Unified retention concept – statistical treatment of Kováts retention index [1]

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Abstract

A detailed analysis of the unified retention index is given. Comparison between the calculated unified retention indices and the measured ones for alkanes, cycloalkanes and alkylbenzenes on squalane, methylsilicone and dinonylphthalate stationary phases has shown that some similarities exist. It is demonstrated that the unified retention index provides a better procedure for the precalculation of retention indices at any desired temperature than any model that has hitherto been published.

Keywords: Retention indices; Unified retention index; Dinonylphthalate phases; Methylsilicone phases; Squalane phases; Poly(propylene glycol) phases; Alkanes; Arenes; Cycloalkanes

1. Introduction

High-resolution capillary gas chromatography is generally the most useful method for the analysis of complex hydrocarbon mixtures. Hydrocarbons are of particular importance in the petrochemical industry and in issues concerning the environment. Much effort has been directed towards the accurate identification of pollution sources. Therefore, analytical chemistry devoted permanent attention to them. For separation and determination, a single column can be used with non-polar, medium polarity and polar stationary phases under isothermal and programmed temperature conditions.

The approach generally applied in the identification of separated hydrocarbons is limited by the lack of standards, published retention data or by their

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insufficient reproducibility, further by insufficient precision of the structure–retention relationships and by the limitations of the combined chromatographic–spectral gas chromatography–mass spectrometry detector–Fourier transform infrared (GC–MSD–FTIR) technique.

The retention index is generally recommended for identification on the basis of retention data. In current gas chromatographs it is possible to achieve high precision of retention index measurement, the repeatability of the experimentally obtained retention values could be ± 0.1 index unit or even better. However, the interlaboratory reproducibility of retention indices is much worse. The accuracy of the gas chromatograph as an instrument has been improved, however the reproducibility of retention time on different columns having the same liquid phase and being supplied from the same manufacturer has not been satisfactory. Further, the selectivity of different phases is seldom the same. The poor reproducibility of capillary columns may be due to

the difference in molecular mass of polymers used as the liquid phase, the efficiency of surface coverage, the film thickness and the surface treatment method of the fused-silica tube, etc.

Low interlaboratory reproducibility of the retention values restricts widespread use of data banks of retention indices in chromatographic practice. The major problem is associated with the determination and/or calculation of the gas holdup (dead) time [1–4]. It can be stated that, if correct retention time data were available, the simple method of applying three n-alkanes is equivalent to the more complicated computer methods. In the literature used, as is usual, the gas holdup time was determined according to Peterson and Hirsch [5]. The other very important reason for the poor interlaboratory reproducibility seems to lie in adsorption of the compounds during analysis [6–8]. The effect is most apparent with non-polar phases where the polar contribution of the phase is low and that of the support relatively high [9]. For example, in Sadtler's library of the retention indices obtained under standard conditions, the re-producibility of retention indices of analytes measured on the polar stationary phase Carbowax 20M is said to be no better than 2 index units (i.u.) [10].

A great limitation to the larger scale use of retention indices is that the values of the studied compounds dealt with are determined experimentally for a given column and only one temperature, although Kováts [11] originally suggested that three values should be given:

- the retention index at the column temperature
- the retention index increment per 10°C
- the temperature range in which the index has been examined

Many researchers have realized the necessity of carrying out measurements at, at least, three different column temperatures for a given isothermal GC system, but this practical solution has not found general application.

Similarly to retention index review papers, attempts to organize a retention index library [10,12–14] have only been of a recapitulatory type, i.e., they contain very few critical elements, if any. Thus it may often happen that different retention index values are given for the same compound measured with a particular GC system. As a consequence, the user has to decide which value to take as the proper

one. Hence, the question of which data is 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 precalculation.

Detailed investigations reported in the literature [15,16] showed that the actual relationship between retention index (I) and column temperature (T) can generally be described by an Antoine-type equation:

$$I = A + B/(T + C) \tag{1}$$

where A, B and C are constants depending on the solute and liquid phase. Eq. (1) corresponds to a hyperbola; however, it has been demonstrated [17–21] that in the temperature interval used in practice the I vs. T plot has a linear section and therefore, we can write that:

$$I \simeq aT + b \tag{2}$$

where a and b are constants. The linear relationship generally covers a larger temperature range with a nonpolar than with a polar phase.

The effect of temperature on retention was recognized early in the history of gas chromatography. The first systematic work on the relation of retention index (I) with column temperature (T) is that of Ettre and Billeb [18]. Mitra and Saha [22] have made an exhaustive study of I–T relationships for all types of hydrocarbons in various stationary liquids and concluded that retention indices not only show a regular and systematic variation, but also follow an approximately linear relation with column temperature, covering the entire working range of the stationary phases. Vernon and Suratman [23] demonstrated that for the temperature ranges used in practice, the linear relationship between I–T may be written as:

$$I = I_0 + mT \tag{3}$$

where I_0 is the theoretical retention index at 0°C and T the working temperature in °C. This assumption of linearity has been verified in a study of n-alkyl-benzene retention on Apiezon L and Carbowax 20M over a wide range of temperatures. The calculated I_0 and temperature gradient m are obtained with correlation coefficients of 0.999 for all studied n-alkyl-benzenes on Apiezon L and with the ones from 0.991–0.999 on Carbowax 20M, respectively.

Due to the approximate linear relationship de-

scribed in Eq. (2) and Eq. (3), one can express the temperature dependency of the retention index by giving the increment for a given temperature range, usually 10°C, and then use this value to calculate the retention index at selected temperatures.

In recent years, the stated conclusion has been applied by Dimov [24–27] and Škrbić [28–33,36] in the form of:

$$UI_T = UI_0 + (dUI/dT)T \qquad (4)$$

where: UI_T is the unified retention index at temperature T (°C), UI_0 is the value of UI_T at 0°C, dUI/dT is the index increment with the analysis temperature (usually given as $dUI/10$°C).

Dimov [24] has used this concept to explain the variation in the retention index of hydrocarbons on squalane which are largely attributed to random errors. In order to remove doubts about the choice of the literature sources for experimental retention data, and to create a bank of data with known confidence interval, all of the existing experimental retention index values for selected phases have been treated statistically.

The unified retention index concept represents the linear regression of the retention data published by various authors at different temperatures. If the differences between the literature data obtained at the same temperature were greater than ±1 index unit, these data were not included in the regression analysis. It is considered that in routine analysis, differences of ±1 i.u. between experimental indices from different laboratories are acceptable [34,35].

The statistical treatment using simple regression analysis of the experimental data allows computation of a unified retention index (UI_T) by Eq. (4). The values of unified retention index (UI_T) obtained and its temperature increment were considered as reliable if the data included in the regression matrix were from two authors and at three temperatures at least, and no more than 33% of all data were excluded.

Therefore, the unified retention index and temperature increment of the unified retention index have the advantage of being a statistical value and thus more reliable than any individual experimental retention value. Furthermore, it is characterized by a standard deviation and the calculation of the confidence interval at any desired level is possible; temperature increment of unified retention index

(dUI/dT) is a more reliable value than the retention index increment (dI/dT) for estimating peak movement with temperature. This concept also permits an easy and convenient way of determining the retention index value at any temperature within the range investigated and the evaluation of the proper column temperature for the analysis of multicomponent mixtures, and demonstrates the change in elution sequence of the sample components.

Tabulated data of the unified retention indices and temperature increment of the unified retention indices were presented for 334 [24,26,27,33] and 191 [25,28–31] hydrocarbons on squalane and methylsilicones phases: OV-101, BP-1 and SE-30, respectively.

2. Results

Concerning the unified retention indices and the measured ones of a particular solute on different stationary phases, the following similarities are observed:

Like the isothermal retention indices of non-polar compounds (alkanes), the unified retention indices also remain almost constant on slightly polar dinonylphthalate phases and on squalane and methylsilicone non-polar phases, as can be seen from Table 1. In most instances the differences between data vary from several tenths of 1 i.u. to 1–3 i.u., the maximum being 5.08 i.u. for 2,5-dimethylhexane. The same conclusion may be drawn if the differences obtained between the experimental retention indices [25,37] are considered. The maximum difference, being 4.3, is again for 2,5-dimethylhexane.

The unified retention indices of some compounds determined on various non-polar stationary phases are identical or very close to one another. This statement does not strictly follow one of the seven Kováts rules concerning retention index – that retention indices of any compounds determined on various non-polar stationary phases are identical or very close to one another.

As can be seen from Table 1 (for alkanes), Table 2 (for cycloalkanes) and Table 3 (for alkylbenzenes), comparison of the unified retention indices on squalane and methylsilicone (OV-101 and BP-1) mostly shows the differences which are larger for

Table 1

Comparison of unified retention indices (UI_0) of alkanes on squalane, methylsilicone and dinonylphthalate (DNP) stationary phases

No.	Alkanes	$(UI_0)_{sq}$ [24]	$(UI_0)_{OV\text{-}101}$ [25]	$(UI_0)_{BP\text{-}1}$ [28]	$(UI_0)_{DNP}$ [36]
1	2,2-dimethylbutane	532.58	533.22	533.89	
2	2,3-dimethylbutane	562.33	559.40	562.95	565.33
3	2-methylpentane	569.19	568.43		569.08
4	3-methylpentane	581.56	581.12	580.95	
5	2,2-dimethylpentane	622.80	621.34		
6	2,4-dimethylpentane	628.14	627.93	628.30	628.96
7	2,2,3-trimethylbutane	632.31	629.65		
8	3,3-dimethylpentane	652.22	648.64		
9	2,3-dimethylpentane	667.90	665.30	664.79	669.02
10	2-methylhexane	665.74	666.61	664.68	664.26
11	3-methylhexane	673.36	674.07	677.05	674.10
12	3-ethylpentane	683.20	683.18		
13	2,2-dimethylhexane	717.00	718.07		
14	2,2,3-trimethylpentane	728.91	730.30		
15	2,4-dimethylhexane	729.45	730.80	732.25	
16	2,5-dimethylhexane	726.72	731.80	731.20	726.55
17	3,3-dimethylhexane	735.35	736.66	737.12	
18	2,3,4-trimethylpentane	743.39	744.74	743.00	
19	2-methyl-3-ethylpentane	754.32	755.19	743.00	
20	2,3-dimethylhexane	755.36	756.76		
21	3,4-dimethylhexane	765.18	764.63		
22	3-methyl-3-ethylpentane	764.38	764.78		
23	2-methylheptane	764.30	765.57		761.87
24	4-methylheptane	765.75	766.11		764.91
25	3-methylheptane	770.53	771.93		769.45

Table 2

Comparison of unified retention indices (UI_0) of cycloalkanes on squalane, methylsilicones and dinonylphthalate (DNP)

No.	Cycloalkanes	$(UI_0)_{sq}$ [24]	$(UI_0)_{OV\text{-}101}$ [25]	$(UI_0)_{BP\text{-}1}$ [28]	$(UI_0)_{DNP}$ [36]
1	cyclopentane	558.70	558.35		569.01
2	methylcyclopentane	621.12	620.18	619.27	628.43
3	cyclohexane	653.50	649.77	648.90	658.23
4	1,1-dimethylcyclopentane	664.70	664.95		
5	1-cis-dimethylcyclopentane	657.30	675.21		
6	1-trans-dimethylcyclopentane	678.10	677.59		
7	methylcyclohexane	714.16	709.47	714.86	720.13
8	1-cis-2-dimethylcyclopentane	711.70	711.11		
9	1,1,3-trimethylcyclopentane	714.00	714.10		
10	ethylcyclopentane	724.44	722.05		
11	1-trans-2-cis-4-trimethylcyclopentane	733.05	732.14		
12	1-trans-2-cis-3-trimethylcyclopentane	740.20	737.91		
13	1,1,2-trimethylcyclopentane	750.64	749.22		
14	1-cis-3-dimethylcyclohexane	773.64	763.98		781.84
15	1-trans-4-dimethylcyclohexane	772.96	765.40		781.35
16	1,1-dimethylcyclohexane	772.50	768.35		
17	1-ethyl-trans-2-methylcyclopentane	780.02	779.15		
18	1-trans-2-dimethylcyclohexane	789.50	783.00		795.86

Table 3
Comparison of unified retention indices (UI_0) of alkylbenzenes on squalane [24], methylsilicone [30], UCON LB-550 (UCON) and dinonylphthalate (DNP) [36]

No.	Alkylbenzene	$(UI_0)_{sq}$	$(UI_0)_{OV-101}$	$(UI_0)_{UCON}$	$(UI_0)_{DNP}$
1	benzene	623.01	643.72	740.12	709.63
2	toluene	732.98	745.95	838.11	817.71
3	ethylbenzene	821.76	831.61	941.63	904.12
4	1,4-dimethylbenzene	836.00	843.17	931.49	918.96
5	1,3-dimethylbenzene	839.42	842.04	938.05	923.15
6	styrene		856.94		967.82
7	1,2-dimethylbenzene	855.61	857.03		945.31
8	isopropylbenzene	883.56	891.14		
9	*n*-propylbenzene	911.61	922.62	1014.17	
10	1-methyl-3-ethylbenzene	923.99	931.52	1031.74	
11	1-methyl-4-ethylbenzene	928.67	930.04	1031.74	
12	1-methyl-2-ethylbenzene	939.69	942.67	1067.56	
13	1,3,5-trimethylbenzene	948.27	938.08	1063.79	
14	*tert.*-butylbenzene	950.93	953.41		
15	isobutylbenzene	954.95	976.78	1058.23	
16	1,2,4-trimethylbenzene	959.06	952.87		
17	*sec.*-butylbenzene	959.89	970.50	1050.64	
18	1,2,3-trimethylbenzene	978.19	981.87		
19	1-methyl-2-isopropylbenzene	978.19	991.84		
20	1-methyl-3-isopropylbenzene	987.56	976.45		
21	1-methyl-4-isopropylbenzene	992.21	989.88		
22	1,3-diethylbenzene	1002.94	1014.57	1113.54	
23	1-methyl-4-*n*-propylbenzene	1007.63	1017.06		
24	1-methyl-3-*n*-propylbenzene	1008.37	1013.43		
25	1,4-diethylbenzene	1010.12	1019.19	1115.77	
26	1,2-diethylbenzene	1011.19	1022.03	1194.72	
27	*n*-butylbenzene	1012.67	1018.48	1126.47	
28	1-methyl-2-*n*-propylbenzene	1015.06	1023.05	1124.75	
29	*tert.*-pentylbenzene	1030.86	1043.04		
30	1,4-dimethyl-2-ethylbenzene	1032.46		1147.33	
31	1,2-diethyl-2-ethylbenzene	1037.71		1156.47	
32	1-methyl-4-*tert.*-butylbenzene	1045.50	1052.97		
33	1,2,4,5-tetramethylbenzene	1071.14	1071.54		
34	1,2,3,5-tetramethylbenzene	1077.48	1073.79		
35	1,2,3,4-tetramethylbenzene	1083.84		1214.16	
36	1,3,5-trimethylbenzene	1161.79	1185.83		
37	pentamethylbenzene	1241.75	1209.07		

alkylbenzenes, although these phases are considered as non-polar in chromatographic practice. Also, the same differences are observed among the experimental retention indices [38]. Hence, the opinion that the elution order on similar phases is the same is not correct and cannot be used with the necessary reliability for separation or identification prediction. That is why the relationship has been studied between the retention on both phases.

Table 3 also gives calculated unified retention indices of some alkylbenzenes on the slightly polar stationary phases UCON LB-550 and dinonylphthalate. The agreement of the data is generally poorer than on squalane and non-polar silicones.

Using linear regression equations, the unified retention indices and temperature increments of unified retention indices on methylsilicone phase (OV-101) may be predicted, with reasonable accuracy, on the basis of unified retention indices and temperature increments obtained on squalane. The prediction possibility of derived equations [29] were verified for 43 hydrocarbons (25 alkanes and 18

cycloalkanes) with a correlation coefficient of 0.9993 and mean standard deviation of 2.62 index units for unified retention indices and, with a correlation coefficient of 0.9353 and mean standard deviation of 0.027 for temperature increments of unified retention indices.

It has been shown [27], as well, that the equations based on the unified retention indices allowed calculation of the values for other phases with reasonable accuracy.

The retention indices of hydrocarbons measured on the methylsilicone oil, and the unified retention indices of the same compounds on squalane (UI_{sq}^t) can be correlated by considering some constants related to the structural elements [27] of the respective hydrocarbons as follows:

$$I_{JXR}^t = b_0 + b_1 UI_{sq}^t + \sum_{i=2}^{n} b_i x_i \qquad (5)$$

where b_i represents the regression estimations of statistically important structural elements x_i. Superscript t indicates the temperature at which the calculations were carried out.

The obtained differences between the experimental and calculated retention indices on methylsilicone oil have show that in 61.5% of the studied cases they are less than 1.0 i.u. and that correlation coefficients are better than 0.9992 in all cases.

The existing relationships allow two independent possibilities for peak identification on the investigated phase. First, the experimental data obtained on one phase could be used to recalculate the expected retention on the other phase. Second, if the unified retention indices are not available, it is possible to precalculate the retention indices from the solute properties only.

A detailed statistical analysis [32], comparing the validity of the best literature, recommended equations [39,40] for prediction of retention indices of alkylbenzenes on squalane and metylsilicone stationary phase, with the unified retention index concept showed that the unified retention index based on the residual mean square as an error-free measure of the goodness of fit and Bards termination criteria [41], provides the smallest residual error and that it could be applied for prediction purposes. It should be noted that in the above mentioned cases, the obtained

results with linear regression are better than the calculated ones with other regression methods by computer.

The advantage of the unified retention index concept over quantitative structure–gas chromatographic retention relations (QSRR) [42] is proved by applying the proposed equation to the methylsilicone OV-101 phase:

$$RI^{OV-101} = c_1 + c_2 M_m + c_3(q_1 + q_2) - c_4 CH_{3br} + c_5 q_{7(8)} + c_6 ST \qquad (6)$$

$c_1 = 334(\pm 45.62)$ $c_4 = 33.7(\pm 4.95)$

$c_2 = 6.76(\pm 0.28)$ $c_5 = 279.5(\pm 101.9)$

$c_3 = 1154(\pm 223)$ $c_6 = 95.21(\pm 64.05)$

where M_m is molecular mass; $q_{7(8)}$ is atom charge at C-8 in o-alkylsubstituents; ST is combined effect of type of substitution; CH_{3br} is the number of branching in the alkylsubstituent; and the published unified retention data [30].

Eq. (6) satisfies the accepted upper limit of 5 i.u. error [42] for any compound. In the comparison, the same data set of selected compounds which has been used for the choice of the literature proposed model [42] is applied. The calculated retention values obtained by Eq. (6) and the unified retention concept are compared with the experimental ones in Table 4. As can be seen the smallest residual deviation, s, is obtained by the unified retention index concept.

Therefore, it is concluded that the unified retention index provides a better procedure for the precalculation of retention index for alkylbenzenes at any desired temperature, than any model that has, hitherto, been published.

3. Conclusion

It is suggested that the unified retention index should be used for the study and explanation of quantitative structure–gas chromatographic retention relationships, dispersion and selectivity indices, etc., since the unified retention index has the advantage of being a statistical value and thus, more reliable than any individual experimental retention value.

Table 4
Comparison of the calculated retention value (I_{calc}) according to Eq. (6) [42] and the unified retention index concept [30] with the experimentally obtained value on OV-101

No.	Alkylbenzenes	I_{exp} [42]	$I_{Eq.3}$ [42]	UI_{100C} [30]	$I_{exp} - I_{Eq.3}$	$I_{exp} - UI_{100C}$
1	n-propylbenzene	947.5	949	949.56	−1.5	−2.03
2	n-butylbenzene	1046	1044	1047.93	2	−1.93
3	i-propylbenzene	919	918	920.03	1	−1.03
4	tert-butylbenzene	986	985	987.15	1	−1.15
5	1,4-dimethylbenzene	866	863	867.96	3	−1.96
6	1,3-dimethylbenzene	866	869	866.46	3	−0.46
7	1-methyl-4-i-propylbenzene	1016.5	1012	1017.28	4.5	−0.78
8	1-methyl-3-i-propylbenzene	1010	1017	1011.37	7	−1.34
9	1-methyl-4-i-propylbenzene	1046.5	1047	1046.39	0.5	0.11
10	1-methyl-3-n-propylbenzene	1042	1042	1042.59	0	0.59
11	1-methyl-2-etylbenzene	973	976	973.66	3	−0.66
12	1,3-diethylbenzene	1038.5	1039	1040.2	0.5	−1.7
13	1,2-diethylbenzene	1051	1049	1053.05	2	−2.05
14	1,3,5-trimethylbenzene	969	966	962.99	3	6.01
15	1,2,4-trimethylbenzene	988	992	987.4	6	0.6
16	1,2,3-trimethylbenzene	1016	1011	1016.36	5	−0.36
	s^2				18	4.37
	s				4.24	2.09

The values of unified retention data obtained could be used as a data bank and with the aid of suitable software computer assisted identification might be possible. In this way, the data of a total of 334 and 191 hydrocarbons separated on squalane and methylsilicone phases, respectively, may be used.

Acknowledgments

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