I_{160} = I_{160}^{XE} - I_{160}^{ApM}$	
		I_{160}	$10 \frac{dI}{dT}$	I_{160}	$10 \frac{dI}{dT}$	ΔI_{160}	$10 \frac{d\Delta I}{dT}$
(MeO) ₄ Si	100-160	658	-2.8	924	-0.5	266	+2.3
(EtO) ₄ Si	100-160	850	-4.5	1024	-4.7	174	-0.2
(PrO) ₄ Si	120-180	1163	-4.5	1315	-5.5	152	-1.0
(BuO) ₄ Si	140-200	1488	-5.5	1630	-7.0	142	-1.5
(AmO) ₄ Si	160-220	1830	-6.0	1972	-7.0	142	-1.0
(HexO) ₄ Si	160-220	2178	-6.5	2318	-8.0	140	-1.5
(HeptO) ₄ Si	160-220	2527	-7.2	2670	-8.7	143	-1.5

Our results are given in Tables I-II. When the same addition method as above was applied to the mixed tetraalkoxysilanes in Table II, results were obtained that were similar to those for the tetraalkylsilanes (see Table III). The calculated values in Table III were obtained by the addition of the group retention indices $I(\text{RO})\text{Si}$, derived from the retention indices of symmetrical tetraalkoxysilanes in Table I by

TABLE II

EXPERIMENTAL AND CALCULATED RETENTION INDICES AND ΔI VALUES OF MIXED TETRAALKOXYSILANES

Compound	I_{160}^{ApM}			I_{160}^{XE}			ΔI_{160}		
	Exptl.	Calcd.	Diff.	Exptl.	Calcd.	Diff.	Exptl.	Calcd.	Diff.
(MeO) ₃ SiOEt	716	715	-1	960	959	-1	244	244	0
(MeO) ₂ Si(OEt) ₂	766	766	0	987	987	0	221	221	0
MeOSi(OEt) ₃	812	811	-1	1008	1009	+1	196	198	+2
(MeO) ₃ SiOPr	803	803	0	1042	1042	0	239	239	0
(MeO) ₂ Si(OPr) ₂	934	935	+1	1147	1146	-1	213	211	-2
MeOSi(OPr) ₃	1056	1055	-1	1236	1237	+1	180	182	+2
(MeO) ₃ SiOBu	894	893	-1	1130	1130	0	236	237	+1
(MeO) ₂ Si(OBu) ₂	1110	1110	0	1318	1317	-1	208	207	-1
MeOSi(OBu) ₃	1306	1308	+2	1484	1483	-1	178	175	-3
(MeO) ₃ SiOAm	991	988	-3	1228	1226	-2	237	236	-1
(MeO) ₂ Si(OAm) ₂	1293	1294	+1	1499	1501	+2	206	207	+1
MeOSi(OAm) ₃	1576	1574	-2	1747	1750	+3	171	176	+5
(MeO) ₃ SiOHex	1086	1085	-1	1321	1322	+1	235	237	+2
(MeO) ₂ Si(OHex) ₂	1477	1480	+3	1686	1687	+1	209	207	-2
MeOSi(OHex) ₃	1847	1845	-2	2019	2019	0	172	174	+2
(MeO) ₃ SiOHept	1183	1181	-2	1419	1420	+1	236	239	+3
(MeO) ₂ Si(OHept) ₂	1667	1667	0	1878	1876	-2	211	209	-2
MeOSi(OHept) ₃	2116	2116	0	2295	2293	-2	179	177	-2
(EtO) ₃ SiOPr	930	933	+3	1102	1101	-1	172	168	-4
(EtO) ₂ Si(OPr) ₂	1010	1013	+3	1174	1176	+2	164	163	-1
EtOSi(OPr) ₃	1088	1089	+1	1245	1247	+2	157	158	+1
(EtO) ₃ SiOBu	1018	1019	+1	1183	1185	+2	165	166	+1
(EtO) ₂ Si(OBu) ₂	1179	1181	+2	1338	1339	+1	159	158	-1

TABLE II (continued)

Compound	J_{160}^{ApM}			J_{160}^{XE}			ΔI_{160}		
	Exptl.	Calcd.	Diff.	Exptl.	Calcd.	Diff.	Exptl.	Calcd.	Diff.
EtOSi(OBu) ₃	1339	1338	-1	1487	1488	+1	148	150	+2
(EtO) ₃ SiOAm	1106	1108	+2	1274	1275	+1	168	167	-1
(EtO) ₂ Si(OAm) ₂	1356	1358	+2	1516	1516	0	160	158	-2
EtOSi(OAm) ₃	1596	1598	+2	1749	1749	0	153	151	-2
(EtO) ₃ SiOHex	1200	1200	0	1366	1366	0	166	166	0
(EtO) ₂ Si(OHex) ₂	1539	1538	-1	1696	1695	-1	157	157	0
EtOSi(OHex) ₃	1864	1864	0	2014	2013	-1	150	149	-1
(PrO) ₃ SiOBu	1247	1247	0	1396	1396	0	149	149	0
(PrO) ₂ Si(OBu) ₂	1328	1329	+1	1476	1476	0	148	147	-1
PrOSi(OBu) ₃	1408	1409	+1	1553	1554	+1	145	145	0
(PrO) ₃ SiOAm	1334	1335	+1	1482	1484	+2	148	149	+1
(PrO) ₂ Si(OAm) ₂	1504	1503	-1	1648	1650	+2	144	147	+3
PrOSi(OAm) ₃	1666	1668	+2	1813	1813	0	147	145	-2
(PrO) ₃ SiOHex	1426	1424	-2	1575	1573	-2	149	149	0
(PrO) ₂ Si(OHex) ₂	1680	1680	0	1826	1826	0	146	146	0
PrOSi(OHex) ₃	1931	1931	0	2076	2074	-2	145	143	-2
(PrO) ₃ SiOHept	1515	1514	-1	1665	1663	-2	150	149	-1
(PrO) ₂ Si(OHept) ₂	1859	1858	-1	2008	2005	-3	149	147	-2
PrOSi(OHept) ₃	2196	2196	0	2345	2341	-4	149	145	-4
(BuO) ₃ SiOAm	1574	1575	+1	1716	1717	+1	142	142	0
(BuO) ₂ Si(OAm) ₂	1661	1661	0	1802	1803	+1	141	142	+1
BuOSi(OAm) ₃	1747	1746	-1	1888	1888	0	141	142	+1
(BuO) ₃ SiOHex	1662	1663	+1	1805	1803	-2	143	140	-3
(BuO) ₂ Si(OHex) ₂	1838	1836	-2	1978	1977	-1	140	141	+1
BuOSi(OHex) ₃	2010	2008	-2	2147	2148	+1	137	140	+3
(MeO) ₃ Si(OPr)OAm	1114	1116	+2	1323	1325	+2	209	209	0
MeOSi(OPr) ₂ OAm	1229	1231	+2	1410	1411	+1	181	180	-1
MeOSi(OPr)(OAm) ₂	1401	1403	+2	1581	1582	+1	180	179	-1
(EtO) ₂ Si(OBu)OHex	1358	1360	+2	1521	1518	-3	163	158	-5
EtOSi(OBu) ₂ OHex	1513	1513	0	1665	1664	-1	152	151	-1
EtOSi(OBu)(OHex) ₂	1688	1690	+2	1841	1839	-2	153	149	-4

TABLE III

COMPARISON OF EXPERIMENTAL RETENTION INDICES (J_{160}^{ApM}) WITH THOSE CALCULATED BY ADDITION OF GROUP RETENTION INDICES

Compound	J_{160}^{ApM}		
	Exptl.	Calcd.	Diff.
(MeO) ₂ Si(OEt) ₂	766	754	12
(MeO) ₂ Si(OHex) ₂	1477	1418	59
(MeO) ₃ SiOAm	991	951	40
(MeO) ₂ Si(OAm) ₂	1293	1244	49
MeOSi(OAm) ₃	1576	1537	39
(EtO) ₃ SiOHex	1200	1182	18
(EtO) ₂ Si(OHex) ₂	1539	1514	25
EtOSi(OHex) ₃	1864	1846	18

TABLE IV

GROUP RETENTION INDICES AND GROUP ΔI VALUES OF *n*-ALKOXY GROUPS BONDED TO SILICON IN SYMMETRICAL TETRAALKOXYSILANES

RO	$I_{160}^{APM}(RO)Si$	$\delta I(CH_2)$	$I_{160}^{XE}(RO)Si$	$\delta I(CH_2)$	$\Delta I_{160}(RO)Si$
MeO	164.5	48.0	231.0	25.0	66.5
EtO	212.5	78.3	256.0	72.8	43.5
PrO	290.8	81.2	328.8	78.7	38.0
BuO	372.0	85.5	407.5	85.5	35.5
AmO	457.5	87.0	493.0	86.5	35.0
HexO	544.5	87.3	579.5	88.0	35.0
HeptO	631.8		667.5		35.7

division by four (see Table IV). From the values in Table III, certain conclusions can be drawn. It is obvious that mixed tetraalkoxysilanes elute later than predicted from the retention indices of the symmetrical counterparts. It can further be seen that for the same combination pattern, the deviation from additivity increases with increased difference in carbon number between the groups (see (a) in Table III). It can also be concluded that for the same difference in carbon numbers, the deviation depends both on the combination pattern and on the size of the groups bonded to the silicon atom (see (b) and (c) in Table III). A detailed analysis of the experimental material showed that the deviations between the experimental retention indices and the values obtained by the addition of group retention indices can be accounted for by correction terms according to eqn. 2:

$$I(RO)_4Si = \Sigma I(RO)Si + \Sigma(n \cdot d \cdot k)_{RO-RO} \quad (2)$$

where

RO denotes a normal alkoxy group;

$I(RO)Si$ = group retention index (see Table IV);

n = combination number;

d = difference in carbon numbers between combined alkoxy groups;

k = constant dependent on the smallest alkoxy group in a combination (see Table V).

The combination number is obtained by multiplying the numbers of the various alkoxy groups bonded to the silicon atom. In order to demonstrate the

TABLE V

VALUES OF CONSTANT k IN EQN. 2

Smallest group present	Values of constant k	
	Calc. of I_{160}^{APM}	Calc. of I_{160}^{XE}
MeO	3.1	3.3
EtO	1.5	1.5
PrO	0.8	0.8
BuO	0.4	0.4

application of eqn. 2, the retention indices of some tetraalkoxysilanes are calculated below.

The first example deals with $(\text{MeO})_2\text{Si}(\text{OHex})_2$.

$$I^{\text{APM}}(\text{MeO})_2\text{Si}(\text{OHex})_2 = 2I^{\text{APM}}(\text{MeO})\text{Si} + 2I^{\text{APM}}(\text{HexO})\text{Si} + (n \cdot d \cdot k)_{\text{MeO-HexO}}$$

The combination number n is equal to 4 (2·2), as there are two MeO groups and two HexO groups. The difference in carbon numbers between Me and Hex is 5 and $k = 3.1$, because MeO is the smallest alkoxy group present. By inserting the group retention indices from Table IV into the equation and adding the correction term ($4 \cdot 5 \cdot 3.1 = 62$), the retention index of $(\text{MeO})_2\text{Si}(\text{OHex})_2$ is calculated to be 1480. The experimental value is 1477.

In the second example, the retention index of $\text{MeOSi}(\text{OPr})_2\text{OAm}$ is calculated.

$$I^{\text{APM}}\text{MeOSi}(\text{OPr})_2\text{OAm} = I^{\text{APM}}(\text{MeO})\text{Si} + 2I^{\text{APM}}(\text{PrO})\text{Si} + I^{\text{APM}}(\text{AmO})\text{Si} + (n \cdot d \cdot k)_{\text{MeO-PrO}} + (n \cdot d \cdot k)_{\text{MeO-AmO}} + (n \cdot d \cdot k)_{\text{PrO-AmO}}$$

By applying the same principles as before when calculating the correction terms, we obtain $(n \cdot d \cdot k)_{\text{MeO-PrO}} = 2 \cdot 2 \cdot 3.1 = 12.4$, $(n \cdot d \cdot k)_{\text{MeO-AmO}} = 1 \cdot 4 \cdot 3.1 = 12.4$, $(n \cdot d \cdot k)_{\text{PrO-AmO}} = 2 \cdot 2 \cdot 0.8 = 3.2$, and $I^{\text{APM}}\text{MeOSi}(\text{OPr})_2\text{OAm} = 1231$. The experimental value is 1229. The retention indices of 54 mixed tetraalkoxysilanes, calculated according to eqn. 2, are given in Table II. The agreement between the experimental and calculated values is surprisingly good, the mean deviation being about 1.2 index units for either column. In fact, in most instances the deviation does not exceed the expected accuracy in the retention index measurement.

As shown in Table IV, in the series of symmetrical tetraalkoxysilanes, the index increment for an added CH_2 group becomes approximately constant, and the same for the two liquid phases, from BuO onwards. Accordingly, approximate group retention indices, not listed in Table IV, can be obtained by the addition of 87 index units to the values of $I(\text{HeptO})\text{Si}$ for each new CH_2 group.

According to the first of Kováts' seven rules¹⁰, the retention index of the higher members of any homologous series increases by 100 for each CH_2 group introduced. However, exceptions from this rule have been reported, e.g. for esters of dibasic acids¹¹. That the first rule of Kováts is not valid for homologous series of tetraalkoxysilanes is easily understood. It was already pointed out that in the series of symmetrical tetraalkoxysilanes the constant difference per CH_2 group is about 87, which is the lowest value that the difference can attain. Using the equation derived for the calculation of retention indices, it can be shown that the difference per CH_2 group will change with the series. Thus the highest difference (97) is found in the $(\text{MeO})_3\text{SiOR}$ series and the differences for other homologous series of tetraalkoxysilanes will lie between the two extreme values.

ΔI values. Kováts¹⁰ denoted the difference between a polar and non-polar index of a substance, its ΔI value, and has shown it to be characteristic of the structure. A formula for calculating ΔI values of tetraalkoxysilanes is obtained by subtracting eqn. 2, valid for Apiezon M, from the same equation, valid for XE-60, giving

$$\Delta I(\text{RO})_4\text{Si} = \Sigma \Delta I(\text{RO})\text{Si} + \Sigma (n \cdot d \cdot k)_{\text{MeO-RO}} \quad (3)$$

where $k = 0.2$ and n and d have the same meaning as in eqn. 2. The group ΔI values, $\Delta I(\text{RO})\text{Si}$, were taken from Table IV. As shown by eqn. 3, the group ΔI values are additive except for $\Delta I(\text{MeO})\text{Si}$, where a correction has to be made. Thus, for $(\text{MeO})_2\text{Si}(\text{OHex})_2$, the correction is 4 ($= 4 \cdot 5 \cdot 0.2$). Table II lists the calculated ΔI values of 54 tetraalkoxysilanes. The decreasing ΔI values in Table I reflect the increased shielding of the polar Si-O and C-O bonds by the alkyl groups. From $(\text{BuO})_4\text{Si}$ onwards, the ΔI values are essentially constant, indicating that the shielding effect has reached a saturation point. The use of ΔI values for the identification of various types of tetraalkoxysilanes is discussed later in this paper.

In the same way as the polarity of a substance can be expressed by its individual ΔI values, the constant ΔI value that the members of a homologous series attain when the carbon chain has reached a certain length can be used as a measure of the polarity of the series. Table VI summarizes the ΔI values of some homologous series, denoted by ΔI_{hom} .

TABLE VI
 ΔI VALUES OF SOME HOMOLOGOUS SERIES

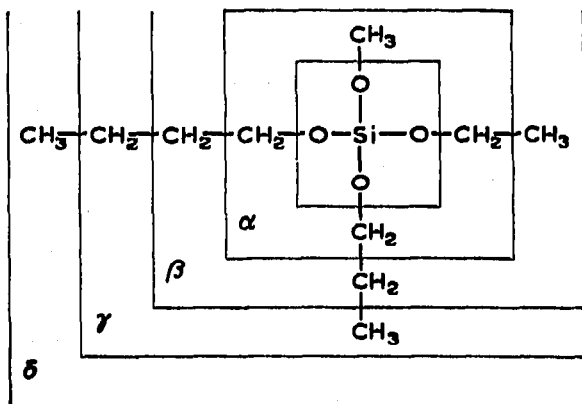
Homologous series	$\Delta I_{\text{hom}}^{\text{XE-APM}}$
$(\text{MeO})_3\text{SiOR}$	236
$(\text{MeO})_2\text{Si}(\text{OR})_2$	208
$\text{MeOSi}(\text{OR})_3$	175
$(\text{EtO})_3\text{SiOR}$	166
$(\text{EtO})_2\text{Si}(\text{OR})_2$	158
$\text{EtOSi}(\text{OR})_3$	149
$(\text{PrO})_3\text{SiOR}$	149
$(\text{PrO})_2\text{Si}(\text{OR})_2$	147
$\text{PrOSi}(\text{OR})_3$	146
$(\text{BuO})_3\text{SiOR}$	143
$(\text{BuO})_2\text{Si}(\text{OR})_2$	141
$\text{BuOSi}(\text{OR})_3$	141
$\text{Si}(\text{OR})_4$	142

It will be noted that the polarity decreases from the methoxysilanes to the butoxysilanes and also within each group of alcoxysilanes. The first change is caused by the increase in size of the groups to the left of the silicon atom in Table VI and the second change by the exchange of RO groups for MeO, EtO, etc., groups. A substantial exchange effect on the ΔI_{hom} value exists only for the methoxysilanes (about 30 index units) and a small effect for the ethoxysilanes (about 10 index units), while it is negligible for the propoxy- and butoxysilanes. This is to be expected considering the differences between the group ΔI values given in Table IV, *i.e.*, $\delta\Delta I(\text{MeOSi-ROSi}) \approx 30$, $\delta\Delta I(\text{EtOSi-ROSi}) \approx 8$ and $\delta\Delta I(\text{PrOSi-ROSi}) \approx 3$.

Theoretical considerations

The retention index of a compound is related to the free energy of solution of the solute molecules in the stationary phase. The fact that the group retention indices of alkoxy groups of different sizes are non-additive means that the dissolution

power of the group in question in the stationary phase changes in the new environment. This change can, at least formally, be explained by assuming that an interaction takes place between certain CH_3 and CH_2 groups in the mixed tetraalkoxysilane. To elucidate this, consider as an example the tetraalkoxysilane $\text{MeO}(\text{EtO})(\text{PrO})(\text{BuO})\text{Si}$, with four dissimilar alkoxy groups bonded to the silicon atom:



CH_3 and CH_2 groups situated at the same distance from the silicon atom belong to the same zone, and the tetraalkoxysilane shown above contains four zones. It is assumed that an interaction between a CH_3 and a CH_2 group in the same zone gives rise to an increase in retention index amounting to $k_{\alpha-\alpha}$, $k_{\beta-\beta}$, $k_{\gamma-\gamma}$ and $k_{\delta-\delta}$ index units. It is also assumed that an interaction between a CH_2 group in an outer zone and a CH_3 group in an inner zone gives rise to an increase in retention index amounting to $k_{\beta-\alpha}$, $k_{\gamma-\alpha}$, $k_{\delta-\alpha}$, $k_{\gamma-\beta}$, $k_{\delta-\beta}$ and $k_{\delta-\gamma}$ index units. Accordingly, the total change in retention index for the tetraalkoxysilane in the figure will be

$$3k_{\alpha-\alpha} + 2k_{\beta-\beta} + k_{\gamma-\gamma} + 2k_{\beta-\alpha} + k_{\gamma-\alpha} + k_{\gamma-\beta}$$

Setting* $k_{\alpha-\alpha} \approx k_{\beta-\alpha} \approx k_{\gamma-\alpha} = k'$, $k_{\beta-\beta} \approx k_{\gamma-\beta} = k''$ and $k_{\gamma-\gamma} = k'''$ makes the change in retention index equal to $6k' + 3k'' + k'''$.

Comparison with the correction term in eqn. 2 for the tetraalkoxysilane in question:

$$\begin{aligned} \Sigma(n \cdot d \cdot k)_{\text{RO-RO}} &= \Sigma(n \cdot d \cdot k)_{\text{MeO-RO}} + \Sigma(n \cdot d \cdot k)_{\text{EtO-RO}} + (n \cdot d \cdot k)_{\text{PrO-BuO}} \\ &= 6k (k = 3.1) + 3k (k = 1.5) + k (k = 0.8) \end{aligned}$$

shows that the correction term can be obtained by adding a number of interaction increments k' , k'' and k''' arising from an assumed interaction between certain CH_3 and CH_2 groups. The value of k' is equal to 3.1, that of k'' equal to 1.5 and that of k''' equal to 0.8 for Apiezon M according to Table V.

Temperature dependence of retention indices and ΔI values

The measured change in retention index with temperature for symmetrical

* It can be shown that these equalities are approximately valid.

tetraalkoxysilanes is given in Table I, which also lists the calculated temperature dependence of the ΔI values. The retention index change is given as 10 times the change of I per degree centigrade ($10dI/dT$). This method of reporting the variation in retention index presupposes an at least approximately linear change of I with T within the indicated 60° temperature range. Thus, linear interpolation within the range to obtain retention indices at temperatures other than 160° is possible, and some extrapolation outside the range is also permitted. In order to demonstrate the use of retention index increments, the retention indices of $(\text{MeO})_4\text{Si}$ at 60° and of $(\text{EtO})_4\text{Si}$ at 100° will be calculated. According to Table I, in the first case $I = 658 + 10 \cdot 2.8 = 686$, and in the second case $I = 850 + 6 \cdot 4.5 = 877$, which are in very good agreement with the values for Apiezon L reported by Garzó *et al.*⁵ (686 and 875, respectively). However, over a wider range, the temperature dependence of the index is non-linear, which has also been shown to be the case for other types of compounds¹².

As seen, the change in index with temperature is negative and increases considerably when the alkoxy group increases in size. Negative temperature increments of this magnitude are exceptional. Comparison with the corresponding tetraalkylsilanes (R_4Si), for which the temperature increment is generally positive and of the same order of magnitude ($10dI/dT \approx 0.5-3$) (ref. 9) as for the corresponding hydrocarbons (R_4C) (ref. 13), warrants the conclusion that the unusual behaviour of the tetraalkoxysilanes is connected with the oxygen atom.

Ettre and Billeb¹⁴ have pointed out the usefulness of retention index *versus* temperature plots for the evaluation of the optimum column temperature when analyzing mixtures of compounds with similar boiling points. For example, plots for the tetraalkoxysilanes $(\text{MeO})_n\text{Si}(\text{OEt})_{4-n}$ ($n = 0-4$) give straight lines that converge towards higher temperatures. Hence, it appears that the best separation of the compounds in question will be obtained at the lowest possible column temperature.

The $10dI/dT$ values of certain mixed tetraalkoxysilanes can be calculated with fair accuracy from those of the corresponding symmetrical compounds in Table I. These values are divided by four to give group values, which are then added. By this method, the following $10dI/dT$ values on XE-60 were obtained, for example, for the methoxyethoxysilanes $(\text{MeO})_n\text{Si}(\text{OEt})_{4-n}$ ($n = 1-3$); for $n = 1$, -3.5 (-3.7 found), for $n = 2$, -2.8 (-2.7 found), and for $n = 3$, -1.5 (-1.6 found). Naturally, the method should not be applied to mixed tetraalkoxysilanes such as methoxyheptoxysilanes for which the temperature dependence of the retention indices of the corresponding symmetrical compounds were measured in separate temperature ranges*. Thus, the retention index *versus* temperature curves can be drawn for every system of mixed tetraalkoxysilanes for which the temperature increments of the corresponding symmetrical tetraalkoxysilanes are known in the same approximate temperature range.

The increments of the ΔI values are far lower than the increments of the retention indices as a consequence of the latter being of the same sign and similar magnitude for Apiezon M and XE-60. They are negative with one exception, the value for $(\text{MeO})_4\text{Si}$ being positive.

* Calculations covering more extensive material will be presented in a forthcoming paper.

Relationship between retention indices and carbon numbers

There will be an approximately linear relationship between retention index and carbon number for any homologous series of tetraalkoxysilanes, e.g., $(RO)_3SiOC_nH_{2n+1}$, counted from $n = 4$. This follows from the fact that the differences between group retention indices become approximately constant from $I(BuO)Si$ onwards and that the same applies to the correction term in eqn. 2. The linear relationship is demonstrated in Fig. 1 for some homologous series of tetraalkoxysilanes.

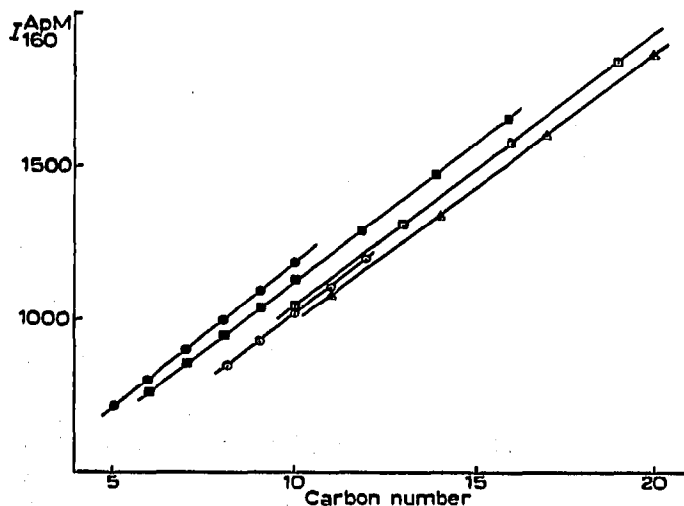


Fig. 1. Retention index on 4% Apiezon M at 160° versus carbon number for homologous series of tetraalkoxysilanes: ●, $(MeO)_3SiOR$; ■, $(MeO)_2Si(OR)_2$; □, $MeOSi(OR)_3$; ○, $(EtO)_3SiOR$; △, $EtOSi(OR)_3$.

Pollard *et al.*¹⁵ have stated that a linear relationship exists between the logarithm of the retention volume and the carbon number for tetraalkylsilanes belonging to the series $R_4Si-R_3SiR'-R_2SiR'_2-RSiR'_3-SiR'_4$. For the corresponding series of tetraalkoxysilanes, an approximately linear relationship between retention index and carbon number will exist only for series with small values of the product $d \cdot k$ in the correction term of eqn. 2. This means that an approximately linear relationship will be found, for example, for the series $(PrO)_nSi(OBu)_{4-n}$ ($n = 4-0$), but not for the series $(MeO)_nSi(OBu)_{4-n}$ ($n = 4-0$) (see Fig. 2).

Retention index versus molar refraction

Vorbjev¹⁶ demonstrated a linear relationship between the logarithm of the retention volume and molar refraction of homologous series of certain aldehydes, ketones, esters, ethers and carboxylic acids. Putnam and Pu¹⁷ plotted retention indices of organotin compounds against their molar refractions but no linear relationship was found, probably because of an inappropriate choice of the compounds investigated.

As the molar refraction of homologous series of tetraalkoxysilanes is linear with the carbon number counted from the second member in a series¹⁸, it follows that

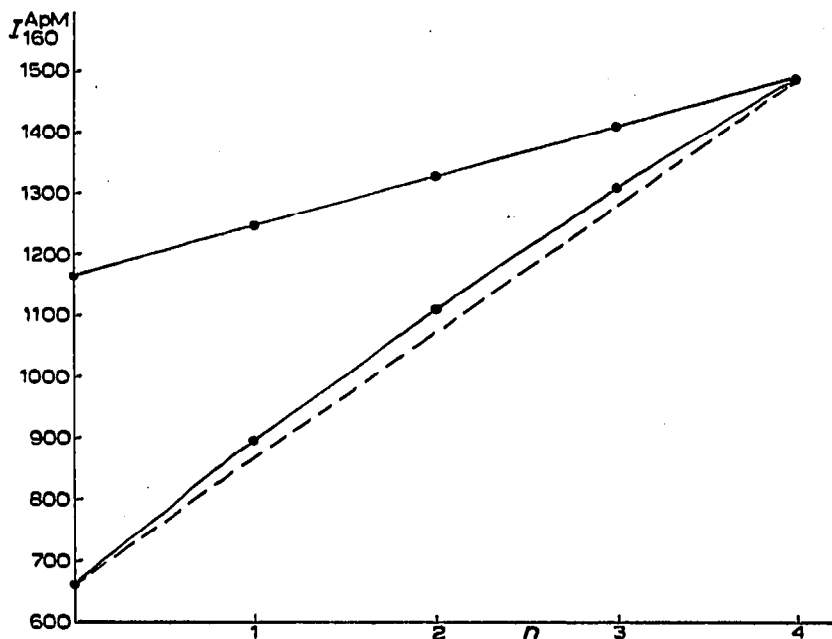


Fig. 2. Retention index on 4% Apiezon M at 160° of the series $(\text{PrO})_n\text{Si}(\text{OBu})_{4-n}$ (upper curve) and $(\text{MeO})_n\text{Si}(\text{OBu})_{4-n}$ (lower curve) plotted against n .

the molar refraction will be linear with the retention index counted from the third or fourth member in a homologous series. However, in order to arrive at the molar refraction, the density, refractive index and molar weight have to be determined. The molar refraction is thus a physical quantity that is difficult to obtain and which, furthermore, cannot be determined by using micro-amounts of substance. A plot of molar refraction (MR_D) against I_{160}^{APM} shows that the spread between different homologous series is small, except for methoxyalkoxysilanes. In fact, a plot of simply the molecular weight against I_{160}^{APM} gives as much information as the plot of MR_D against I_{160}^{APM} .

It therefore appears that the molar refraction is of limited value for identification purposes. Of the above-mentioned physical quantities, the refractive index (n_D) is most easily established by using an Abbe refractometer, only a small drop of liquid being required, and furthermore values have been tabulated for a very large number of organic compounds. It would therefore be convenient if the refractive index could be utilized in conjunction with the retention index for identification purposes. The manner in which this can be achieved will be described in a subsequent paper.

Retention index versus boiling point

When the boiling points of tetraalkoxysilanes are plotted against I_{160}^{APM} , the points align themselves along a slightly curved line. However, the Kováts' relationship¹⁰ ($\delta T \approx 0.2 \delta I$) seems to be applicable to the calculation of approximate boiling points from I_{160}^{APM} values. Here δT denotes the difference between the boiling points of two tetraalkoxysilanes and δI the difference between their I_{160}^{APM}

values. Table VII gives the differences between the calculated and experimental boiling points. In the calculation, the difference to the lowest boiling compound in a series, $(\text{MeO})_4\text{Si}$, was taken as the reference. It should be pointed out that the precision of the experimental values of the boiling points is low in certain instances, as they were recalculated to atmospheric pressure from boiling points measured at reduced pressure.

TABLE VII

COMPARISON OF EXPERIMENTAL AND CALCULATED BOILING POINTS OF TETRAALKOXY-SILANES

Compound	Boiling point ($^{\circ}\text{C}$)		
	Exptl.	Calcd.	Diff. (calcd.-exptl.)
$(\text{MeO})_4\text{Si}$	120		
$(\text{MeO})_3\text{SiOPr}$	150	149	-1
$(\text{MeO})_2\text{Si}(\text{OPr})_2$	177	175	-2
$\text{MeOSi}(\text{OPr})_3$	198	200	+2
$\text{Si}(\text{OPr})_4$	225	221	-4
$(\text{MeO})_3\text{SiOBu}$	167	167	0
$(\text{MeO})_2\text{Si}(\text{OBu})_2$	205	210	+5
$\text{MeOSi}(\text{OBu})_3$	250*	250	0
$\text{Si}(\text{OBu})_4$	280*	286	+6

* These boiling points were calculated to atmospheric pressure from values measured at reduced pressure¹⁸ using a nomogram valid for *n*-alkanes¹⁹.

Retention indices of homologous series of mixed tetraalkoxysilanes versus retention indices of the symmetrical counterparts

When the J_{160}^{ApM} values of homologous series of mixed tetraalkoxysilanes were plotted against the J_{160}^{ApM} values of the symmetrical counterparts, the points were found to lie on straight lines (see Fig. 3). In this instance, there is no deviation from linearity for the first members in a series as in, for example, the plots of retention index versus carbon number.

The slopes of the lines in the graph depend on whether one, two or three alkoxy groups are exchanged at a time. Similar plots are obtained for J_{160}^{XE} . The linear relationship may be utilized for refining the previously described method for calculating retention indices of mixed tetraalkoxysilanes from those of the symmetrical counterparts. The procedure used will be described in a subsequent paper.

J_{160}^{ApM} versus J_{160}^{XE} . In the two-phase plot of J_{160}^{ApM} versus J_{160}^{XE} , two main linear relationships exist (see Fig. 4). The first refers to so-called homologous lines, which connect points in homologous series of tetraalkoxysilanes. Four homologous lines are drawn in Fig. 4 for the series with the formula codes 111X, 112X, 122X and 222X (the formula code simply denotes the alkoxy groups bonded to the central silicon atom, 1 = MeO, 2 = EtO, 3 = *n*-PrO and so on; the formula code 1111 thus refers to $(\text{MeO})_4\text{Si}$). The linear relationship in homologous series is a consequence of the previously established linear relationship between the carbon number and J_{160}^{ApM} and J_{160}^{XE} , respectively.

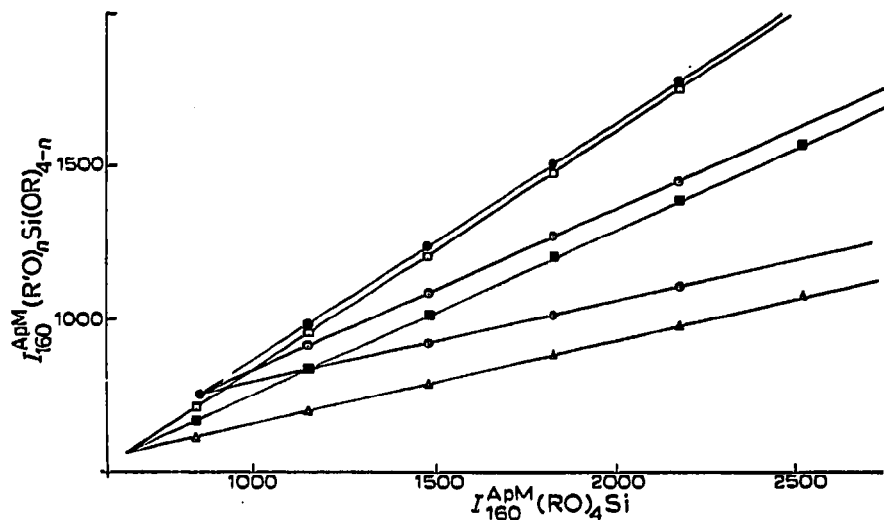


Fig. 3. Retention indices on 4% Apiezon M of homologous series of mixed tetraalkoxysilanes versus retention indices of symmetrical counterparts. ●, EtOSi(OR)_3 ; ○, $(\text{EtO})_2\text{Si(OR)}_2$; ⊕, $(\text{EtO})_3\text{SiOR}$; □, MeOSi(OR)_3 ; ■, $(\text{MeO})_2\text{Si(OR)}_2$; △, $(\text{MeO})_3\text{SiOR}$.

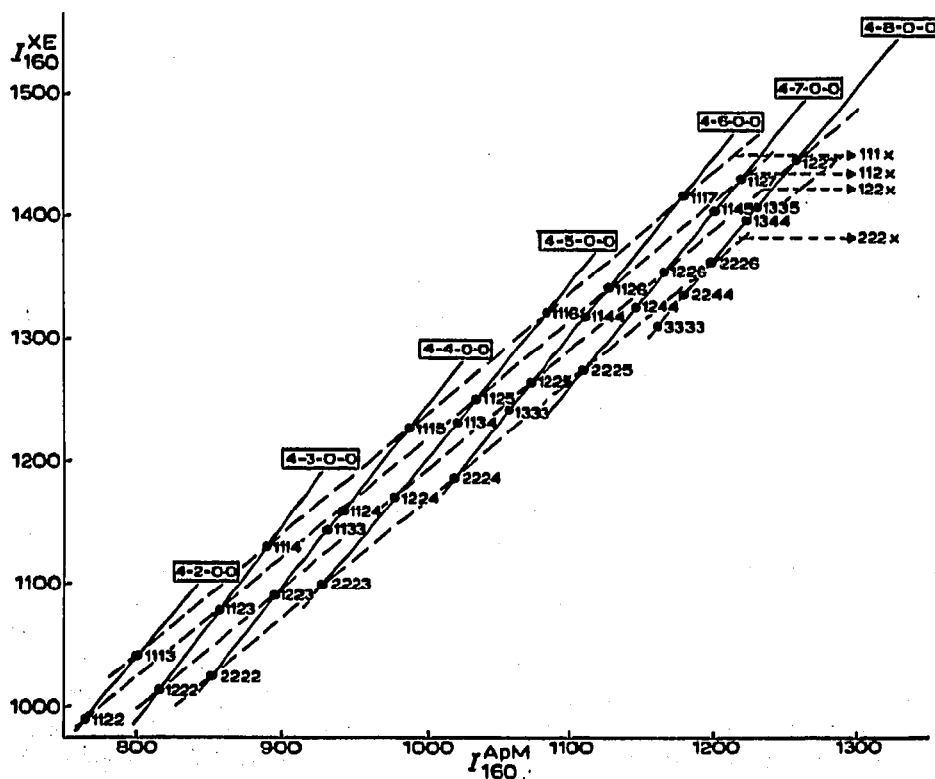


Fig. 4. Two-phase plot of I_{160}^{ApM} versus I_{160}^{XE} . ---, homologous lines; —, structure lines.

The second linear relationship in Fig. 4 was more unexpected and refers to so-called structure lines. It appears that these structure lines connect points that have the same structure code. The structure code is written $a-b-d-e$ where a , b , d and e are the number of CH_3 , CH_2 , CH and C groups, respectively. As this work concerns only normal alkoxy groups, d and e are always zero. Along each structure line, the tetraalkoxysilanes, all of equal molecular weight, are arranged according to decreasing formula code. Furthermore, the compounds that belong to the same structure series are grouped together with interspaces between the groups. The first group comprises compounds without MeO groups, the second group compounds with one MeO group, the third group compounds with two MeO groups, and the fourth group compounds with three MeO groups. The above alignment means that within a structure series, the compounds are eluted according to symmetry, the most symmetrical being eluted first and the least symmetrical last.

Although the linear relationship in the structure series is reasonable (see Table VIII), closer inspection indicates that an imbrication exists between the separate groups within a series. In the original structure code, no differentiation was made

TABLE VIII

CONSTANTS IN AND CORRELATION COEFFICIENTS OF THE LINEAR RELATION $I_{160}^{\text{XE}} = k \cdot I_{160}^{\text{ApM}} + l$ FOR TETRAALKOXY-SILANES WITH THE SAME STRUCTURE CODE 4-b-0-0

Structure code	Number of compounds	k	l	Correlation coefficient
4-2-0-0	2	1.486	-152	
4-3-0-0	3	1.476	-188	0.99990
4-4-0-0	5	1.458	-217	0.9998
4-5-0-0	6	1.455	-257	0.99998
4-6-0-0	8	1.449	-292	0.99997
4-7-0-0	9	1.427	-308	0.99990
4-8-0-0	11	1.420	-337	0.99995
4-9-0-0	5	1.411	-364	0.99991
4-10-0-0	8	1.403	-388	0.99990
4-11-0-0	5	1.376	-385	0.9998
4-12-0-0	8	1.381	-427	0.9998

between CH_3 and CH_2 groups bonded to oxygen and carbon. If this differentiation is made, we obtain, instead of the code $a-b-d-e$, a new code a' , $a''-b'$, $b''-d-e$, where a' and b' are the numbers of CH_3 and CH_2 groups bonded to oxygen and a'' and b'' the numbers of the same groups bonded to carbon; d and e are zero, as before. If this subcode is applied, it is found that the various groups within a structure series have the same subcode number, e.g., in the series 4-6-0-0, the subcode numbers will become 0,4-4,2-0-0, 1,3-3,3-0-0, 2,2-2,4-0-0 and 3,1-1,5-0-0.

There is also an indication that the order of imbrication changes with the number of CH_2 groups in the molecule. Thus, tetraalkoxysilanes with an even number of CH_2 groups like those in the structure series 4-6-0-0 exhibit a normal imbrication order, while tetraalkoxysilanes with an odd number of CH_2 groups like those in the structure series 4-7-0-0 show an inverse order of imbrication. Structural

relationships similar to those found here have been reported for hydrocarbons and some other types of organic compounds^{20,21}.

Identification of tetraalkoxysilanes

The most useful aid in the identification of tetraalkoxysilanes is the two-phase plot in Fig. 4. As I_{160}^{APM} and I_{160}^{XE} can be calculated for any tetraalkoxysilane with normal alkoxy groups by using eqn. 2, the two-phase plot can be expanded as required. However, with increasing molecular weight, the differentiation between neighbouring compounds within each sub-group in a structure series will become increasingly difficult, and chemical methods must be resorted to, e.g. hydrolysis combined with gas chromatographic investigation of the alcohols formed.

The ΔI values are also of value for identification purposes (see Fig. 5). It is

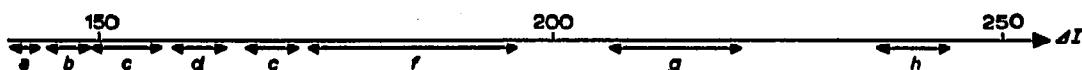


Fig. 5. $\Delta I_{160} = I_{160}^{XE} - I_{160}^{APM}$ for homologous series of tetraalkoxysilanes. $a = (\text{BuO})_n\text{Si}(\text{OR})_{4-n}$ ($n = 1-4$); $b = (\text{PrO})_n\text{Si}(\text{OR})_{4-n}$ ($n = 1-4$); $c = \text{EtOSi}(\text{OR})_3$; $d = (\text{EtO})_2\text{Si}(\text{OR})_2$; $e = (\text{EtO})_3\text{SiOR}$; $f = \text{MeOSi}(\text{OR})_3$; $g = (\text{MeO})_2\text{Si}(\text{OR})_2$ and $h = (\text{MeO})_3\text{SiOR}$.

possible to distinguish between the series $(\text{MeO})_3\text{SiOR}$, $(\text{MeO})_2\text{Si}(\text{OR})_2$ and $\text{MeOSi}(\text{OR})_3$ and also between some of the higher series of tetraalkoxysilanes. The varying temperature dependence of the retention indices of tetraalkoxysilanes can also be utilized in identification work, as will be discussed in a subsequent paper.

REFERENCES

- 1 C. R. Thrash, *J. Gas Chromatogr.*, 2 (1964) 390.
- 2 M. Wurst, *Mikrochim. Acta*, (1966) 379.
- 3 M. Wurst and J. Churáček, *Collect. Czech. Chem. Commun.*, 36 (1971) 3497.
- 4 J. H. Taylor, *J. Gas Chromatogr.*, 6 (1968) 557.
- 5 G. Garzó, J. Fekete and M. Blazsó, *Acta Chim. Acad. Sci. Hung.*, 51 (1967) 359.
- 6 I.-B. Peetre, *Chromatographia*, 6 (1973) 257.
- 7 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 5 (1961) 300.
- 8 J. A. Semlyen and C. S. G. Phillips, *J. Chromatogr.*, 18 (1965) 1.
- 9 I.-B. Peetre, *J. Chromatogr.*, in press.
- 10 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 11 J. Zulaica and G. Guichon, *Bull. Soc. Chim. Fr.*, (1963) 1242.
- 12 G. D. Mitra and W. C. Saha, *Chromatographia*, 6 (1973) 93.
- 13 G. Castello, M. Berg and M. Lunardelli, *J. Chromatogr.*, 79 (1973) 23.
- 14 L. S. Ettre and K. Billeb, *J. Chromatogr.*, 30 (1967) 112.
- 15 F. H. Pollard, G. Nickless and P. C. Uden, *J. Chromatogr.*, 19 (1965) 28.
- 16 L. N. Vorbjev, *Collect. Czech. Chem. Commun.*, 27 (1962) 1045.
- 17 R. Putnam and H. Pu, *J. Gas Chromatogr.*, 3 (1965) 160.
- 18 B. Smith, *Dissertation*, Gothenburg, 1951.
- 19 S. W. Ferris, *Handbook of Hydrocarbons*, Academic Press, New York, 1955, p. 324.
- 20 J. J. Walraven, A. W. Ladon and A. I. M. Keulemans, *Chromatographia*, 1 (1968) 195.
- 21 J. J. Walraven, *Dissertation*, Eindhoven University of Technology, Eindhoven, 1968.