

## Note

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### Unified retention index of hydrocarbons separated on squalane

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(First received April 11th, 1985; revised manuscript received July 22nd, 1985)

The general identification approach applied over many years in gas chromatographic (GC) practice is to compare the retention of a compound of interest with that of a reference substance or standard. It is not easy, however, to maintain the necessary collection of standards, so comparison is commonly made with literature data. Unfortunately, the published retention data are given in many forms and their usefulness is limited. Even the Kováts retention index,  $I^1$ , did not solve the problem, in spite of it being considered to be the most representative characteristic of retention<sup>2,3</sup>, as the temperature dependence of  $I$  and its high sensitivity with respect to stationary phase composition changes<sup>4,5</sup>. The temperature dependence,  $dI/dT$ , is an additional source of information about structure<sup>6</sup> and is used to confirm the identification<sup>7,8</sup>. Hence, the determination of its correct value is as important as the determination of the value of  $I$  itself.

Studies on the influence of the GC conditions on the retention of hydrocarbons were completed in about 1973 with the comprehensive work of Rijks<sup>9</sup>. He showed that the repeatability of the experimentally obtained  $I$  values could be  $\pm 0.1$  index units (i.u.) or even better. This was confirmed later for GC with temperature programming<sup>10,11</sup>. Unfortunately, the inter-laboratory reproducibility remains unsatisfactory, except for a few special cases<sup>9</sup>. The actual discrepancies between the experimental values of  $I$  for identical compounds obtained in different laboratories in routine analysis we assume to be  $\pm 1$  i.u.<sup>12,13</sup>. Cases in which these discrepancies are up to 10 i.u. or more have been explained<sup>13</sup>.

We consider that the observed discrepancies should not be accepted as a disadvantage of the retention index system and it is time to establish better the reliability of this identification approach. The existing uncertainty is connected with the discrepancies between the published data. We assume that the existing numerous experimental data could be unified by using them as inputs for a regression analysis. The values obtained should be more reliable and could be used for a calibration procedure in which the column would be checked in a manner similar to spectral calibration. Then the GC identification could be considered as more reliable than it is at present. This paper gives equations for the calculation of such unified retention indices. They can be used further in the comparison with the experimentally obtained  $I$  values at any analysis temperature. The equations given refer to the calculation of unified retention indices of hydrocarbons separated on squalane.

## EXPERIMENTAL

Comparison of the  $I_{\text{exp}}$  of the same hydrocarbon obtained in different laboratories shows that the discrepancy varied in magnitude and sign. Such comparisons are given in the literature<sup>14</sup>, and the differences reported varied from 0.2 to 1.3 i.u. We also compare in Table I  $I_{\text{exp}}$  values taken from the publications of workers whose activity in the field is well known<sup>13</sup>; even greater differences were found. Hence, the question of which data are the more correct is reasonable. Any practical chromatographer who has to identify the peaks he has obtained is faced with such a question, and so does any theoretician who works on retention index pre-calculation. Thus, Altenburg compared the values of  $I_{\text{calc}}$ , calculated according to his equations<sup>15</sup>, with the  $I_{\text{exp}}$  values obtained by Evans<sup>16</sup>, Martinov and Vidergauz<sup>17</sup> and later Randić<sup>18</sup> used in their comparison the  $I_{\text{exp}}$  values of Tourres<sup>19</sup>. Hammers and De Ligny<sup>20</sup> cited the  $I_{\text{exp}}$  values of Hively and Hinton<sup>21</sup>, and Chrétien and Dubois<sup>22</sup> those of Rijks<sup>9</sup>.

We consider that the differences between the  $I_{\text{exp}}$  values of the different workers result from random errors, because in most instances they have neither equal magnitude nor the same signs. On this basis and in order to remove doubts about the choice of the literature source for  $I_{\text{exp}}$  data, and to create a bank of data with known confidence intervals, we treated all of the existing  $I_{\text{exp}}$  values statistically. If we denote the unified retention index at any analysis temperature  $T$  (°C) by  $UI_T$ , its value could be calculated by the following equation:

$$UI_T = UI_0 + (dUI/dT)T$$

where  $UI_0$  is the value of  $UI_T$  at 0°C. Using the  $I_{\text{exp}}$  values at the corresponding temperatures and the least-squares approach, we obtain the values of  $UI_0$ ,  $dUI_0/dT$  and the standard deviations. The value of the slope,  $-dUI/dT$ , is of great interest: it is used for confirmation of the identification made on the basis of  $I^{\text{R},23}$ , it is correlated with the structure of the substance<sup>24,25</sup> or it is used for the prediction the best separation temperature<sup>26</sup>. The general relationship between  $I$  and temperature is

TABLE I

$I_{\text{SQ}}^{\text{R}0}$  VALUES OF SOME HYDROCARBONS AND MAXIMAL DISCREPANCES ( $d$ ) BETWEEN RESULTS OF DIFFERENT WORKERS

No.	Hydrocarbon	$I^{\text{Lit}}$	$d$
1	2,3,3-Trimethyl-1-butene	630.7 <sup>9</sup> ; 631.3 <sup>21</sup>	0.6
2	Methylcyclopentane	630.8 <sup>19</sup> ; 631.0 <sup>9</sup> ; 632.7 <sup>21</sup>	1.0
3	Benzene	641.8 <sup>9</sup> ; 642.8 <sup>29</sup> ; 642.9 <sup>32</sup> ; 645.3 <sup>21</sup>	3.5
4	2,3-Dimethyl-1-pentene	652.2 <sup>9</sup> ; 653.4 <sup>17</sup>	1.2
5	Cyclohexane	666.95 <sup>14</sup> ; 667.2 <sup>9</sup> ; 668.0 <sup>32</sup> ; 668.6 <sup>21</sup>	1.6
6	1-Heptene	682.3 <sup>9</sup> ; 682.5 <sup>29</sup> ; 682.8 <sup>21</sup>	0.5
7	3-Methyl- <i>cis</i> -3-hexene	685.3 <sup>9</sup> ; 691.7 <sup>21</sup>	6.7
8	Toluene	750.2 <sup>9</sup> ; 750.5 <sup>32</sup> ; 750.7 <sup>29</sup> ; 751.9 <sup>21</sup>	1.7
9	3-Methylheptane	772.3 <sup>9</sup> ; 772.5 <sup>21</sup> ; 772.9 <sup>14</sup> ; 773.6 <sup>19</sup>	1.3
10	3-Methyloctane	870.6 <sup>17</sup> ; 870.7 <sup>9</sup> ; 871.0 <sup>19</sup>	0.4
11	3,3-Diethylpentane	882.4 <sup>9</sup> ; 882.7 <sup>17</sup> ; 884.2 <sup>19</sup> ; 885.4 <sup>33</sup>	3.0

TABLE II

VALUES OF  $U_{10}$ ,  $(dU/dT) \cdot 10$ , THE STANDARD DEVIATION ( $s$ ), THE NUMBER ( $n$ ) OF  $I_{\text{exp}}$  TAKEN IN THE REGRESSION AND  $(dI/dT) \cdot 10$  VALUES TAKEN FROM DIFFERENT REFERENCES

No.	Hydrocarbon	$U_{10}$	$(dU/dT) \cdot 10$	$s$	$n$	Literature $(dI/dT) \cdot 10$
1	<i>trans</i> -2-Pentene	501.20	-0.195	0.30	8	-0.13 <sup>30</sup> ;
2	3,3-Dimethyl-1-butene	503.30	0.741	0.30	4	0.63 <sup>30</sup> ;
3	<i>cis</i> -2-Pentene	504.48	0.073	0.26	8	0.03 <sup>30</sup> ;
4	2-Methyl-2-butene	513.64	0.130	0.17	5	0.06 <sup>30</sup> ;
5	2,2-Dimethylbutane	532.58	0.863	0.27	13	0.82 <sup>9</sup> ;
6	4-Methyl-1-pentene	546.60	0.561	0.42	9	0.58 <sup>21</sup> ;
7	3-Methyl-1-pentene	547.30	0.834	0.30	9	0.79 <sup>9</sup> ;
8	4-Methyl- <i>cis</i> -2-pentene	554.49	0.340	0.35	5	0.21 <sup>30</sup> ;
9	2,3-Dimethyl-1-butene	556.20	0.490	0.14	8	0.43 <sup>9</sup> ;
10	Cyclopentane	558.70	1.475	0.37	14	1.23 <sup>30</sup> ;
11	4-Methyl- <i>trans</i> -2-pentene	562.25	-0.100	0.16	5	-0.10 <sup>30</sup> ;
12	2,3-Dimethylbutane	562.33	1.055	0.21	9	0.72 <sup>7</sup> ;
13	2-Methylpentane	569.19	0.102	0.19	12	0.10 <sup>19</sup> ;
14	2-Methyl-1-pentene	579.06	0.210	0.23	8	0.22 <sup>9</sup> ;
15	1-Hexene	580.99	0.262	0.35	12	0.24 <sup>9</sup> ;
16	3-Methylpentane	581.56	0.568	0.31	14	0.45 <sup>9</sup> ;
17	<i>cis</i> -3-Hexene	591.80	0.161	0.26	14	0.19 <sup>9</sup> ;
18	2-Ethyl-1-butene	592.00	0.008	0.17	9	0.01 <sup>30</sup> ;
19	<i>trans</i> -3-Hexene	593.40	-0.216	0.40	9	-0.17 <sup>30</sup> ;
20	<i>trans</i> -2-Hexene	597.50	-0.077	0.36	11	-0.07 <sup>9</sup> ;
21	4,4-Dimethyl-1-pentene	600.50	0.876	0.30	8	0.92 <sup>21</sup> ;
22	2-Methyl-2-pentene	600.98	-0.020	0.28	10	-0.08 <sup>30</sup> ;
23	3-Methyl- <i>cis</i> -2-pentene	600.98	0.432	0.52	6	0.33 <sup>9</sup> ;
24	<i>cis</i> -2-Hexene	602.45	0.243	0.24	9	0.25 <sup>9</sup> ;
25	3-Methyl- <i>trans</i> -2-pentene	612.38	0.130	0.37	5	0.08 <sup>9</sup> ;
26	3,3-Dimethyl-1-pentene	620.70	1.124	0.45	7	1.17 <sup>9</sup> ;
27	Methylcyclopentane	621.12	1.380	0.40	8	1.26 <sup>30</sup> ;
28	2,3,3-Trimethyl-1-butene	622.70	1.177	0.24	6	1.12 <sup>9</sup> ;
29	2,2-Dimethylpentane	622.80	0.621	0.28	15	0.52 <sup>31</sup> ;
30	Benzene	623.01	2.744	0.41	11	2.43 <sup>6</sup> ;
31	2,3-Dimethyl-2-butene	623.55	0.326	0.43	8	0.26 <sup>9</sup> ;
32	2,4-Dimethylpentane	628.14	0.352	0.28	10	0.32 <sup>19</sup> ;
						-0.25 <sup>21</sup>
						0.65 <sup>9</sup> ;
						0.06 <sup>30</sup> ;
						0.10 <sup>9</sup> ;
						0.83 <sup>21</sup> ;
						0.58 <sup>21</sup> ;
						0.81 <sup>21</sup> ;
						0.36 <sup>30</sup>
						0.86 <sup>30</sup>
						0.32 <sup>21</sup> ;
						0.69 <sup>21</sup>
						1.54 <sup>21</sup>
						0.12 <sup>21</sup>
						0.90 <sup>21</sup>
						0.17 <sup>9</sup>
						0.34 <sup>21</sup>
						0.49 <sup>21</sup>
						0.58 <sup>21</sup>
						0.28 <sup>21</sup>
						0.05 <sup>9</sup> ;
						-0.22 <sup>9</sup> ;
						-0.15 <sup>30</sup> ;
						0.94 <sup>9</sup> ;
						-0.11 <sup>9</sup> ;
						0.42 <sup>21</sup>
						0.35 <sup>30</sup> ;
						0.15 <sup>21</sup> ;
						1.20 <sup>30</sup> ;
						1.52 <sup>9</sup> ;
						1.63 <sup>4</sup>
						1.16 <sup>30</sup> ;
						0.65 <sup>9</sup> ;
						2.47 <sup>21</sup> ;
						0.40 <sup>30</sup> ;
						0.34 <sup>21</sup> ;

33	4,4-Dimethyl- <i>cis</i> -2-pentene	629.94	1.144	0.35	7	1.02 <sup>1</sup> ;	1.05 <sup>9</sup> ;	1.09 <sup>30</sup>
34	3,4-Dimethyl-1-pentene	631.8	1.125	0.59	5	1.12 <sup>9</sup> ;	1.22 <sup>21</sup>	
35	2,2,3-Trimethylbutane	632.31	1.538	0.30	12	1.44 <sup>9</sup> ;	1.49 <sup>21</sup> ;	1.55 <sup>19</sup>
36	2,4-Dimethyl-1-pentene	634.00	0.728	0.24	6	0.65 <sup>9</sup> ;	0.68 <sup>30</sup> ;	0.75 <sup>21</sup>
37	2,4-Dimethyl-2-pentene	641.00	-0.100	0.32	6	-0.17 <sup>21</sup> ;	-0.30 <sup>9</sup>	
38	3-Methyl-1-hexene	641.84	0.655	0.48	5	0.68 <sup>9</sup> ;	0.93 <sup>21</sup>	
39	3-Ethyl-1-pentene	642.45	1.017	0.60	6	1.01 <sup>9</sup> ;	1.15 <sup>21</sup> ;	
40	2,3-Dimethyl-1-pentene	645.90	0.884	0.30	7	0.96 <sup>30</sup> ;	0.99 <sup>9</sup> ;	1.12 <sup>21</sup>
41	5-Methyl-1-hexene	647.50	0.517	0.47	8	0.44 <sup>9</sup> ;	0.45 <sup>30</sup> ;	0.51 <sup>21</sup>
42	2-Methyl- <i>trans</i> -3-hexene	648.10	-0.173	0.40	8	-0.15 <sup>21</sup> ;	-0.16 <sup>90</sup> ;	-0.19 <sup>9</sup>
43	3,3-Dimethylpentane	652.22	1.356	0.33	13	1.31 <sup>21</sup> ;	1.32 <sup>9</sup> ;	1.45 <sup>19</sup>
44	4-Methyl- <i>cis</i> -2-hexene	653.00	0.483	0.60	7	0.60 <sup>9</sup> ;	0.71 <sup>21</sup>	
45	Cyclohexane	653.50	1.909	0.64	12	1.89 <sup>7</sup> ;	2.05 <sup>31</sup> ;	2.22 <sup>9</sup>
46	4-Methyl- <i>trans</i> -2-hexene	654.30	0.463	0.45	9	0.38 <sup>9</sup> ;	0.42 <sup>21</sup> ;	0.44 <sup>30</sup>
47	4-Methyl-1-hexene	654.81	0.663	0.45	8	0.63 <sup>9</sup> ;	0.64 <sup>21</sup> ;	0.71 <sup>30</sup>
48	1,1-Dimethylcyclopentane	664.70	1.824	0.46	11	1.83 <sup>9</sup> ;	1.84 <sup>31</sup> ;	1.95 <sup>21</sup>
49	2-Methylhexane	665.74	0.171	0.24	14	0.15 <sup>21</sup> ;	0.17 <sup>9</sup> ;	0.18 <sup>31</sup>
50	2,3-Dimethylpentane	667.90	0.801	0.30	14	0.85 <sup>9</sup> ;	0.86 <sup>21</sup> ;	1.01 <sup>19</sup>
51	3,4-Dimethyl- <i>cis</i> -2-pentene	668.80	0.428	0.34	7	0.44 <sup>9</sup> ;	0.56 <sup>21</sup>	
52	3-Methylhexane	674.38	0.344	0.28	11	0.31 <sup>21</sup> ;	0.35 <sup>19</sup> ;	0.36 <sup>9</sup>
53	1- <i>cis</i> -3-Dimethylcyclopentane	675.30	1.568	0.38	12	1.32 <sup>30</sup> ;	1.63 <sup>9,31</sup> ;	1.69 <sup>21</sup>
54	2-Methyl-1-hexene	677.00	0.200	0.25	3	0.15 <sup>21</sup> ;	0.23 <sup>9</sup> ;	0.25 <sup>30</sup>
55	1- <i>trans</i> -3-Dimethylcyclopentane	678.10	1.637	0.44	8	1.65 <sup>9</sup> ;	1.66 <sup>31</sup> ;	1.76 <sup>21</sup>
56	1-Heptene	680.70	0.248	0.27	12	0.17 <sup>21</sup> ;	0.25 <sup>9</sup> ;	0.27 <sup>30</sup>
57	2-Ethyl-1-pentene	681.14	0.237	0.44	7	0.22 <sup>1</sup> ;	0.25 <sup>9</sup> ;	
58	1- <i>trans</i> -2-Dimethylcyclopentane	681.30	1.634	0.45	12	1.34 <sup>30</sup> ;	1.59 <sup>9</sup> ;	1.78 <sup>21</sup>
59	3-Ethylpentane	683.20	0.580	0.25	12	0.57 <sup>9</sup> ;	0.62 <sup>19,21</sup>	
50	2,2,4-Trimethylpentane	684.36	1.168	0.32	13	1.09 <sup>9</sup> ;	1.17 <sup>7</sup> ;	1.18 <sup>19</sup>
51	<i>trans</i> -3-Heptene	688.10	-0.059	0.28	9	-0.06 <sup>9</sup> ;	-0.11 <sup>19</sup>	
52	<i>cis</i> -3-Heptene	689.40	0.287	0.43	10	0.34 <sup>9</sup> ;		
53	2-Methyl-2-hexene	691.15	0.36	0.55	10	0.02 <sup>9</sup>		
54	3-Methyl- <i>cis</i> -2-hexene	691.70	0.406	0.35	6	0.45 <sup>9</sup>		

(Continued on p. 370)

TABLE II (continued)

Vo.	Hydrocarbon	U <sub>10</sub>	(dU <sub>10</sub> /dT) · 10	s	n	Literature (dU <sub>10</sub> /dT) · 10
65	3-Ethyl-2-pentene	694.90	0.420	0.25	7	0.30 <sup>9</sup>
66	<i>trans</i> -2-Heptene	698.60	0.006	0.43	12	0.002 <sup>9</sup> ;
67	2,3-Dimethyl-2-pentene	700.50	0.578	0.43	11	0.38 <sup>9</sup>
68	<i>cis</i> -2-Heptene	700.61	0.395	0.25	5	
69	2,2-Dimethyl- <i>cis</i> -3-hexene	711.70	0.975	0.20	4	1.03 <sup>9</sup>
70	1- <i>cis</i> -2-Dimethylcyclopentane	711.70	1.967	0.38	8	2.03 <sup>4</sup> ;
71	2,4,4-Trimethyl-2-pentene	712.50	0.546	0.13	5	0.44 <sup>9</sup>
72	2,2,3,3-Tetramethylbutane	713.30	2.552	0.26	5	2.36 <sup>7</sup> ;
73	1,1,3-Trimethylcyclopentane	714.00	1.967	0.32	7	1.91 <sup>9</sup> ;
74	Methylcyclohexane	714.16	2.308	0.38	9	2.23 <sup>4</sup> ;
75	2,2-Dimethylhexane	717.00	0.520	0.26	17	0.472 <sup>1</sup> ;
76	Ethylcyclopentane	724.44	1.940	0.35	13	1.83 <sup>4</sup> ;
77	2,5-Dimethylhexane	726.72	0.336	0.27	15	0.33 <sup>9,7</sup>
78	2,2,3-Trimethylpentane	728.91	1.698	0.30	11	1.52 <sup>9</sup> ;
79	2,4-Dimethylhexane	729.45	0.550	0.28	14	0.51 <sup>8</sup> ;
80	Toluene	732.98	2.465	0.35	8	2.40 <sup>9</sup> ;
81	1- <i>trans</i> -2- <i>cis</i> -4-Trimethylcyclopentane	733.05	1.676	0.40	7	1.63 <sup>4</sup> ;
82	3,3-Dimethylhexane	736.66	1.349	0.33	12	1.30 <sup>19</sup> ;
83	1- <i>trans</i> -2- <i>cis</i> -3-Trimethylcyclopentane	740.20	1.575	0.30	7	1.33 <sup>4</sup> ;
84	2,3,4-Trimethylpentane	744.74	1.533	0.33	11	1.38 <sup>9</sup> ;
85	2,3,3-Trimethylpentane	748.16	2.287	0.31	9	2.02 <sup>9</sup> ;
86	1,1,2-Trimethylcyclopentane	750.64	2.190	5.2	9	2.03 <sup>4</sup> ;
87	2-Methyl-3-ethylpentane	754.32	1.437	0.30	9	1.07 <sup>9</sup> ;
88	2,3-Dimethylhexane	756.76	0.707	0.25	15	0.70 <sup>7</sup> ;
89	1- <i>cis</i> -2- <i>trans</i> -4-Trimethylcyclopentane	761.23	2.674	1.76	6	1.93 <sup>4</sup> ;
90	3-Methyl-3-ethylpentane	764.38	1.944	0.31	5	1.952 <sup>1</sup> ;
91	2-Methylheptane	764.30	0.128	0.30	15	0.098 <sup>7</sup> ;
92	3,4-Dimethylhexane	765.18	1.145	0.32	12	1.002 <sup>1</sup> ;
93	4-Methylheptane	765.75	0.290	0.34	14	0.27 <sup>19</sup> ;
94	2,2,4,4-Tetramethylpentane	766.00	1.478	0.45	4	1.87 <sup>9</sup> ;
95	3-Ethylhexane	769.92	0.535	0.37	9	0.37 <sup>19</sup> ;
96	3-Methylheptane	770.63	0.354	0.33	15	0.31 <sup>9</sup> ;
97	1,1-Dimethylcyclohexane	772.50	2.916	0.57	7	2.763 <sup>1</sup> ;
98	1- <i>trans</i> -4-Dimethylcyclohexane	772.96	2.657	0.57	5	2.343 <sup>1</sup> ;

0.01<sup>9</sup>2.09<sup>9</sup>;2.30<sup>19</sup>2.392<sup>1</sup>;2.62<sup>19</sup>

2.0034,31

2.43<sup>9</sup>;0.52<sup>9</sup>;1.83<sup>4</sup>;0.33<sup>9,7</sup>1.66<sup>19</sup>;

0.5319,31

2.4536;

1.69<sup>9</sup>;1.313<sup>1</sup>;1.65<sup>9</sup>1.50<sup>19</sup>;2.08<sup>7</sup>;2.293<sup>1</sup>;1.253<sup>1</sup>;

0.729,15

2.143<sup>1</sup>;1.973<sup>1</sup>;0.15<sup>9</sup>;1.002<sup>1</sup>;0.27<sup>19</sup>;1.90<sup>19</sup>0.403<sup>4</sup>;0.342<sup>1</sup>;2.91<sup>9</sup>;2.63<sup>4</sup>

99	2,2,5-Trimethylhexane	773.10	0.674	0.25	4	0.62 <sup>9</sup> ;	0.65 <sup>19</sup>
100	1- <i>cis</i> -3-Dimethylcyclohexane	773.64	2.363	0.41	7	2.30 <sup>31</sup> ;	2.43 <sup>9</sup> ;
101	1-Octane	779.40	0.309	0.21	8	0.20 <sup>29</sup> ;	0.28 <sup>9</sup>
102	1-Ethyl- <i>trans</i> -2-methylcyclopentane	780.02	2.223	0.51	6	2.2 <sup>34</sup> ;	
103	1-Methyl-1-ethylcyclopentane	782.07	2.539	0.13	5	3.8 <sup>34</sup>	
104	2,2,4-Trimethylhexane	782.40	1.358	0.30	4	1.32 <sup>9</sup> ;	1.35 <sup>19</sup>
105	<i>trans</i> -4-Octene	782.60	0.158	0.30	6	0.00 <sup>29</sup> ;	0.14 <sup>9</sup>
106	<i>cis</i> -3-Octene	786.00	0.386	0.30	4	0.2 <sup>29</sup>	
107	<i>cis</i> -4-Octene	786.20	0.209	0.08	4	0.2 <sup>29</sup>	
108	1- <i>cis</i> -2- <i>cis</i> -3-Trimethylcyclopentane	788.45	2.850	0.50	4		
109	1- <i>trans</i> -2-Dimethylcyclohexane	789.50	2.562	0.45	6	2.8 <sup>34</sup> ;	2.87 <sup>9</sup>
110	<i>trans</i> -3-Octene	789.09	-0.090	0.10	4	-0.1 <sup>29</sup>	
111	1- <i>cis</i> -4-Dimethylcyclohexane	791.64	2.760	0.40	7	2.5 <sup>34</sup> ;	2.67 <sup>9</sup> ;
112	1- <i>trans</i> -3-Dimethylcyclohexane	793.90	2.350	0.43	7	2.45 <sup>34</sup> ;	2.5 <sup>31</sup> ;
113	<i>trans</i> -2-Octene	798.80	-0.130	0.25	5	0.00 <sup>9</sup> ;	-0.1 <sup>29</sup>
114	Isopropylcyclopentane	799.64	2.568	0.27	7	2.35 <sup>31</sup> ;	2.47 <sup>9</sup>
115	<i>cis</i> -2-Octene	799.67	0.346	0.19	3		
116	2,2,4-Trimethylhexane	800.23	1.567	0.30	8	1.57 <sup>9</sup> ;	1.60 <sup>19</sup>
117	2,3,5-Trimethylhexane	808.20	0.807	0.25	4	0.84 <sup>9</sup> ;	0.85 <sup>19</sup>
118	2,2,3,4-Tetramethylpentane	808.50	2.260	0.33	5	2.18 <sup>9</sup> ;	2.25 <sup>19</sup>
119	1-Methyl- <i>cis</i> -2-ethylcyclopentane	809.20	2.400	0.20	4	2.31 <sup>31</sup> ;	2.33 <sup>9</sup>
20	2,2-Dimethyl-1-3-ethylpentane	812.03	2.028	0.16	4	2.00 <sup>9</sup> ;	2.10 <sup>19</sup>
21	2,2-Dimethylheptane	813.60	0.425	0.25	5	0.45 <sup>19</sup> ;	0.51 <sup>9</sup>
22	2,2,3-Trimethylhexane	814.00	1.500	0.35	7	1.38 <sup>9</sup> ;	1.60 <sup>19</sup>
23	1- <i>cis</i> -2-Dimethylcyclohexane	814.17	3.096	0.40	7	3.08 <sup>9</sup> ;	3.11 <sup>31</sup>
24	2,4-Dimethylheptane	820.60	0.172	0.15	5	0.20 <sup>19,21</sup>	
25	Ethylcyclohexane	820.60	2.759	0.53	7	2.69 <sup>9</sup> ;	2.70 <sup>31</sup>
26	<i>n</i> -Propylcyclopentane	820.75	1.936	0.25	9	1.84 <sup>9</sup> ;	1.95 <sup>31</sup>
27	Ethylbenzene	821.76	2.575	0.24	8	2.4 <sup>29</sup> ;	2.61 <sup>31</sup> ;
28	4,4-Dimethylheptane	821.90	1.150	0.10	4	1.15 <sup>19</sup>	2.62 <sup>9</sup>
29	2-Methyl-4-ethylhexane	822.60	0.319	0.55	4	0.55 <sup>19</sup>	
30	2,6-Dimethylheptane	826.20	0.175	0.30	6	0.25 <sup>19</sup>	
31	1,1,3-Trimethylcyclohexane	826.84	2.796	0.47	5		
32	1,1,1-Trimethylcyclohexane	827.60	2.688	0.56	6		
33	2,4-Dimethyl-3-ethylpentane	827.70	1.750	0.10	5	1.71 <sup>9</sup> ;	1.80 <sup>19</sup>
34	2,3,3-Trimethylhexane	830.30	1.965	0.20	5	1.85 <sup>19</sup>	
35	3,5-Dimethylheptane	831.20	0.501	0.20	4	0.55 <sup>19</sup>	
36	3,3-Dimethylheptane	831.30	0.974	0.20	5	1.10 <sup>9</sup> ;	1.15 <sup>19</sup>
37	2,5-Dimethylheptane	831.70	0.258	0.40	7	0.30 <sup>19</sup>	

(Continued on p. 372)

TABLE II (continued)

No.	Hydrocarbon	$U_{I_0}$	$(dU/dT) \cdot 10^5$	$s$	$n$	Literature ( $dI/dT$ ) $\cdot 10$
38	<i>p</i> -Xylene	836.00	2.593	0.45	8	2.32 <sup>9</sup> ;
39	2-Methyl-3-ethylhexane	838.50	1.043	0.10	4	1.05 <sup>19</sup>
40	2,3,4-Trimethylhexane	838.60	1.600	0.10	6	1.46 <sup>9</sup>
41	<i>m</i> -Xylene	839.42	2.497	0.54	10	2.32 <sup>9</sup> ;
42	2,2,3,3-Tetramethylpentane	839.42	2.615	0.50	5	2.70 <sup>19</sup> ;
43	3,3,4-Trimethylhexane	842.40	2.144	0.25	4	2.21 <sup>19</sup> ;
44	3-Methyl-3-ethylhexane	845.30	1.631	0.30	4	1.75 <sup>19</sup>
45	2,3,3,4-Tetramethylpentane	845.52	2.651	0.42	4	2.57 <sup>9</sup> ;
46	3-Methyl-4-ethylhexane	847.50	1.455	0.50	4	1.55 <sup>19</sup>
47	2,3-Dimethylheptane	852.30	0.525	0.35	8	0.65 <sup>19</sup> ;
48	3,4-Dimethylheptane	853.20	1.018	0.35	5	0.80 <sup>19,31</sup>
149	4-Ethylheptane	855.30	0.450	0.10	5	0.40 <sup>9</sup> ;
150	<i>o</i> -Xylene	855.61	2.836	0.47	12	2.72 <sup>9</sup> ;
151	2,3-Dimethyl-3-ethylpentane	859.11	2.630	0.17	5	2.71 <sup>9</sup>
152	2,2,4,5-Tetramethylpentane	860.70	1.900	0.05	4	0.30 <sup>19,31</sup>
153	4-Methyloctane	861.90	0.174	0.15	7	
154	2,2,4-Trimethylheptane	862.80	2.146	0.25	4	
155	2-Methyloctane	864.00	0.100	0.40	11	0.15 <sup>9</sup> ;
156	3,3-Diethylpentane	864.30	2.634	0.15	4	2.62 <sup>9</sup> ;
157	3-Ethylheptane	865.00	0.395	0.24	6	0.45 <sup>19</sup>
158	3-Methyloctane	869.00	0.274	0.25	9	0.30 <sup>31,9</sup> ;
159	1-Nonene	880.70	0.181	0.05	4	
160	<i>cis</i> -4-Nonene	881.25	0.414	0.05	3	
161	<i>trans</i> -4-Nonene	883.55	0.071	0.08	3	
162	Isopropylbenzene	883.61	2.373	0.49	9	2.53 <sup>9</sup> ;
163	<i>cis</i> -3-Nonene	883.73	0.379	0.20	3	
164	<i>trans</i> -3-Nonene	886.83	-0.033	0.12	3	
165	<i>trans</i> -2-Nonene	895.34	0.117	0.31	3	
166	3,3,5-Trimethylheptane	895.70	2.000	0.05	4	
167	<i>cis</i> -2-Nonene	896.36	0.554	0.40	3	2.55 <sup>31</sup> ;
						2.65 <sup>36</sup>

hyperbolic<sup>27,28</sup>, but for  $dI/dT$  for non-polar substances separated on non-polar stationary phases, the linear regression gives more accurate results<sup>13</sup>. Experimentally obtained values of  $dI/dT$  are given in many papers, but the determinations are made over more or less limited temperature intervals<sup>7,19,29-31</sup>. It is evident that the  $dI/dT$  values calculated for two or three temperatures cannot be exact. The regression equations given in this paper combine more experimental data and are considered adequate if  $dUI/dT$  is calculated from  $I_{\text{exp}}$  values obtained by at least two groups of workers and at three temperatures. In most instances, however, the data obtained relate to more than five studies. The comparison with the experimental  $dI/dT$  values of different workers is given in Table II and the advantage is clear.

The following example explains the calculations made. For cis-2-heptene, retention indices at five temperatures ( $n = 5$ ) from two different sources are as follows: 30°C, 701.9<sup>19</sup>; 50°C, 702.5<sup>19</sup>; 70°C, 703.1<sup>19</sup>; 86°C, 704.3<sup>29</sup>; and 115°C, 705.1<sup>29</sup>. The equation obtained is  $UI_T = 700.61 + 0.0395T$  with a standard deviation  $s = 0.247$ . The calculated values of  $UI_T$  agreed well with the corresponding  $I_{\text{exp}}$  values, the difference varying between +0.30 and -0.27 i.u. in the range 30-115°C. All values obtained satisfied the linear regression. If necessary, however, a statistical exclusion of wrong data should be made.

## RESULTS AND DISCUSSION

The values of  $UI_0$ ,  $dUI/dT$ ,  $s$  and  $n$ , the number of  $I_{\text{exp}}$ , taken in the regression are summarized in Table II. The hydrocarbons are arranged in order of increasing  $UI_0$ . The values of  $dUI/dT$  are compared with some similar values of  $dI/dT$  quoted in the literature. If one now uses the given values for  $UI_0$  and  $dUI/dT$ , one could calculate  $UI_T$  for the temperature of the analysis. The  $UI_T$  value obtained and that calculated according to the given  $s$  confidence limit can be used further in the identification.

If the experimentally obtained  $I_T$  value is statistically equal to  $UI_T$ , one could decide with known reliability the peak from the chromatogram to which the hydrocarbon belongs. The  $UI_T$  value gives an even better possibility. If one checks the chromatographic column with a limited set of known hydrocarbons and obtains  $I_{\text{exp}}$  equal to  $UI_T$ , one can be confident in using this column for identification purposes. We consider this test of the column to be similar to the adjusting procedure in spectroscopy.

On the basis of the above results and the discussion, we conclude that the proposed unified retention index possesses the following advantages:  $UI_T$  is a statistically obtained value and, hence, it is more reliable than any individual  $I_{\text{exp}}$  value;  $UI_T$  is characterized by a standard deviation and the calculation of the confidence interval at any desired level is possible;  $dUI/dT$  is a more reliable value than  $dI/dT$  for estimating the peak movement with temperature; and both  $UI_T$  and  $dUI/dT$  can be used as a test to check the reliability of the column for identification purposes.

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