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## ELIMINATION OF THE REFERENCE STATIONARY PHASE IN CLASSIFICATION SCHEMES USING THE MOLECULAR RETENTION INDEX

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### SUMMARY

The applicability of the molecular retention index ( $\Delta Me$ ) as a means of classifying stationary phases in gas chromatography is discussed. The difficulties in using the poorly thermally stable basic stationary phase squalane are eliminated, while the relationship between the retention parameter and temperature allows a numerical value for the stationary phase to be calculated at the operating temperature. Like the McReynolds and Rohrschneider schemes, comparison of stationary phases is simple but classification relies on a series of values characteristic of selected functional groups.

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### INTRODUCTION

The molecular retention index ( $\Delta Me$ ) was developed by Evans and Smith<sup>1,2</sup> in 1961 for the prediction of retention data as an alternative to the use of the retention index ( $I$ )<sup>3</sup>. The retention index is defined as the carbon number of a hypothetical  $n$ -alkane having the same retention as the solute under consideration. The formula the hypothetical  $n$ -alkane equivalent to the solute is  $C_{I'}H_{2I'+2}$  and will have an effective molecular weight given by the relationship

$$\begin{aligned} Me &= 14.026 I' + 2.016 \\ &= 0.14026 I + 2.016 \end{aligned} \quad (1)$$

where

- $I$  = 100  $I'$ ;
- $Me$  = effective molecular weight of the solute or the molecular weight of a hypothetical  $n$ -alkane with  $I'$  carbon atoms;
- $I'$  = number of carbon atoms in hypothetical  $n$ -alkane;
- $\Delta Me$  = is defined as

$$\Delta Me = Me - M \quad (2)$$

where  $M$  is the true molecular weight.

The difference between the effective and true molecular weights of the solute

( $\Delta Me$ ) were suggested in the early report<sup>1</sup> to be a useful parameter for the correlation of chemical structure and chromatographic retention. The propositions outlined almost two decades ago are detailed below and are followed by some mention of the subsequent development of the scheme by Evans and his co-workers.

(1)  $\Delta Me$  is a conceptually simple parameter having the familiar dimensions of molecular weight.

(2) It is virtually constant throughout a homologous series.

(3) It has no, or only a slight linear, variation with temperature.

(4)  $\Delta Me$  is an additive function of the structural features of a molecule (except when specific group-group interactions occur.)

(5) For a proposed structure,  $M$  can be calculated and  $\Delta Me$  for the various structural features obtained from correlation tables. Thus  $Me$  can be predicted. This has proved invaluable in identifying the products of a reaction where only a few alternatives are possible. Thus, once  $\Delta Me$  functional group correlation charts are available, retention times can be predicted without any prior chromatography. This is not practicable with the methods at present available.

(6)  $\Delta Me$  values of selected functional groups can be used to characterize chromatographic columns, particularly when the retention data are to be published. Thus, it should be possible to use the gas-liquid chromatographic data in the literature confidently for the solution of everyday analytical problems.

(7) In general,  $\Delta Me$  values need to be expressed to fewer significant figures than  $I'$  contributions.

While certain of the above features (1-4) were examined in early works<sup>1,2</sup>, it became evident that the molecular shape was of importance and allowance was possible for steric hindrance by the use of geometrically similar model compounds<sup>4</sup>, and later the use of the  $\Delta Me$  concept for phase classification was briefly reported<sup>5</sup>.

Development of the concept has been slow, although a very similar relationship was reported by Piringer *et al.*<sup>6</sup> in 1976 but was not further investigated.

The problems of stationary phase classification are well known. Evans<sup>5</sup> has recently reiterated the limitations of squalane<sup>7-9</sup>, the introduction of acceptable alternative base materials, namely a C<sub>87</sub> branched-chain hydrocarbon<sup>10-12</sup> and exhaustively hydrogenated Apiezon M<sup>13-15</sup>, and modification<sup>16</sup> of the Rohrschneider scheme to allow the use of any thermally stable stationary phase as a reference phase, and has reported an alternative scheme based on the molecular retention index which is independent of a base stationary phase.

The essentially constant values of  $\Delta Me$  for low-polarity phases, *i.e.*, squalane or dinonyl phthalate<sup>1,2</sup>, and for polyethylene glycol columns<sup>5</sup> have been reported, together with the use of  $\Delta Me$  values. In this work, the values of  $\Delta Me$  for homologous series of varying functional class, *i.e.*, alcohols, aldehydes, esters and ketones, have been established at various temperatures using a series of eight polysiloxane stationary phases of increasing polar character. The values of  $\Delta Me$  and  $\Delta Me_0$  obtained are compared and their utility discussed in relation to McReynolds constants for the classification of stationary phases.

## EXPERIMENTAL

The analyses were carried out using 10% of the stationary phases on

Chromosorb W AW DMCS. Aluminium and stainless-steel columns of O.D. 1/8 and 1/4 in. were employed, there being no variation in the retention indices of test compounds on squalane with either column material, provided that the support is inactive. Determinations were carried out at 120, 140, 160 and 180°C.

To increase the speed and accuracy of the determination of retention data, a Hewlett-Packard 5750 research gas chromatograph was interfaced with a 16 K PDP 11/40 digital computer. The chromatograph employed a splitter and individually operated detectors with injection by a Hewlett-Packard 7670A automatic sampler. Calculations of dead time and retention indices were conducted mathematically within the system.

## RESULTS

The molecular retention indices ( $\Delta Me$ ) were found to be essentially constant for a particular homologous series. Table I shows data for four homologous series (acetates, ketones, alcohols and aldehydes) on columns of low (SE-30), medium (OV-25) and reasonably high polarity (Silar 10C) determined at 120°C, the constancy being equivalent to that reported previously<sup>1,2</sup> and being little influenced by the polarity of the stationary phase.

TABLE I  
CONSTANCY OF  $\Delta Me$  WITHIN HOMOLOGOUS SERIES

Substance	Column		
	SE-30	OV-25	Silar 10C
<i>n</i> -Butyl acetate	-21.38	2.52	47.97
<i>n</i> -Amyl acetate	-21.77	2.19	48.36
<i>n</i> -Hexyl acetate	-21.29	2.59	48.11
<i>n</i> -Heptyl acetate	-21.54	2.67	49.03
<i>n</i> -Pentanone	10.89	31.90	92.51
<i>n</i> -Hexanone	10.45	32.95	92.94
<i>n</i> -Heptanone	10.23	32.36	92.74
<i>n</i> -Octanone	10.57	32.19	91.99
<i>n</i> -Nonanone	10.83	32.62	92.62
<i>n</i> -Butanol	19.87	37.26	110.24
<i>n</i> -Pentanol	19.15	37.41	111.76
<i>n</i> -Hexanol	19.54	37.97	111.89
<i>n</i> -Heptanol	19.04	37.94	111.62
<i>n</i> -Octanol	19.77	37.57	111.01
<i>n</i> -Butanal	66.94	88.81	145.96
<i>n</i> -Pentanal	67.01	88.93	145.02
<i>n</i> -Hexanal	67.24	88.09	145.71
<i>n</i> -Heptanal	67.93	88.62	145.85
<i>n</i> -Octanal	67.54	89.00	145.97

The temperature dependence of  $\Delta Me$  has been represented<sup>1,2</sup> by the relationship

$$\Delta Me_{\theta} = \Delta Me_0 + \mu\theta$$

where

$\Delta Me_{\theta}$  = the value at  $\theta^{\circ}\text{C}$ ;

$\Delta Me_0$  = the value at  $0^{\circ}\text{C}$  determined by graphical or other extrapolation;

$\mu$  = a constant.

A series of  $\Delta Me$  values determined at 120–180°C are shown in Table II, and it is evident that with each functional class increasing values of  $\Delta Me$  occur with increasing stationary phase polarity according to the McReynolds scheme or to the general polarity, as indicated by a summation of the McReynolds solute values.

TABLE II

MOLECULAR RETENTION INDICES FOR *n*-ALKYL HOMOLOGOUS SERIES DETERMINED AT 120–180°C

Compounds	Column	Temperature ( $^{\circ}\text{C}$ )			
		120	140	160	180
Acetates	$\text{C}_{37}\text{H}_{176}$	-21.6297	-22.5091	-22.4003	-21.9580
	SE-30	-17.7058	-18.5958	-18.9078	-19.9075
	OV-17	-8.3156	-6.9360	-8.6368	-8.3031
	OV-25	-2.5426	2.0827	2.6781	2.4280
	QF-1	28.9900	29.3901	34.7710	35.6872
	Silar 5CP	33.5771	36.0665	36.4707	44.0809
	Silar 7CP	37.7845	40.1217	42.0749	47.2796
	Silar 9CP	43.4847	48.0868	51.8532	52.7337
	Silar 10C	49.5801	53.5676	56.7464	58.1990
	Ketones	$\text{C}_{37}\text{H}_{176}$	9.2650	8.0238	9.1771
SE-30		10.3080	10.1597	10.3527	9.7992
OV-17		26.5886	26.7840	26.5857	26.8536
OV-25		32.2517	32.1253	32.0095	32.0662
QF-1		54.4775	55.7932	56.0787	58.0011
Silar 5CP		77.3516	80.8275	83.0727	87.9992
Silar 7CP		81.3112	84.7699	88.3176	92.4677
Silar 9CP		87.9454	92.5792	99.1762	104.5313
Silar 10C		93.7774	101.5413	107.6088	113.5220
Alcohols		$\text{C}_{37}\text{H}_{176}$	19.3440	19.2700	19.1500
	SE-30	19.5615	19.5882	18.9252	18.3550
	OV-17	32.4685	32.5180	32.6121	33.2467
	OV-25	38.0334	37.9749	38.3998	37.9426
	QF-1	41.52	44.7401	45.6249	47.2850
	Silar 5CP	91.4491	94.0441	95.3817	99.9271
	Silar 7CP	95.8547	98.7092	101.2585	104.8146
	Silar 9CP	104.5001	106.1991	114.0032	119.4995
	Silar 10C	111.6243	121.3408	123.4385	127.9702
	Aldehydes	$\text{C}_{37}\text{H}_{176}$	67.1528	67.8464	67.6613
SE-30		68.3687	68.2881	68.0580	68.2900
OV-17		84.3182	85.0364	85.0883	84.9065
OV-25		88.590	88.6915	89.2590	89.7639
QF-1		51.694	52.9410	54.7523	56.8496
Silar 5CP		131.3735	134.9178	138.4813	144.6711
Silar 7CP		134.9609	138.9263	143.2659	148.4458
Silar 9CP		139.4285	145.7856	153.6589	158.3068
Silar 10C		145.9553	153.8995	160.7622	166.1612

A comparison of the  $\Delta Me$  values at 120°C for the alcohol and ketone functional group and the retention of the McReynolds solutes is shown in Table III. It is evident with the range of stationary phases that the  $Y'$  values appropriate to *n*-butanol are generally higher than the  $Z'$  values appropriate to 2-pentanone, while the  $\Delta Me$  values for the hydroxyl functional group of alcohols is generally higher than the  $\Delta Me$  values for the ketone carbonyl group. The possession of definite specific retention characteristics of a stationary phase is rather vague, except for QF-1<sup>17</sup>, for which an increased retention of ketones obviously occurs. The McReynolds data show a higher  $Z'$  than  $Y'$  value, while the  $\Delta Me$  value for the carbonyl group is much higher than for the hydroxyl group, this being the only one of the stationary phases considered that shows this result.

The value of  $\Delta Me$  on all of the lower polarity stationary phases increased in the order acetates, ketones, alcohols and aldehydes. However, the selectivity of the polar stationary phases is indicated by the greater increases in  $\Delta Me$  values from esters to ketones to alcohols, while with the aldehyde functional group the increase is between that of esters and ketones.

Evans and Smith<sup>1,2</sup> suggested that the retention characteristics of a functional group may be defined by two simple parameters,  $\Delta Me$  and  $\mu$ , and that the retention characteristic or polar character of a solute may be defined by  $\Delta Me_0$  values for various functional groups.

Table IV gives values for  $\Delta Me_0$  and  $\mu$  for the four functional classes, considered together with correlation coefficients that indicate that many of the relationships were only approximately linear. It is evident that the correlation coefficients indicate reasonable relationships with the more polar stationary phases. This is unusual, as correlations of chromatographic retention and molecular structure have tended to be much more satisfactory with low-polarity solutes.

Despite the varying correlation coefficients, a numerical value defining a stationary phase relevant to the temperature of operation can be calculated. This is currently not possible with the McReynolds and Rohrschneider schemes owing to the thermal limitations of squalane, and therefore the  $\Delta Me$  scheme allows a comparison of stationary phase constants at low temperature appropriate to low-molecular-weight homologues of a functional class with phase constants appropriate to the temperature required to separate higher molecular weight homologues of the same functional class. This situation is clearly of value when considering stationary phases with similar McReynolds constants but which show different performances at higher operating temperatures.

Table IV shows values of  $\Delta Me_0$  that follow the values of  $\Delta Me$  in Table II, but that are influenced by the temperature dependence of the polar character of the stationary phase as indicated by the relative slopes of retention *versus* temperature plots. The values of  $\mu$  also increase with stationary phase polarity; the variations, although small, are much greater with the more polar acceptor type phases.

## DISCUSSION

The use of molecular retention indices is of some value in stationary phase classification as it eliminates the necessity for comparison of the performance of a stationary phase against the thermally unstable base stationary phase squalane as a

TABLE III

COMPARISON OF STATIONARY PHASE POLARITY AS INDICATED BY McREYNOLDS CONSTANTS AND  $\Delta Me$  VALUES FOR HYDROXYL AND CARBONYL FUNCTIONAL GROUPS

Stationary phase	McReynolds constant										$\Delta Me$
	X' (benzene)	Y' (1-butanol)	Z' (2-pentanone)	U' (nitropropane)	S' (pyridine)	T5	OH	C=O			
C <sub>18</sub> H <sub>17</sub> S	21	10	3	12	25	71	19.34	9.26			
SE-30	16	53	44	65	42	220	19.56	10.30			
OV-17	119	158	162	243	202	884	32.47	26.59			
OV-25	178	204	208	305	280	1175	38.03	32.36			
QF-1	144	233	355	463	305	1500	41.52	54.48			
Silar 5CP	319	495	446	637	530	2427	91.45	77.35			
Silar 7CP	440	638	605	844	673	3200	95.86	81.31			
Silar 9CP	489	725	631	913	778	3536	104.5	87.95			
Silar 10C	523	755	659	942	800	3679	111.62	93.78			

TABLE IV

$\Delta Me_0$  AND U VALUES CALCULATED FROM DATA OBTAINED AT 120-180°C

Stationary phase	Acetates		Ketones		Alcohols		Aldehydes		
	$\Delta Me_0$	$\mu \cdot 10^3$	r	$\Delta Me_0$	$\mu \cdot 10^3$	r	$\Delta Me_0$	$\mu \cdot 10^3$	r
C <sub>18</sub> H <sub>17</sub> S	-21.47	-0.44	-0.28	8.27	0.42	0.18	19.90	65.25	1.67
SE-30	-13.59	-3.46	-0.98	11.15	-0.67	-0.69	22.32	63.60	-0.23
OV-17	-6.80	-0.83	-0.28	26.26	0.30	0.56	30.89	83.47	0.91
OV-25	2.24	0.13	0.13	32.62	-0.34	-0.84	37.97	86.01	2.04
QF-1	13.11	12.74	0.94	47.95	5.43	0.96	31.16	41.10	8.64
Silar 5CP	13.61	15.96	0.91	56.67	17.09	0.99	75.12	104.77	21.73
Silar 7CP	18.99	15.22	0.97	58.95	18.57	1.00	78.09	107.80	22.40
Silar 9CP	25.40	15.76	0.96	53.73	28.21	1.00	71.45	100.91	32.25
Silar 10C	32.75	14.52	0.98	55.14	32.65	1.00	82.74	106.08	33.74

means of subtracting non-polar interactions, as proposed by Rohrschneider<sup>18</sup>. Here, however, acceptance of either of the available thermally stable non-polar base stationary phases<sup>9-15</sup> such as the branched-chain hydrocarbon C<sub>87</sub>H<sub>176</sub> as used in this work or additional material may be developed such as a paraffin wax recently proposed by Evans and Osborn<sup>25</sup> to be thermally acceptable to 150°C, may remove this objection. The same workers also demonstrate what is fundamentally evident that all hydrocarbons are susceptible to oxidation with use of oxygen as carrier gas. Under these severe conditions squalane and Apiezon MH display similar oxidation tendencies while the C<sub>87</sub>H<sub>176</sub> showed greater oxidation resistance. These results would clearly suggest that to obtain optimum results in retention measurements oxygen free carrier gas should be used and also columns have a limited life if optimum results are to be obtained. Also, a nearly linear relationship allowing the calculation of a numerical value for the stationary phase appropriate to the temperature required for a separation and using the functional class of interest is not possible with the Rohrschneider and McReynolds schemes and is potentially of considerable value and will be evaluated in due course.

With both schemes, *i.e.*,  $\Delta Me$  or  $I$ , a series of numerical values for compounds of different functional classes are necessary to specify a stationary phase and in both instances there is considerable difficulty in relating the ability to effect a specific separation with the numerical values available. It has been shown previously<sup>19</sup> that use of particular test solutes relevant to the functional classes under consideration will allow a better prediction of retention to be made using the McReynolds and Rohrschneider schemes, and this applies also to the use of  $\Delta Me$  values. Alternatively, the use of a wide range of reference compounds or classes with either scheme reduces the general application and in the extreme reverts to the unsatisfactory reporting of relative retention as in early papers, where the number of standards was so numerous that comparison was not possible in many instances. A recent report by Heldt and Köser<sup>26</sup> indicates the use of nine different homologous series as the reference line for a retention index scheme. The work is an application of the generalised retention index expression of Novák and Růžičková<sup>27</sup> where a functional constant appropriate to the homologous series is calculated. Heldt and Köser<sup>26</sup> have determined the constants for the nine series so as to allow interconversion between systems. With increasing sophistication of operation computer controlled automatic injection and data reduction as is carried out in these laboratories would readily allow reference to multiple reference standards.

It is evident that the McReynolds values for  $Y'$  and  $Z'$  and the  $\Delta Me$  values for the OH and CO groups increase similarly for the stationary phases considered and for a particular stationary phase show the same relative trends. The exception is QF-1, with enhancement of ketone retention, which shows a  $Z'$  greater than  $Y'$  and  $\Delta Me$  (C=O) substantially greater than  $\Delta Me$  (OH). Since completion of this work, Evans and Osborn<sup>25</sup> have reported a series of  $\Delta Me$  values for the various McReynolds solutes on polysiloxane phases calculated from the work of McReynolds<sup>20</sup> who used approximately 20% stationary phase.

While some doubts exist concerning certain of the data of McReynolds<sup>20,28</sup> regarding the effect of additives used it is apparent that the trend with QF-1 is observed, together with the generally increasing values of  $\Delta Me$  with increasing phase polarity. Despite the differences in the operating conditions a surprising similarity

exists with the present work, both with respect to the  $\Delta Me$  (C=O) and  $\Delta Me$  (OH) values and to comparison of the general polarity using the McReynolds values and to what is described as the McReynolds polarity index this being a summation of the  $\Delta Me$  values for the first five McReynolds solutes. The values as are comparable are shown in Table V. The table also includes a comparison of SILAR 5CP and XF-1150 which with 50% substitution of cyanopropyl and cyanoethyl groups, respectively, are obviously not equivalent but with such similar groups both exhibit the same strong acceptor activity. The increased polar character of SILAR 5CP over XF-1150 is shown both by the higher values according to the McReynolds constants and to the relative  $\Delta Me$  (C=O) and (OH) values. The concept of general polarity by summation of the five terms in each instance may indicate a considerable similarity between both schemes as the phase ranking is in the same order with the limited number of solutes available for comparison and may suggest that the use of a base stationary phase as suggested by Rohrschneider<sup>18</sup> and subsequently by McReynolds<sup>28</sup> is not necessary. In this regard it is of interest that the proposal of Rohrschneider that the retention index differences,  $\Delta I$ , for a particular compound due to polar interactions as determined by elimination of non-polar interactions by subtraction of interactions due to a low-polarity base stationary phase is an oversimplification, and it has been shown that Rohrschneider-type schemes are based on differences in intermolecular interactions rather than polar interactions alone, as originally proposed<sup>21,22</sup>.

TABLE V

COMPARISON OF MOLECULAR RETENTION INDICES OF HYDROXYL AND CARBONYL FUNCTIONS, AND OF GENERAL POLARITY AND McREYNOLDS POLARITY INDEX<sup>25</sup>

Stationary phase	$\Delta Me(OH)^*$	$\Delta Me(CO)^*$	$\sum_{1}^5 I^{**}$	$\Delta Me$ (butanol) <sup>***</sup>	$\Delta Me$ (pentanone) <sup>***</sup>	$\sum_{1}^5 \Delta Me^{***}$
SE-30	19.56	10.3	220	18.67	10.15	87.0
OV-17	32.47	26.59	884	32.82	26.56	179.34
OV-25	38.03	32.36	1175	39.27	33.01	220.15
QF-1	41.52	54.48	1500	43.34	53.63	265.5
SILAR-5CP	91.45	77.35	2427			
XF-1150				83.59	69.76	405.3

\* Determined experimentally (Table III).

\*\* From Table III.

\*\*\* From Evans and Osborn<sup>25</sup>.

It is on reflection apparent with the McReynolds and similarly the Rohrschneider scheme that the retention of the alkane standards alter very significantly with phase polarity while the retention of the test solutes are much less susceptible to solvent polarity variation. Thus according to these schemes it is alkane retention that determines the position of a phase in the polarity scale. This situation has recently been briefly reiterated by Aue and Paramasignamani<sup>29</sup> and has previously been described by Littlewood<sup>30</sup> and by Ashes and Haken<sup>31</sup>. The similarity of the results between the present study and the work of McReynolds may again indicate the significance of the alkane retention.



The work of Evans and Carmi<sup>23</sup> has shown a marked dependence of stationary phase loading on the  $\Delta Me$  values and in a general scheme this is a disadvantage, particularly as the Rohrschneider and McReynolds schemes are relatively independent of stationary phase concentration. Many sets of Rohrschneider and McReynolds constants in the literature determined at 10% loadings are essentially identical with those in earlier reports obtained using columns with a 20% stationary phase loading. The variation in  $\Delta Me$  with stationary phase loading differs greatly, while studies with different supports with a polar stationary phase show much less variation and are comparable to the variations with support shown by Rohrschneider and McReynolds constants. The dependence on concentration introduces a difficulty which occurs with the use of specific retention volumes<sup>24</sup>, where the determination of concentration in the extreme requires destruction of the column. Modification of the molecular retention index approach using a superior reference material might eliminate the concentration dependence.

Clearly, it is apparent that the hypotheses indicated are worthy of further study and may lead to improved methods of stationary phase classification.

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