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GAS CHROMATOGRAPHIC INVESTIGATION OF ORGANOMETALLIC COMPOUNDS AND THEIR CARBON ANALOGUES

V. USE OF REFRACTIVE INDEX IN CONJUNCTION WITH KOVÁTS' RETENTION INDEX FOR THE IDENTIFICATION OF ORGANOSILICON COMPOUNDS

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SUMMARY

A method is described in which the refractive index is utilized in conjunction with the Kováts' retention index for the identification of organosilicon compounds. The refractive index is converted into a quantity known as the refractive number by linear interpolation between refractive indices of *n*-alkanes. As this quantity is a linear function of the retention index for homologous series of compounds, the refractive number–retention index plot can be utilized for identification purposes.

INTRODUCTION

Refractive indices have for a long time been used in combination with densities for the calculation of specific and molar refractions and in the past these quantities have been of considerable value for the identification of organic structures. However, a drawback of this method of identification is that the determination of density is a laborious procedure which requires relatively large amounts of substance. As the working scale in analysis has undergone a steady reduction during recent years and improved identification methods have been introduced, the specific and molar refractions are now of little importance for identification purposes.

The refractive index alone has been less used in identification work although it is probably one of the most easily obtainable physical constants. A determination requires only a small drop of liquid and can be performed in about 1 min using an inexpensive refractometer. Furthermore, refractive indices are tabulated for a vast number of organic compounds. It was thought that by combining the refractive index with another easily obtainable physical quantity, its utility for identification purposes could be considerably increased. The quantity in question should preferably be a linear function of the refractive index for homologous series in order to make it possible to identify an unknown compound from its position in a diagram.

One of the most powerful identification and separation methods today is gas chromatography, and because of our previous experience with this method it was convenient to try to combine the refractive index with the Kováts' retention index,

which is a measure of the position of an eluted substance in a chromatogram. In this paper we demonstrate how the two physical quantities can be advantageously utilized together for the identification of organosilicon compounds. In a subsequent paper, the application of the new method to other types of organic compounds will be described.

EXPERIMENTAL

Refractive index

The refractive indices (n_D^{20}) given in Table I were either determined by means of an Abbe refractometer or taken from previous work by one of the present authors¹ or from other sources²⁻⁶. The mixed tetraalkoxysilanes were prepared by alcoholysis of symmetrical tetraalkoxysilanes using hydrogen chloride as a catalyst. For the final purification, a preparative gas chromatograph was employed.

Although the general procedure for the determination of refractive indices by means of an Abbe refractometer requires only a small drop of liquid, it may sometimes be advantageous to be able to decrease the amount needed in the standard method. Of the several micro-methods that have been described, we have found the method of Blohm⁷ particularly easy to apply.

Retention index

All retention indices collected in Table I were determined in this laboratory⁸⁻¹¹. They all relate to 4% Apiezon M on Chromosorb G (AW, DMCS), 80-100 mesh, at 160°.

Identification procedure

If a pure compound is available, the refractive and retention indices can be simply determined. If a mixture of compounds is present, the components are separated, preferably by gas chromatography, and enough of the compounds of interest are collected to permit a refractive index determination to be made. In a separate run, the retention indices are measured after admixture of appropriate *n*-alkanes.

RESULTS AND DISCUSSION

Refractive number (N_D^{20})

The first difficulty encountered when trying to devise an identification system based on the refractive and retention indices is the fact that they are not linear functions of each other for homologous series of compounds, which was previously considered to be desirable. However, we have found that the refractive index can be converted into another quantity, known as the refractive number, which is a linear function of the retention index for homologous series of compounds. The refractive number is obtained by linear interpolation between refractive indices of the *n*-alkanes, the refractive numbers of which are defined as 100 times their carbon number. Thus, the refractive number of *n*-pentane is 500, of *n*-hexane 600, etc. The refractive number (N_D^{20}) of a compound A whose refractive index is $n_D^{20}(A)$ is obtained from the following equation:

$$N_D^{20}(A) = 100p + \frac{n_D^{20}(A) - n_D^{20}(C_p)}{n_D^{20}(C_{p+1}) - n_D^{20}(C_p)} \quad (1)$$

where C_p and C_{p+1} denote two n -alkanes with carbon numbers p and $p+1$ and between the refractive indices of which n_D^{20} (A) occurs. The n_D^{20} values for n -alkanes were taken from ref. 12. The refractive numbers of the organosilicon compounds investigated are collected in Table I.

TABLE I

REFRACTIVE INDICES (n_D^{20}), REFRACTIVE NUMBERS (N_D^{20}), RETENTION INDICES (I_{160}^{APM}) AND REFRACTIVE RETENTIONS (R_R) FOR ORGANOSILICON COMPOUNDS

Compound	n_D^{20}	Ref.	N_D^{20}	I_{160}^{APM}	Ref.	R_R
<i>Tetraalkoxysilanes</i>						
(MeO) ₄ Si	1.3682	This work	561	658	8	-15
(EtO) ₄ Si	1.3833	This work	666	850	8	-22
(PrO) ₄ Si	1.4011	This work	846	1163	8	-27
(iso-PrO) ₄ Si	1.3852	1	681	915	9	-26
(BuO) ₄ Si	1.4133	This work	1027	1488	8	-31
(iso-BuO) ₄ Si	1.4070	1	925	1304	9	-29
(sec.-BuO) ₄ Si	1.4074	1	931	1264	9	-26
(AmO) ₄ Si	1.4220	This work	1213	1830	8	-34
(HexO) ₄ Si	1.4292	1	1409	2178	8	-35
(MeO) ₃ SiOPr	1.3807	This work	646	803	8	-20
(MeO) ₃ SiOBu	1.3878	This work	702	894	8	-21
(MeO) ₃ SiOAm	1.3938	This work	763	991	8	-23
(MeO) ₂ Si(OPr) ₂	1.3898	This work	722	934	8	-23
(MeO) ₂ Si(OBu) ₂	1.3996	This work	828	1110	8	-25
(MeO) ₂ Si(OAm) ₂	1.4077	This work	935	1294	8	-28
MeOSi(OPr) ₃	1.3961	This work	787	1056	8	-25
MeOSi(OBu) ₃	1.4073	This work	929	1306	8	-29
MeOSi(OAm) ₃	1.4163	This work	1083	1574	8	-31
(EtO) ₃ SiOBu	1.3937	This work	762	1018	8	-25
(EtO) ₃ Si(OBu) ₂	1.4018	This work	855	1179	8	-27
EtOSi(OBu) ₃	1.4078	This work	937	1339	8	-30
<i>Methyltrialkoxysilanes, MeSi(OR)₃</i>						
R = Me	1.3678	2	559	626	11	-11
Et	1.3836	1	666	772	11	-14
Pr	1.3992	1	822	1015	11	-19
Bu	1.4109	1	984	1271	11	-23
Am	1.4194	1	1150	1538	11	-25
Hex	1.4264	1	1325	1808	11	-27
Hept	1.4314	1	1483	2085	11	-29
<i>Dimethyldialkoxysilanes, Me₂Si(OR)₂</i>						
R = Me	1.3706	1	575	576	11	0
Et	1.3814	1	651	678	11	-4
Pr	1.3953	1	778	847	11	-8
Bu	1.4055	1	901	1024	11	-12
Am	1.4138	1	1036	1209	11	-14
Hex	1.4206	1	1177	1396	11	-16
Hept	1.4254	1	1296	1587	11	-18

(Continued on p. 386)

TABLE I (continued).

Compound	n_D^{20}	Ref.	N_D^{20}	$I_{160}^{A_p M}$	Ref.	R_R
<i>Trimethylalkoxysilanes, Me₃SiOR</i>						
R = Me	1.3678	2	559	506	11	10
Et	1.3743	2	596	558	11	7
Pr	1.3838	2	670	645	11	4
Bu	1.3925	2	750	742	11	1
Am	1.4010	2	845	836	11	1
Hex	1.4058	2	906	932	11	- 3
Hept	1.4108	2	983	1030	11	- 5
<i>Tetraalkylsilanes</i>						
Me ₄ Si	1.3582	2	504	420	10	20
Et ₄ Si	1.4267	1	1334	922	10	45
Pr ₄ Si	1.4384	1	1770	1193	10	48
Bu ₄ Si	1.4465	1	> 1900	1486	10	
Am ₄ Si	1.4494	5	> 1900	1820	10	
Me ₃ SiEt	1.3828	6	662	550	10	20
Me ₃ SiPr	1.3935	6*	760	634	10	20
Me ₃ SiBu	1.4028	6*	867	723	10	20
Me ₃ SiAm	1.4096	3	965	814	10	19
Me ₃ SiHex	1.4154	3	1067	904	10**	18
Me ₃ SiHept	1.4201	3	1166	994	10**	17
Me ₃ SiOct	1.4242	3	1265	1084	10**	17
Me ₂ SiEt ₂	1.4001	6*	834	677	10	23
Me ₂ SiEtPr	1.4082	6*	942	759	10	24
Me ₂ SiPr ₂	1.4143	6*	1045	839	10	26
Me ₂ SiBu ₂	1.4240	4	1260	1008	10	25
MeSiEt ₃	1.4160	3	1078	800	10	35
MeSiPr ₃	1.4280	2	1373	1026	10	34
MeSiBu ₃	1.4382	4	1760	1264	10	39
Et ₃ SiPr	1.4309	6*	1463	994	10	47
Et ₃ SiBu	1.4342	6*	1587	1076	10	47
Et ₂ SiPr ₂	1.4339	2	1577	1064	10	48
EtSiPr ₃	1.4362	2	1671	1130	10	48

* Recalculated to 20°.

** Obtained by addition of 90 index units to the previous value.

Calculation of refractive number

One of the properties of the refractive number is its linear relationship with the carbon number for homologous series of organosilicon (and other) compounds, except for the first one or two members in a series:

$$N_D^{20} = k_1 \times \text{carbon number} + l_1 \quad (2)$$

Fig. 1 demonstrates the extent of the linearity between the refractive number and the carbon number for some homologous series of organosilicon compounds*. A consequence of this relationship is that the refractive numbers, and accordingly the

* The points for the series (MeO)₂Si(OR)₂ nearly coincide with the points for the series MeSi(OR)₃.

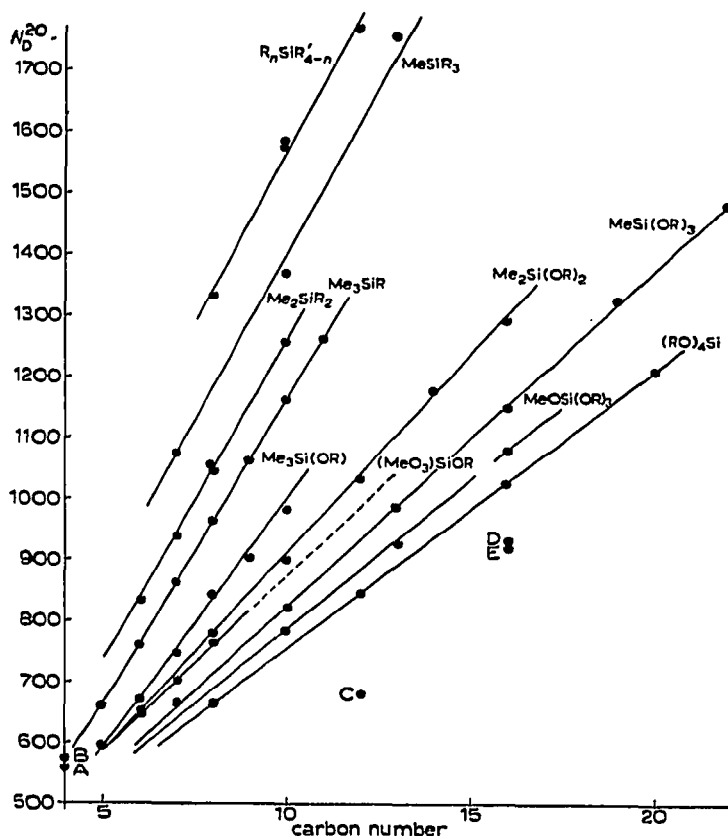


Fig. 1. Refractive numbers versus carbon numbers for homologous series of organosilicon compounds. A = $(\text{MeO})_4\text{Si}$; B = $\text{Me}_2\text{Si}(\text{OMe})_2$; C = $(\text{iso-PrO})_4\text{Si}$; D = $(\text{sec.-BuO})_4\text{Si}$; E = $(\text{iso-BuO})_4\text{Si}$.

refractive indices, of missing members in a homologous series of compounds can be calculated. The constants in the linear equation valid for homologous series of some silicon compounds are given in Table II.

For mixed tetraalkoxysilanes, there is another method of obtaining refractive numbers. It appears that the method utilized in a previous paper⁸ for the calculation of retention indices for mixed tetraalkoxysilanes from retention indices for the symmetrical counterparts is also applicable to refractive number calculation:

$$N_D^{20}[(\text{RO})_4\text{Si}] = \Sigma N_D^{20}(\text{ROSi}) + \Sigma(n \cdot d \cdot k)_{\text{RO-RO}} \quad (3)$$

where

RO denotes a normal alkoxy group;

$N_D^{20}(\text{ROSi})$ = group refractive number, obtained from the refractive numbers of symmetrical tetraalkoxysilanes by division by four;

n = combination number, obtained by multiplying the numbers of the alkoxy groups in a combination. A combination is formed between any two unlike alkoxy groups bonded to the silicon atom (see further ref. 8);

TABLE II

CONSTANTS IN AND CORRELATION COEFFICIENTS FOR THE LINEAR RELATIONSHIP $N_D^{20} = k_1 \cdot \text{CARBON NUMBER} + l_1$, VALID FOR HOMOLOGOUS SERIES OF ORGANOSILICON COMPOUNDS

Series	Compounds	k_1	l_1	Correlation
$(\text{RO})_4\text{Si} + (\text{EtO})_n\text{Si}(\text{OBu})_{4-n}$	R = Et-Hex, $n = 1-3$	46.05	296.6	0.9998
$\text{MeOSi}(\text{OR})_3^*$	R = Pr-Am	49.33	291.7	0.9997
$(\text{MeO})_2\text{Si}(\text{OR})_2^*$	R = Pr-Am	53.25	295.8	1.0000
$(\text{MeO})_3\text{SiOR}^*$	R = Pr-Am	58.50	294.0	0.9997
$\text{MeSi}(\text{OR})_3$	R = Et-Hept	54.86	276.2	0.9999
$\text{Me}_2\text{Si}(\text{OR})_2$	R = Et-Hept	65.10	257.1	0.9998
Me_3SiOR	R = Et-Hept	78.24	204.9	0.9991
MeSiR_3	R = Et-Bu	113.7	267.0	0.997**
Me_2SiR_2	$R_2 = \text{Et}_2\text{-Bu}_2, \text{EtPr}$	106.3	196.3	0.99997
Me_3SiR	R = Et-Oct	100.8	158.6	0.99995
$\text{Et}_n\text{SiPr}_{4-n} + \text{Et}_3\text{SiBu}$	$n = 0-4$	108.0	487.0	0.996**

* Compounds with R=Et have not been investigated.

** The poor correlation is caused by the high n_D^{20} values with consequent uncertainty in N_D^{20} .

d = carbon number difference between alkoxy groups in a combination;

k = constant dependent on the smallest alkoxy group in a combination and to a certain extent on the carbon number difference.

The last term in eqn. 3 may be regarded as a correction term which accounts for the deviation from additivity of the group refractive numbers. In the corresponding correction term in the equation for the calculation of retention indices, the k values are dependent only on the smallest alkoxy group present in a combination. In the present case, however, there is a small but distinct increase in the k value when the carbon number difference (d) increases. Thus, for the combination MeO-PrO $k = 2.2$, for MeO-BuO $k = 2.5$ and for MeO-AmO $k = 3.0$. Whether a similar increase in k values occurs for EtO as the smallest group in a combination is unknown, as only ethoxybutoxysilanes have been investigated. The k value for the combination EtO-BuO is 0.8.

In another method for calculating the retention indices of mixed tetraalkoxysilanes¹³, the retention index difference was substituted for the carbon number difference in the correction term. The same procedure can be applied in the present case:

$$N_D^{20}[(\text{RO})_4\text{Si}] = \Sigma N_D^{20}(\text{RO})\text{Si} + \Sigma(n \cdot k \cdot \Delta N_D^{20})_{\text{RO-RO}} \quad (4)$$

where

ΔN_D^{20} = refractive number difference of the two symmetrical tetraalkoxysilanes, the groups of which appear in a combination;

k = constant dependent on the smallest alkoxy group in a combination.

TABLE III
COMPARISON OF EXPERIMENTAL AND CALCULATED REFRACTIVE NUMBERS
FOR MIXED TETRAALKOXYLSILANES

Compound	N_D^{20}		Diff.	N_D^{20}		Diff.	N_D^{20}	
	Exp.	Calcd. from eqn. 2		Calcd. from eqn. 3	Calcd. from eqn. 4			
(MeO) ₃ SiOPr	646	645	-1	645	-1	647	+1	
(MeO) ₂ Si(OPr) ₂	722	722	0	721	-1	723	+1	
MeOSi(OPr) ₃	787	785	-2	788	+1	789	+2	
(MeO) ₃ SiOBu	702	704	+2	700	-2	701	-1	
(MeO) ₂ Si(OBu) ₂	828	828	0	824	-4	826	-2	
MeOSi(OBu) ₃	929	933	+4	933	+4	934	+5	
(MeO) ₃ SiOAm	763	762	-1	760	-3	757	-6	
(MeO) ₂ Si(OAm) ₂	935	935	0	935	0	931	-4	
MeOSi(OAm) ₃	1083	1081	-2	1086	+3	1083	0	
(EtO) ₃ SiOBu	762	757	-5	761	-1	761	-1	
(EtO) ₂ Si(OBu) ₂	855	849	-6	852	-3	852	-3	
EtOSi(OBu) ₃	937	941	+4	941	+4	941	+4	

In this case there is no change in the k value with the carbon number difference, k being equal to 0.017 for MeO as the smallest group and to 0.005 for EtO as the smallest group.

Table III gives the values for the refractive numbers calculated by eqns. 3 and 4 and, for comparison, also using the linear relationship in eqn. 2. The fact that the same type of equations can be applied for calculation of refractive numbers and retention indices for mixed tetraalkoxysilanes indicates that the same interaction forces are responsible for the deviation from additivity of the group values in the two cases. A possible type of interaction is discussed elsewhere⁸.

N_D^{20} versus I_{460}^{APM}

In Fig. 2, refractive numbers are plotted against retention indices for some homologous series. For the sake of clarity, some series present in the N_D^{20} -carbon number plot have been omitted, namely the series MeOSi(OR)₃, (MeO)₂Si(OR)₂ and (MeO)₃SiOR, the values of which are very close to the line for the series (RO)₄Si. That the refractive number should be a linear function of the retention index for homologous series was to be expected, as the two quantities are both linear functions of the carbon number. However, the extent of linearity is better than in the corresponding carbon number plots, and even the values for the first members in a series are positioned on or near the straight line. This is also borne out by the correlation coefficients in Table IV, where the constants in the linear equation are also given.

The main use of the refractive number-retention index plot is for identification purposes. Of special interest is the fact that the tetraalkylsilane series MeSiR₃, Me₂SiR₂ and Me₃SiR are separated from each other and from the series R₄Si (R ≠ Me). It was previously shown¹⁰ that in the two-phase plot where retention indices measured on a non-polar phase are plotted against retention indices obtained on a polar phase, the spread for tetraalkylsilanes is rather small. Only three compounds

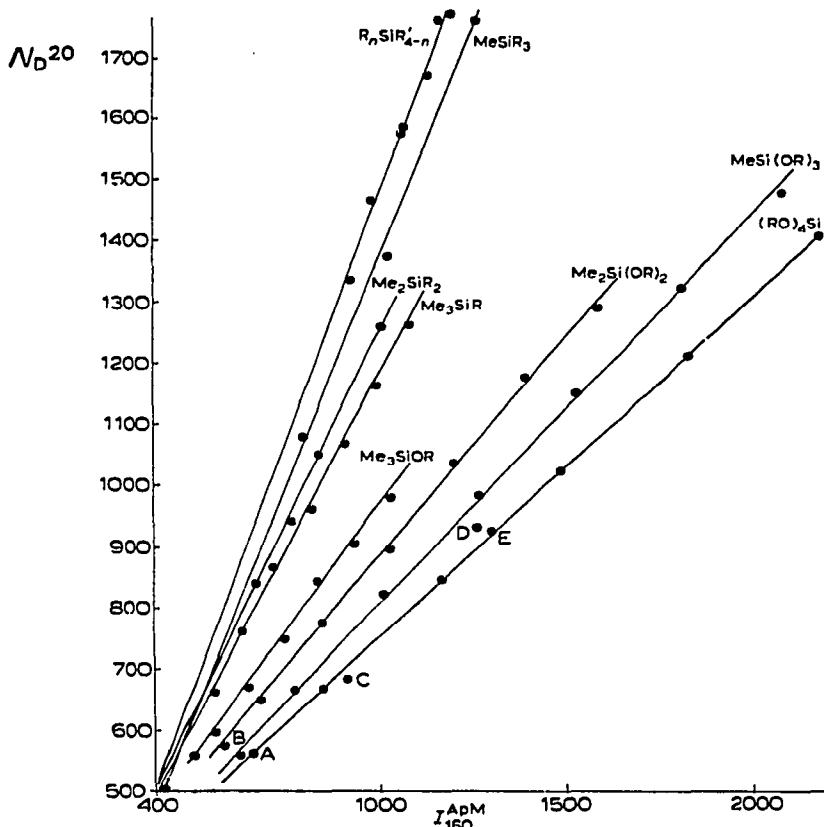


Fig. 2. Refractive numbers *versus* retention indices on 4% Apiezon M at 160° for homologous series of organosilicon compounds. A=(MeO)₄Si; B=Me₂Si(OMe)₂; C=(iso-PrO)₄Si; D=(*sec.*-BuO)₄Si; E=(iso-BuO)₄Si.

TABLE IV

CONSTANTS IN AND CORRELATION COEFFICIENTS FOR THE LINEAR RELATIONSHIP $N_D^{20} = k_2 \cdot I_{160}^{ApM} + I_2$, VALID FOR HOMOLOGOUS SERIES OF ORGANOSILICON COMPOUNDS

Series	Compounds	k_2	I_2	Correlation
(RO) ₄ Si + (EtO) _n Si(OBu) _{4-n}	R = Me-Hex, $n = 1-3$	0.5576	194.5	0.99991
MeOSi(OR) ₃ *	R = Me, Pr-Am	0.5696	185.8	1.00000
(MeO) ₂ Si(OR) ₂ *	R = Me, Pr-Am	0.5890	173.0	0.99998
(MeO) ₃ SiOR*	R = Me, Pr-Am	0.6062	160.9	0.9998
MeSi(OR) ₃	R = Me-Hept	0.6350	172.2	0.9997
Me ₂ Si(OR) ₂	R = Me-Hept	0.7183	165.4	0.9998
Me ₃ SiOR	R = Et-Hept	0.8232	141.1	0.999
MeSiR ₃	R = Me-Bu	1.4738	-114.5	0.9995**
Me ₂ SiR ₂	R ₂ = Me ₂ -Bu ₂ , EtPr	1.2873	-36.3	0.99999
Me ₃ SiR	R = Me-Oct	1.1269	46.5	0.9999
Et _n SiPr _{4-n} + Et ₃ SiBu	$n = 0-4$	1.5943	-128.0	0.999**

* Compounds with R=Et have not been investigated.

** The poor correlation is caused by the high n_D^{20} values with consequent uncertainty in N_D^{20} .

in Fig. 2 contain branched RO groups [(RO)₄Si with R = isopropyl, isobutyl and *sec.*-butyl]. The values for these tetraalkoxysilanes lie not too far from the (RO)₄Si line, in contrast to the case for the refractive number-carbon number plot in Fig. 1, where they are some distance from this line. It thus appears that the refractive number-retention index plot may form a useful adjunct to the two-phase plot in organosilicon identification work.

Refractive retention

The *N* versus *I* plot discussed in the previous section undoubtedly presents the best means of identifying a compound on the basis of its refractive index and retention index. However, sometimes it is of advantage to be able to assign them a composite quantity. For this purpose, the so-called refractive retention

$$R_R = \frac{N - I}{I} \cdot 100 \quad (5)$$

has been defined. It has been found that, with the exception of the first one or two compounds, the refractive retention for members of a homologous series attains characteristic values, often within narrow limits. Fig. 3 demonstrates the refractive retention ranges for various series of organosilicon compounds studied in this work (see also Table I). Although a certain amount of overlap exists, the refractive retention makes possible the differentiation between several types of organosilicon compounds.

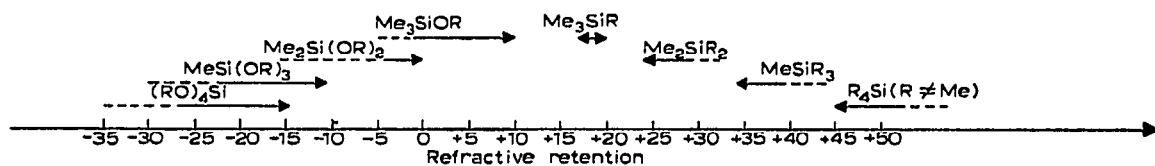


Fig. 3. Refractive retention ranges for series of organosilicon compounds.

Limitations of the method

The fact that the refractive number is calculated by interpolation between the refractive indices of *n*-alkanes imposes certain limitations on the use of the refractive index in conjunction with retention index for identification purposes. Thus, the method cannot be used with confidence for compounds with too high refractive indices because of the decreased accuracy in the refractive number calculation in this case. The reason for this is the decreased interpolation interval. For the C₅- and C₆-alkanes, the difference between their refractive indices is 0.0174, but for the C₂₂- and C₂₃-alkanes the difference is only 0.0013. If the error in the measured refractive index is 0.0002, this means that the error in the calculated refractive number will be about 1 unit between refractive numbers 500 and 600 but about 15 units between refractive numbers 2200 and 2300. On this account, it is not recommended to calculate the refractive number if the refractive index is higher than about 1.44. There is also a lower limit for the refractive index, as the smallest reported refractive index for an *n*-alkane is 1.3326. Accordingly, the refractive number cannot be calculated for compounds that have a refractive index below this value.

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