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A SYSTEM OF STANDARD RETENTION INDICES AND ITS USES  
THE CHARACTERISATION OF STATIONARY PHASES AND  
THE PREDICTION OF RETENTION INDICES

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**SUMMARY**

A method for the calculation of "standard" retention indices from boiling point data has been proposed. The uses of standard retention indices and standard retention index differences for the characterisation of stationary phases and the prediction of retention indices on any stationary phase at any temperature have been discussed. A "cyclic" effect on retention data has been found on squalane and SE-30.

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**INTRODUCTION**

In recent years the use of the KOVATS retention index<sup>1</sup> has become an accepted procedure for the identification of gas chromatographic peaks. Methods have been proposed for the prediction of these retention indices, either from chromatographic data as in SCHOMBURG's method<sup>2,3</sup> which involves "homomorphic" factors, or, following DIMOV AND SHOPOV<sup>4</sup>, from physical data such as vapour pressures, molecular weights and densities. Both of these methods require a considerable amount of data before any prediction of the retention indices can be attempted and for many compounds this data is not available.

We propose that "standard" retention indices can be calculated from boiling point data using a formula similar to that proposed by KOVATS.

The classification of stationary phases according to their polarity has been investigated by many workers<sup>5</sup>. It has been shown that a simple classification can not be achieved on this basis. We show here that a stationary phase may be characterised by comparing observed and standard retention indices of various compounds on that phase.

**EXPERIMENTAL**

The hydrocarbons used were obtained from either Fluka A.G. or Koch-Light Laboratories.

Retention indices were determined using a Varian Model 1800 gas chromatograph with flame ionisation detector. The carrier gas was oxygen-free nitrogen.

Columns were operated either isothermally or using a non-linear temperature program (NLTP)<sup>6</sup>. The columns and NLTP operating conditions were as follows.

### SQUAL

A 10 ft.  $\times$  1/4 in. 5 % squalane on 60/100 Embacel column of 2000 theoretical plates. The carrier gas flow rate was 30 ml/min and the temperature program was as follows: 5 min at 25°, 5 min at 2°/min, 15 min at 4°/min, hold at 95°.

### SE-30

A 20 ft.  $\times$  3/8 in. 30 % SE-30 on 30/60 Chrom W column of 2900 theoretical plates. Carrier gas flow rate was 170 ml/min with the following temperature program: 10 min at 50°, 2 min at 20°/min, 6 min at hold (90°), 6 min at 10°/min, hold at 150°.

### SBDP

A 4 ft. 6 in.  $\times$  1/4 in. 30 % benzyldiphenyl on 60/100 Embacel column of 1900 theoretical plates. Carrier gas flow rate of 60 ml/min. Temperature program: 5 min at 30°, 15 min at 4°/min, 20 min at hold (90°), 10 min at 2°/min, hold at 110°.

### LBDP

A 10 ft.  $\times$  1/4 in. 5 % benzyldiphenyl on 60/100 Embacel column of 1350 theoretical plates. Carrier gas flow rate of 30 ml/min with a temperature program of: 5 min at 50°, 5 min at 2°/min, 10 min at 4°/min, hold at 100°.

### CWX20

A 10 ft.  $\times$  3/8 in. 10 % Carbowax 20M on 60/100 Embacel column of 2700 theoretical plates. Carrier gas flow of 80 ml/min. The temperature program was: initial temperature 25°, 25 min at 4°/min, 5 min at hold (125°), 20 min at 2°/min, hold at 165°.

## RESULTS AND DISCUSSION

(a) *The calculation of standard retention indices and comparison with experimental values*

We define the standard retention index as

$$I_{std} = 100n + 100 \cdot \frac{\log BP_x - \log BP_n}{\log BP_{n+1} - \log BP_n}$$

where  $BP_x$ ,  $BP_n$  and  $BP_{n+1}$  refer to the boiling points of the compound and the  $n$ -alkanes with  $n$  and  $n + 1$  carbon atoms respectively similar to the method of KOVATS<sup>1</sup>. The selected values for  $I_{std}$  are given in Table I.

A standard retention index difference ( $\Delta I^*$ ) may now be obtained by comparison of the standard and experimental retention indices.

$$\Delta I^* = I_{std} - I_x^T$$

where  $I_x^T$  is the retention index of the compound at temperature  $T$  on stationary phase  $x$ .

TABLE I

BOILING POINTS AND STANDARD RETENTION INDICES OF HYDROCARBONS

Compound	b.p. (°C)	<i>I</i> <sub>std</sub>	Compound	b.p. (°C)	<i>I</i> <sub>std</sub>
Methane	-161.6	100	2-Methylhexane	89.7	674
Ethylene	-102.4	175	2,3-Dimethylpentane	89.7	674
Ethane	-88.5	200	2,3-Dimethylpentane	89.7	674
Propylene	-47.7	283	3-Methylhexane	91.8	680
Propane	-42.2	300	Hept-1-ene	93.1	684
Cyclopropane	-33.0	305	3-Ethylpentane	93.3	685
2-Methylpropane	-12.2	327	<i>trans</i> -Hept-2-ene	98.3	699
2-Methylpropene	-6.6	341	<i>n</i> -Heptane	98.4	700
But-1-ene	-6.3	342	<i>cis</i> -Hept-2-ene	99.0	702
1,3-Butadiene	-4.8	349	2,2,4-Trimethylpentane	99.3	703
<i>n</i> -Butane	-0.5	400	Methylcyclohexane	100.3	707
<i>trans</i> -But-2-ene	0.9	413	4-Methylcyclohex-1-ene	102.8	717
<i>cis</i> -But-2-ene	3.7	446	Ethylcyclopentane	103.4	720
2,2-Dimethylpropane	9.5	468	3-Methylcyclohex-1-ene	104.4	724
3-Methylbut-1-ene	20.1	486	1-Methylcyclohex-1-ene	109.5	743
2-Methylbutane	28.0	494	Toluene	110.6	747
Pent-1-ene	29.2	495	2,3,4-Trimethylpentane	113.4	758
2-Methylbut-1-ene	31.0	496	Cycloheptatriene	117.0	770
<i>trans</i> -Pent-2-ene	35.9	499	2-Methylheptane	117.2	771
<i>n</i> -Pentane	36.1	500	4-Methylheptane	118.0	774
<i>cis</i> -Pent-2-ene	37.0	503	Cycloheptane	118.5	776
2-Methylbut-2-ene	38.6	510	3-Methylheptane	119.0	777
Cyclopentene	44.4	532	<i>cis</i> -Oct-2-ene	123.0	791
Cyclopentane	49.3	548	2,2,5-Trimethylhexane	124.1	795
2,2-Dimethylbutane	49.7	549	<i>trans</i> -1,2-Dimethylcyclohexane	124.5	796
2-Methylpent-1-ene	53.6	561	<i>n</i> -Octane	125.6	800
3-Methylpent-1-ene	53.6	561	2,3,5-Trimethylhexane	130.0	818
4-Methylpent-1-ene	53.8	561	<i>cis</i> -1,2-Dimethylcyclohexane	130.1	819
<i>trans</i> -4-Methylpent-2-ene	54.7	564	Ethylcyclohexane	131.8	826
2,3-Dimethylbut-1-ene	55.8	567	Ethylbenzene	136.1	844
2,3-Dimethylbutane	58.0	573	<i>p</i> -Xylene	138.5	853
<i>cis</i> -4-Methylpent-2-ene	58.0	573	<i>m</i> -Xylene	138.8	854
2-Methylpentane	60.2	579	4-Methyloctane	142.5	869
3-Methylpentane	63.2	586	Cyclooctatetraene	142.5	869
Hex-1-ene	63.5	587	1,3-Cyclooctadiene	143.0	871
2-Methylpent-2-ene	66.0	593	<i>o</i> -Xylene	144.0	875
2-Ethylbut-1-ene	66.0	593	Styrene	145.3	879
<i>cis</i> -3-Methylpent-2-ene	66.0	593	Cyclooctane	145.8	881
<i>trans</i> -Hex-3-ene	66.5	594	<i>n</i> -Nonane	150.7	900
<i>trans</i> -Hex-2-ene	68.1	598	<i>cis,cis</i> -1,5-Cyclooctadiene	150.8	900
<i>n</i> -Hexane	68.8	600	Isopropylbenzene	152.5	908
<i>cis</i> -Hex-2-ene	69.0	600	1,3,5-Trimethylbenzene	164.6	961
<i>trans</i> -3-Methylpent-2-ene	69.0	600	<i>tert.</i> -Butylbenzene	169.0	979
3-Methylcyclopent-1-ene	70.0	604	1,2,4-Trimethylbenzene	169.8	983
Methylcyclopentane	71.9	612	<i>tert.</i> -Butylcyclohexane	170.0	983
2,3-Dimethylbut-2-ene	73.3	617	<i>sec.</i> -Butylbenzene	172.5	993
1-Methylcyclopent-1-ene	75.1	624	<i>n</i> -Decane	174.0	1000
2,2-Dimethylpentane	78.9	638	<i>p</i> -Methyl-isopropylbenzene	176.9	1014
Benzene	80.1	642	<i>n</i> -Butylcyclohexane	179.0	1024
Cyclohexane	80.7	644	<i>n</i> -Butylbenzene	183.3	1044
2,4-Trimethylbutane	80.8	644	<i>n</i> -Undecane	195.8	1100
1,3-Cyclohexadiene	81.5	647	<i>n</i> -Undec-1-ene	189.0	1070
Cyclohexene	83.0	652	<i>n</i> -Dodecane	216.2	1200
1,4-Cyclohexadiene	85.5	660	<i>n</i> -Dodec-1-ene	213.0	1184
3,3-Dimethylpentane	86.0	662			

Values for  $\Delta I^*$  on squalane at  $100^\circ$  and SE-30 at  $75^\circ$  are given in Table II. Agreement between standard and observed values is good for alkanes and alkenes.

TABLE II

 $\Delta I^*$  VALUES ON SQUALANE AND SE-30

Class	Compound	$\Delta I_{squal}^*$ ( $100^\circ$ )	$(10 \times dI/dT)_{squal}$	$\Delta I_{SE-30}^*$ ( $75^\circ$ )	$(10 \times dI/dT)_{SE-30}$
Alkanes	2-Methylbutane	+17	+0.6	+12	-0.2
	2,2-Dimethylbutane	+8	+0.8	+9	+0.8
	2,3-Dimethylbutane	+2	+0.6	+4	+0.8
	2-Methylpentane	+1	+0.2	+9	0
	3-Methylpentane	0	+0.4	+1	-0.4
	2,4-Dimethylpentane	+13	+0.2	+13	+0.4
	2-Methylhexane	+6	+0.2	+6	-0.4
	2,3-Dimethylpentane	+1	+0.2	+1	+1.0
	3-Methylhexane	+2	+0.4	+3	+1.2
	3-Ethylpentane	-4	+0.6	+6	+0.8
	2,2,4-Trimethylpentane	+4	+1.0	+8	+1.0
	2-Methylheptane	+6	+0.6	+4	0
	4-Methylheptane	+5	+0.4	—	—
	3-Methylheptane	+3	+0.4	+2	+0.4
2,2,5-Trimethylhexane	+16	+0.6	+9	+0.6	
Alkenes	Pent-1-ene	+21	-1.6	+4	+0.4
	2-Methylbut-1-ene	-4	+3.4	-4	0
	2-Methylpent-1-ene	-18	+2.6	-27	0
	4-Methylpent-1-ene	+10	0	+2	+0.2
	<i>trans</i> -4-Methylpent-2-ene	+7	-0.8	-3	+0.4
	Hex-1-ene	+7	-0.6	-2	0
	2-Methylpent-2-ene	-7	0	-7	0
	Hept-1-ene	+1	+0.4	-1	+1.2
Cyclic alkanes	Cyclopentane	-27	+2.0	-23	+2.4
	Methylcyclopentane	-24	+1.4	-21	+1.2
	Cyclohexane	-30	+2.0	-23	+2.2
	Cycloheptane	-36	+0.2	-8	+0.6
Cyclic alkenes	Cyclopentene	-24	+1.8	-28	+1.4
	3-Methylcyclopent-1-ene	-5	+1.4	-11	+1.2
	1,3-Cyclohexadiene	-15	+1.6	-41	+2.4
	Cyclohexene	-28	+1.6	-27	+2.6
	1,4-Cyclohexadiene	-40	+1.8	-40	+3.0
	1-Methylcyclohex-1-ene	-24	+1.0	-28	+2.0
	Cycloheptatriene	-4	+2.2	—	—
	1,3-Cyclooctadiene	-22	+2.0	—	—
Aromatics	Benzene	-6	+1.6	-14	+1.8
	Toluene	-11	+1.8	-12	+2.4
	Ethylbenzene	-4	+2.0	—	—
	Styrene	+3	+3.0	+1	+0.8

## (b) The "cyclic" effect

The hydrocarbons studied have been grouped (Table II) according to their structure. Table II shows that  $\Delta I^*$  values vary little within a group but that there are marked differences between some groups. This table also shows that the standard retention index differences are much greater for some groups (notably cyclic alkenes and cyclic alkanes). The stationary phases (squalane and SE-30) thus have an enhanced retaining effect on cyclic (except aromatic) compounds, the retention indices

of these compounds being higher than the standard values. We have called this the "cyclic" effect.

Since squalane has usually been taken as the reference stationary phase for comparison of chromatographic data this "cyclic" effect has hitherto escaped notice. Because of this effect we consider squalane to be unsatisfactory as a reference stationary phase and we propose that standard retention indices be used in future to define behaviour.

(c) *A method for the characterisation of stationary phases*

Departures from ideality as measured by  $\Delta I^*$  values may be used to characterise stationary phases as described below.

The hydrocarbons studied were divided into seven classes according to their structure. These classes were: 0, *n*-alkanes; I, branched alkanes; II, *n*-alkenes; III, branched alkenes; IV, cycloalkanes; V, cycloalkenes; VI, aromatics.

If the range of  $\Delta I^*$  values for each class of hydrocarbon is determined on a stationary phase then the retention characteristics of that phase for these classes may be tabulated. A method similar to this has been proposed by WEHRLI AND KOVATS<sup>7</sup> who used Apiezon L as a reference stationary phase.

Table III gives the standard retention index differences ( $\Delta I^*$ ) for compounds arranged in the above classes, together with the average values for each class and the corresponding standard deviations on each of five columns. Only eight of the thirty standard deviation values given lie outside  $\pm 5.0$ , which is the accepted value for reproducibility of retention indices, and none is greater than  $\pm 8.1$ . The values obtained on two different benzyldiphenyl (BDP) columns have been included to indicate the agreement found for different columns of the same stationary phase. In all cases except class VI (aromatics) the values lie within the standard deviation limits shown.

The size of the average  $\Delta I^*$  values for the different classes on a given stationary phase gives an indication of how the phase behaves with respect to these compounds. For instance the large negative value for aromatics on BDP shows that aromatic compounds are retarded in their passage through the column in comparison with, say, alkanes or alkenes.

(d) *A simplified method for the characterisation of stationary phases*

A simpler method than that proposed in section (c) is to use only one member from each class as the basis for characterisation. The  $\Delta I^*$  values could be determined at either one or a number of column temperatures.

The hydrocarbons containing six carbon atoms were chosen as being representative of their classes and the  $\Delta I^*$  values for these, determined at 50°, along with the average values and standard deviations for each class are given in Table IV. The agreement is good enough to permit approximate predictions from the representative  $\Delta I_{50}^*$  values but more accurate predictions must be made using the average value for the particular class being studied.

An example of the use of Table IV is in choosing a stationary phase to separate compounds of similar boiling point, e.g., benzene (b.p. 80.1°), cyclohexane (80.7°) and 1,3-cyclohexadiene (81.5°). These compounds belong to different classes and inspection of Table IV shows that the largest differences between these classes occur

TABLE III

STANDARD RETENTION INDEX DIFFERENCES ( $\Delta I^*$ ) OF HYDROCARBONS

Class	Compound	$I_{std}-I_{SE-30}$	$I_{std}-I_{SBDP}$	$I_{std}-I_{LBDP}$	$I_{std}-I_{squal}$	$I_{std}-I_{CWX20}$
I	2-Methylpropane	(-41)	(-62)	(-34)	22	(-46)
	2,2-Dimethylpropane	(53)	34	34	39	30
	2-Methylbutane	18	14	7	18	18
	2,2-Dimethylbutane	7	30	26	12	-18
	2,3-Dimethylbutane	2	13	11	2	9
	2-Methylpentane	3	11	15	10	-5
	3-Methylpentane	-2	5	4	2	4
	2,2-Dimethylpentane	3	18	20	5	-21
	2,4-Dimethylpentane	4	29	22	3	-8
	2,2,3-Trimethylbutane	-3	14	13	-7	-16
	3,3-Dimethylpentane	9	12	9	-7	-2
	2-Methylhexane	-2	10	10	0	-2
	2,3-Dimethylpentane	1	6	5	-6	10
	3-Methylhexane	-3	18	9	-5	6
	3-Ethylpentane	-7	-4	-1	-6	16
	2,2,4-Trimethylpentane	3	30	23	-	-31
	2,3,4-Trimethylpentane	-3	6	4	-2	-4
	2-Methylheptane	-4	3	7	-1	9
	4-Methylheptane	4	1	4	-1	10
	3-Methylheptane	0	0	3	-2	-2
2,2,5-Trimethylhexane	-	-	29	-	-5	
2,3,5-Trimethylhexane	-7	18	11	0	0	
4-Methyloctane	-12	2	0	6	11	
Average		0.5	12.8	12.0	3.9	0.4
Standard deviation		1.5	2.5	2.1	2.5	3.0
II	Ethylene	-13	-58	-55	-5	-25
	Propylene	-7	(-109)	-64	14	19
	But-1-ene	(-50)	(-105)	(-83)	(-62)	(-71)
	1,3-Butadiene	-46	-80	(-104)	(-54)	(-54)
	<i>trans</i> -But-2-ene	2	-49	-40	-8	-3
	<i>cis</i> -But-2-ene	19	-16	-21	18	29
	Pent-1-ene	3	-21	-5	16	-5
	<i>trans</i> -Pent-2-ene	-13	-35	-36	-1	-1
	<i>cis</i> -Pent-2-ene	-14	-47	-47	3	3
	Hex-1-ene	-5	-28	-24	5	-13
	<i>trans</i> -Hex-3-ene	-6	-29	-30	1	-11
	<i>trans</i> -Hex-2-ene	-22	-37	-30	-2	-2
	<i>cis</i> -Hex-2-ene	-20	-42	-38	0	0
	Hept-1-ene	-8	-34	-32	33	-16
	<i>trans</i> -Hept-2-ene	-1	-44	-33	-1	-1
	<i>cis</i> -Hept-2-ene	-13	-48	-37	2	15
	<i>cis</i> -Oct-2-ene	-22	-55	-52	-9	-9
	<i>n</i> -Undec-1-ene	(48)	-54	-43	-13	-30
	<i>n</i> -Dodec-1-ene	-6	-	-	2	-16
	Average		-10.1	-42.3	-36.6	3.2
Standard deviation		3.3	4.9	4.5	2.8	3.7
III	2-Methylpropene	-49	(-103)	(-87)	(-59)	(-71)
	3-Methylbut-1-ene	(29)	(1)	(4)	27	3
	2-Methylbut-1-ene	3	-26	-30	9	-4
	2-Methylbut-2-ene	-15	-40	-	-	-
	2-Methylpent-1-ene	-33	-50	-55	10	19
	3-Methylpent-1-ene	-2	-61	-55	10	19
	4-Methylpent-1-ene	0	-18	-6	10	-13
	<i>trans</i> -4-Methylpent-2-ene	-10	-36	-46	(45)	-25
	2,3-Dimethylbut-1-ene	-4	-46	-62	5	-1

TABLE III (continued)

Class	Compound	$I_{std}-I_{SE-80}$	$I_{std}-I_{SBDP}$	$I_{std}-I_{LBDP}$	$I_{std}-I_{squal}$	$I_{std}-I_{CWX20}$
	<i>cis</i> -4-Methylpent-2-ene	1	-27	-45	14	-8
	2-Methylpent-2-ene	-34	-42	-37	-7	-7
	2-Ethylbut-1-ene	-7	-35	-33	-1	-7
	<i>cis</i> -3-Methylpent-2-ene	-21	-57	-52	-7	-5
	<i>trans</i> -3-Methylpent-2-ene	-27	-53	-52	-19	-16
	2,3-Dimethylbut-2-ene	-32	—	—	-14	—
	Average	-16.4	-40.9	-43.0	3.0	-3.7
	Standard deviation	4.1	3.8	4.9	3.8	3.7
IV	Cyclopropane	-46	(-104)	(-163)	16	(-19)
	Cyclopentane	-25	-52	-52	-16	17
	Methylcyclopentane	-28	-44	-44	-23	-11
	Cyclohexane	-31	-49	-46	-25	44
	Methylcyclohexane	-30	-51	-42	-28	48
	Ethylcyclopentane	-43	-91	-101	-33	-5
	Cycloheptane	-37	-77	-69	-24	48
	<i>trans</i> -1,2-Dimethylcyclohexane	-16	-36	-33	-11	17
	<i>cis</i> -1,2-Dimethylcyclohexane	-68	-51	-52	-17	19
	Ethylcyclohexane	-24	-44	-44	-14	(80)
	Cyclooctane	-66	-102	-95	-46	29
	<i>tert.</i> -Butylcyclohexane	-31	-37	-30	-17	24
	<i>n</i> -Butylcyclohexane	-24	-76	-38	(61)	24
	Average	-36.0	-59.1	-53.8	-19.8	23.0
	Standard deviation	4.3	6.1	6.5	4.3	5.8
V	Cyclopentene	-23	-85	-68	-15	(51)
	3-Methylcyclopent-1-ene	-15	(-54)	(-29)	6	4
	1-Methylcyclopent-1-ene	-38	-87	—	-29	-38
	1,3-Cyclohexadiene	-31	-120	-107	-45	-2
	Cyclohexene	-37	-99	-86	-27	-3
	1,4-Cyclohexadiene	-48	-140	-134	—	-5
	4-Methylcyclohex-1-ene	-34	-83	-126	—	-7
	3-Methylcyclohex-1-ene	-24	-76	(-49)	-15	1
	1-Methylcyclohex-1-ene	-36	-99	-91	-29	25
	Cycloheptatriene	-30	-142	-130	-2	27
	Cyclooctatetraene	-20	-90	-129	23	(-64)
	1,3-Cyclooctadiene	-49	-129	-113	-21	-29
	<i>cis,cis</i> -1,5-Cyclooctadiene	-48	(-144)	-127	-17	(-125)
	Average	-33.3	-104.5	-111.1	-15.5	-2.7
	Standard deviation	2.3	6.8	7.1	5.7	6.4
VI	Benzene	-23	-132	-128	-3	9
	Toluene	-23	-123	-135	-8	15
	Ethylene	-20	-135	-130	-1	12
	<i>p</i> -Xylene	-21	-136	-128	-11	-47
	<i>m</i> -Xylene	-20	-146	-132	-4	-46
	<i>o</i> -Xylene	-25	-148	-132	-5	(-58)
	Styrene	-21	-161	-149	8	(-121)
	Isopropylbenzene	-21	-123	-116	4	12
	1,3,5-Trimethylbenzene	-12	-144	-128	-7	19
	<i>tert.</i> -Butylbenzene	-21	(-83)	(6)	8	-16
	1,2,4-Trimethylbenzene	-17	-149	-126	-9	-17
	<i>sec.</i> -Butylbenzene	-27	-135	-113	-1	-63
	<i>p</i> -Methylisopropylbenzene	-17	-133	-111	3	14
	<i>n</i> -Butylbenzene	—	-136	-116	11	5
	Average	-20.6	-138.5	-126.4	-0.9	-8.1
	Standard deviation	1.0	3.0	2.8	1.6	8.1

TABLE IV

$\Delta I^*$  VALUES FOR REPRESENTATIVE HYDROCARBONS, AVERAGE  $\Delta I^*$  VALUES FOR EACH CLASS AND AVERAGE TEMPERATURE DEPENDENCE FOR EACH CLASS

Column	Class I		Class II		Class III		Class IV		Class V		Class VI	
	$\Delta I^*$	T.D. <sup>a</sup>	$\Delta I^*$	T.D.	$\Delta I^*$	T.D.	$\Delta I^*$	T.D.	$\Delta I^*$	T.D.	$\Delta I^*$	T.D.
	2-Methylpentane		Hex-1-ene		2-Methylpent-1-ene		Cyclohexane		Cyclohexene		Benzene	
SE-30	9 <sup>b</sup> 0.5 ± 1.5 <sup>c</sup>	0.4	-2 -10.1 ± 3.3	0.5	-27 -16.4 ± 4.1	0.1	-20 -36.0 ± 4.3	1.6	-26 -33.3 ± 2.3	2.1	-12 -20.6 ± 1.0	1.7
SBDP	11 12.8 ± 2.5	-0.6	-28 -42.3 ± 4.9	-0.6	-50 -40.9 ± 3.8	-0.4	-56 -59.1 ± 6.1	3.0	-95 -104.5 ± 6.8	2.0	-132 -138.5 ± 3.0	0.4
LBDF	13 12.0 ± 2.1	-0.6	-13 -36.6 ± 4.5	-0.6	-39 -43.0 ± 4.9	-0.4	-44 -58.8 ± 6.5	3.0	-80 -111.1 ± 7.1	2.0	-125 -126.4 ± 2.8	0.4
SQUAL	9 3.9 ± 2.5	0.5	4 3.2 ± 2.8	-0.6	-5 3.0 ± 3.8	1.0	-20 -19.8 ± 4.3	1.4	-20 -15.5 ± 5.7	1.7	2 0.9 ± 1.6	2.1
CWx20M	-5 0.4 ± 3.0	0.7	-13 -3.8 ± 3.7	0.3	3 -3.7 ± 3.7	0.2	44 23.0 ± 5.8	1.2	-33 -2.7 ± 6.4	1.0	-17 -8.1 ± 8.1	3.0

<sup>a</sup> T.D. =  $(10 \times dI/dT)$  assuming a linear dependence of  $I$  on temperature. The values for Carbowax 20M are approximate as the shape of the temperature dependence curve is uncertain.

<sup>b</sup>  $\Delta I^*$  value for representative hydrocarbon.

<sup>c</sup> Average  $\Delta I^*$  values for the members of the class which were studied.



for BDP (79 units) and Carbowax 20M (77 units). Thus either one of these columns would separate these compounds. Actual retention indices obtained on BDP were 774, 693 and 767 and, on Carbowax 20M, 633, 600 and 649 for benzene, cyclohexane and 1,3-cyclohexadiene respectively.

(e) *The effect of temperature on standard retention index values*

Retention indices have been shown to have a linear dependence on temperature with squalane<sup>8</sup> and SE-30<sup>6</sup> as stationary phases. Other workers have reported the temperature variation in the form  $(10 \times dI/dT)$  (refs. 7 and 9).

Our investigations have shown that the variation of  $\Delta I^*$  with temperature is similar for the members of a particular class of hydrocarbons with either squalane or SE-30 as stationary phase, but the values for different classes may vary considerably. This temperature variation is the negative of the variation of the retention indices of the same compounds and these values, as  $(10 \times dI/dT)$ , are given in Table II.

The average values for the temperature variation of the retention indices of each class on each column are given in Table IV.

(f) *The prediction of retention indices*

The values given in Table IV may now be used to predict the retention index of any compound which belongs to one of the classes considered at any temperature required on one of the four stationary phases used. The method is as follows:

Step 1. Determine the standard retention index of the compound from its b.p.

Step 2. Subtract the average  $\Delta I^*$  value given in Table IV for the appropriate class. This gives the predicted retention index at 50°.

Step 3. Adjust the value to the appropriate temperature using the values for  $(10 \times dI/dT)$ .

*Example.* The calculation of the retention index of methylcyclohexane on squalane at 70°. (Step 1) From Table I the standard retention index is 707. (Step 2) The average  $\Delta I^*$  for cycloalkanes (class IV) on squalane is  $-19.8 \pm 4.3$ . This gives  $726.8 \pm 4.3$  at 50°. (Step 3) The average temperature dependence of  $I$  for cycloalkanes on squalane is 0.14 units/1°C. Thus the adjustment is +2.8 units to give a value of  $729.6 \pm 4.3$  units at 70°. The observed value<sup>10</sup> is 731 units.

Other values for compounds chosen at random by fellow workers are given in Table V.

TABLE V

COMPARISON OF PREDICTED AND OBSERVED RETENTION INDICES

	$I_{\text{predicted}}$	$I_{\text{obs}}$
Cyclooctane on SE-30 at 150°	$933.0 \pm 4.3$	(950)
Cyclohexane on SE-30 at 100°	672	(675)
1,3,5-Trimethylbenzene on SE-30 at 125°	$994.4 \pm 1.0$	(975)
Benzene on SE-30 at 125°	$666.8 \pm 1.0$	(668)
1,3,5-Trimethylbenzene on LBDP at 100°	$1074.1 \pm 7.1$	(1074)
Cycloheptane on LBDP at 75°	$842.3 \pm 6.5$	(842)
2,3,4-Trimethylpentane on LBDP at 100°	$858.9 \pm 1.6$	(855)
3-Ethylpentane on squalane at 100°	$682.6 \pm 2.5$	(689) <sup>10</sup>
Methylcyclopentane on squalane at 22°	$627.9 \pm 4.3$	(623)

(g) *The simplified method for the prediction of retention indices on a stationary phase not included in Table IV*

If the retention indices of the representative hydrocarbons are found on the stationary phase in question and their standard retention index differences ( $\Delta I^*$ ) are calculated then an estimate of the retention index of a compound belonging to the same class as one of the representative hydrocarbons may be obtained. The method of calculation is the same as that described in section (f). The representative hydrocarbon retention indices must be determined experimentally at the temperature at which the analysis is to be carried out unless the temperature variation of these retention indices is also obtained.

For the most useful results it is necessary to average the standard hydrocarbons belonging to the same class. This tends to balance out any experimental errors in the determination of the retention indices.

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