New Method for Measuring the Polarity and the Selectivity of the Capillary Gas Chromatography Columns

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An alternative method to McReynolds' method is introduced in this work to measure the column's polarity and selectivity. McReynolds' method was developed primarily for measuring the polarity of packed columns, so it suffers from inaccuracy in measuring the polarity of capillary columns, especially those with a high phase ratio. The new method utilizes the plot of logarithm of adjusted retention times for different homologous series versus the number of carbons in each member multiplied by a hundred. The intercept of the alkane (RH) used as a reference was subtracted from the other series intercepts ($RX_1, RX_2, \ldots$). The sum of differences divided by the mean value of slopes of each series predicts the calculated overall polarity. Selectivity, from the other side, was related to the ratio of each individual intercept divided by the mean value of the slope as shown in eqn. (4). The correlation between the new method and McReynolds' either in polarity or selectivity measurements indicates that there is a high correlation in all cases less than 1% significant error.

Key Words: Polarity, Selectivity, Measurement, Capillary gas chromatography column.

INTRODUCTION

The classification of liquid phases currently used in gas chromatography has been attempted using several methods, which were found to be more or less adequate depending on the type of liquid phase. Many "absolute" and "relative" methods have been used to determine the polarity of columns, which require reference phases as well as a set of specific reference probes.

Some attempts have been made to use the column test mixtures as an indicator of column polarity. The typical elution order of Grob's mixtures I and II[1-3] has been proposed as an aid to determining the type of stationary phase in a column; but since these mixtures are analyzed in programmed temperature mode, parameters related to geometrical properties of columns can change the elution pattern. For similar phases, such as SE-30 and SE-54 columns, mixture II provides almost identical elution patterns.

The so-called Rohrschnieder/McReynold constants[4,5] are based on the determination of the Kovats retention indices of several probe compounds, and on the use of a squalane reference column. Since they were developed mainly for the characterization of the stationary phases in packed columns, and the usual probe compounds are very volatile and their retention indices are often difficult to

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determine with accuracy in capillary columns, especially in those with a very high phase ratio. Furthermore, some porous polymer beads react with nitro-compounds, and therefore 1-nitromethane and 1-nitropropane cannot be used as reference probes in columns packed with porous polymer beads. So the polarity in these columns is indicated as the sum of the remaining four McReynold probes[6] which is not satisfactory. The 'retention polarity' method, which is based on the ratios of the retention index values instead of the differences, also has been suggested[7].

The main problem with these procedures is that it is necessary to normalize the data with respect to squalane as the reference column, and to *n*-alkanes as the reference homologous series. The temperature limit of squalane (120°C) is rather low. It has sometimes been suggested that squalane could be replaced with the synthetic phase, a polane $C_{87}H_{176}$[8,9] for high temperature analysis. Also the use of linear alkanes as reference has been criticized[10–12] for polar phases and for porous polymers.

The "CP index" which has been proposed by Chrompack International[13], for the classification of the polarity of capillary columns, requires the determination of the difference in retention indices values on the stationary phase of interest and (a) squalane as the reference of low polarity and (b) OV-275 cyanosilicon as a reference of high polarity. This method suffers from the disadvantage that it is more complex as it requires two reference columns; also in the classification of porous polymer stationary phases negative values were obtained when squalane was used as the reference phase[9–12].

The Snyder selectivity triangle, originally developed for optimization of liquid chromatography[14,15], was extended to gas-liquid chromatography by Klee *et al.*[16]. Only three probes (*n*-butanol, 1-nitropropane and 1,4-dioxane) were used, but this trio of solutes seems to be poor for gas chromatographic applications as they plot low-polarity phases such as SE-30 near to highly polar phases such as carbowax[17].

"Absolute" method, based only on the retention values of a set of homologous *n*-alkanes, was suggested by Fernandez-Sanchez *et al.*[18]. This method uses the ratio of the intercept to the slope of the straight line obtained by plotting the logarithm of the specific retention volumes (V_g) of the series of *n*-alkanes as a function of the number of carbon atoms. Linear alkanes only are necessary as probes, and no reference column is used, but the calculation of V_g values is complex as it requires knowledge of the exact amount of liquid phase in the column and the application of the pressure correction factors of James and Martin[19]. Furthermore, only the effect of dispersive forces is taken into account, whereas most of the polarity of a liquid phase is often due to hydrogen bonding, and dipolar interactions.

Another method proposed by Castello *et al.*[17,20] for the classification of the polarity order of gas chromatography columns was based on the difference in apparent carbon number of homologous series of alkanes and alcohols (ΔC) with the same retention time, as shown in Fig. 1. This method can classify packed and capillary columns as well as porous polymer packings. The classification depends on the effect of the dispersive forces (from the behaviour of alkanes), and of hydrogen bonding (from the behaviour of alcohols). However, columns whose

action mainly depends on dipole interactions are not correctly classified, and this method cannot indicate anything about the selectivity of the columns.
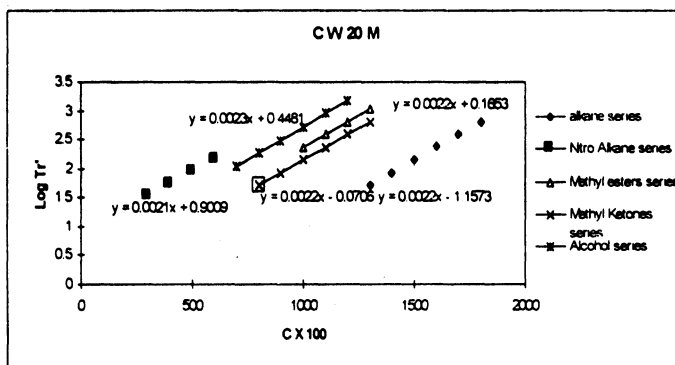

Fig. 1.   Plot log $t_{R/S}$ of the homologous series vs. C × 100 for CW 20 M column

EXPERIMENTAL

All chemicals were of analytical grade and were used as obtained from different sources, Aldrich Chemical Company Ltd. (England), Lancaster Chemical Company Ltd. (England), BDH Chemicals Ltd. (England), Fluca AG Chemische Fabrik (Switzerland) and Koch-Light Laboratories Ltd. The chemicals include n-alkanes (C_9H_{20}–$C_{21}H_{44}$), 1-nitroalkanes ($C_2H_5NO_2$–$C_6H_{15}NO_2$), 2-methylketones ($C_5H_{10}O$–$C_{13}H_{26}O$), methyl esters ($C_8H_{16}O_2$–$C_{15}H_{30}O_2$) and 1-alkanols ($C_7H_{14}O$–$C_{12}H_{24}O$).

The Shimadzu GC-17A chromatograph was used, fitted with an AOC-20 Os autosampler and an AOC-20 I autoinjector and a capillary control unit and splitter injection port. The latter and the flame ionization detector were both operated at 250°C. The new method was applied to different dimensions and film thickness of capillary columns coated with different stationary phases. Helium was used as the carrier gas. The analyses were carried out isothermally at 120°C in order to permit a comparison with previously published McReynolds polarity values.

Procedere

In the present work the polarity of the capillary column stationary phases was characterized by injecting approximately 0.2 v/v % solutions of the different five homologous series in dichloromethane. Each homologous series contains several members: at least four members from n-alkanes (C_9H_{20}–$C_{21}H_{44}$) 1-nitroalkanes ($C_2H_5NO_2$–$C_6H_{15}NO_2$), 2-methylketones ($C_5H_{10}O$–$C_{13}H_{26}O$), methyl esters ($C_8H_{16}O_2$–$C_{15}H_{30}O_2$) and 1-alkanols ($C_7H_{14}O$–$C_{12}H_{24}O$). The choice of the members of each homologous series injected in each column depends on the polarity of the stationary phase.

The new method was used as absolute method (without reference column) and as relative method using OV-1 as reference column instead of squalane.

RESULTS AND DISCUSSION

It is common in capillary columns to plot the logarithms of the adjusted retention times/second of the individual members of the various homologous series as a function of hundred times their carbon number, as shown in Fig. 2.
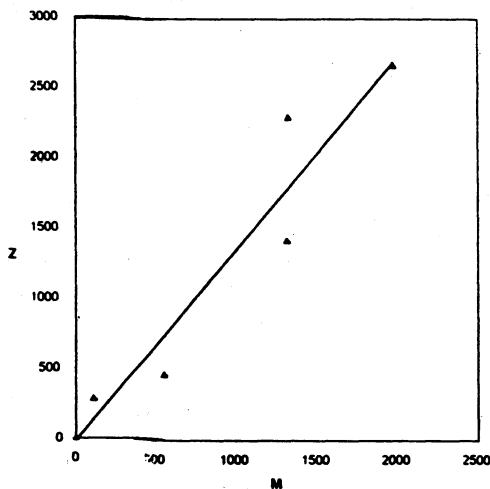

Fig. 2. Regression plot of Z-OVI upon M-OVI (forced through origin)

The resulting lines for each series are virtually parallel, as indicated by Haken *et al.*[21]. Isothermal Kovats retention indices are based on the linear relationship of log (t_R/time unit) *vs.* carbon number for the homologous series of the *n*-alkanes. Such a linear relationship may be represented by Eqn. (1).

$$Y_{RH} = a_{RH} + b_{RH}I_x \qquad \qquad \ldots (1)$$

where a, b are the intercept and slope, respectively, and Y_{RH} is the value of

$$\log (t_R/s).$$

Rearranging, eqn. (1) becomes

$$I_x = (y_{RH} - a_{RH})/b_{RH}$$

For a non-alkane member of other homologous series, the relationship shown by eqn. (2) holds, in which $C_{RX} = 100 \times$ carbon number of RX)

$$Y_{RX} = a_{RX} + b_{RX} \cdot C_{RX} \qquad \qquad \ldots (2)$$

Since Y_{RH} and Y_{RX} are the same for the same compound, thus substitution into eqn. (1) gives

$$I_x = (a_{RX} + b_{RX}C_{RX} - a_{RH})/b_{RH} = (b_{RX}/b_{RH})C_{RX} + (a_{RX} - a_{RH})/b_{RH}$$

where C_{RX} is a constant ($100 \times$ the carbon number of RX for compound x).

Since within the experimental error, the data for all the series exhibit the same slope under the same conditions and the same column, it follows that:

$$I_x = C_{RX} + (a_{RX} - a_{RH})/b \qquad \qquad \ldots (3)$$

The average 'b' values are used to compensate the slight experimental fluctuations in the slope due to the measurement of the retention times of peaks that may have different shapes due to the different polarities of the homologous series.

It also follows from eqn. (3) that, for the same compound RX, the differences in Kovats index (ΔI_x) on any two stationary phases (I_{x1} and I_{x2}) is given by:

$$I_{x1} - I_{x2} = \Delta I_x = \{(a_{RX} - a_{RH})/b\}_1 - \{(a_{RX} - a_{RH})/b\}_2 \qquad \ldots (4)$$

In other meaning, the McReynolds polarity values can therefore be determined for any set of probes, directly from the slopes and intercepts of the Kovats linear plots for their respective homologous series and that of the n-alkanes; when measured in this way, they should also be more accurate.

Correlation

Polarity: The above method that has been applied is correlated with McReynold's, because it is the most popular classification used by producers of liquid phases to characterize their products. We have experimentally measured a polarity index by calculating the sum of the differences in Kovats indices for four different homologous series and the series of the n-alkanes. This is obtained by subtracting the intercept of the fitted line for the n-alkane (RH) from the intercepts of the best fitted lines for other series ($RX_1, RX_2, RX_3, \ldots$). The sum of the differences divided by the mean value of slopes using the relationship shown in eqn. (4) uses OV-1 as the non-polar reference column in place of squalane. This value gives overall polarity index for each column under a given set of operating conditions. Therefore, these measurements can be used as an accurate method to determine the polarity of the columns.

The comparison of the values calculated by the new method with the McReynolds' values published before[5,21,22] is shown in Table-1. The new method seems reproducible. The correlation plot between the McReynolds' values published and the result of this method, for all the phases in the case of OV-1 as non-polar reference column is shown in Fig. 3, gives a correlation coefficient 0.983, even with 5 points. This corresponds to less than 1% significant level. This indicates there is a highly significant correlation between the two methods as shown in Table-2.
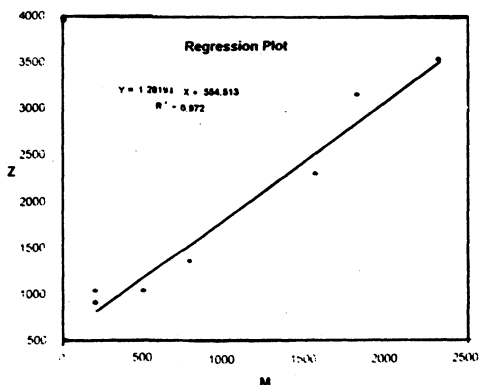

Fig. 3.   Regression plot of Z-sum upon McR-sum

TABLE-1

POLARITY VALUES CALCULATED BY THE NEW METHOD WITH PREVIOUSLY PUBLISHED McREYNOLDS' VALUES[5, 21, 22]

Columns	Result of new method	Σ_{McR}^5 (squalane)
CP-Sil 5	123	95
SE-54	32	115
OV-1701	473	567
OV-215	1409	1323
OV-225	2259	1591
CW 20 M	2627	2086

TABLE-2

CORRELATION COEFFICIENT, r, FOR PAIR OF VARIABLES

Variable 1	Variable 2	No. of points	r	Significant at
Z-ol	M-ol	7	0.954	< 1%
Z-one	M-one	7	0.928	< 1%
Z-NA	M-NA	7	0.914	< 1%
Z-sum	M-sum	7	0.986	< 0.1%
Z-OVI	M-OVI	5	0.983	< 1%

where Z = new index, M = McReynolds index, -ol = alcohol, -one = ketone, -NA = nitroalkane, -sum = sum of {-ol, -one, and -NA} -OVI = (-sum) −'(-OVI sum)

This method can also be used as an absolute method on the same basis as the method of Castello[21, 24] without the need to use a reference column, by using the sum of the difference between the intercepts of the various homologous series and the intercepts of the *n*-alkanes homologous series divided by the mean value of the slope of the different homologous series. The correlation plot between the McReynolds' values published and the result of this method, for all the phases (without subtracting the value of the reference column OV-1) as shown in Fig. 4, gives a correlation coefficient 0.986 (with 7 points). This correspond to less than 0.1% significant level. This indicates that there is a higher significant correlation in the case of non-using OV-1 as reference column than in the case using OV-1 as reference column as shown in Table-2.

Selectivity: This method can also be used to classify the stationary phases depending on the type of the specific interactions between the stationary phase and the functional groups of the members of the homologous series. For example, the effects of dispersive forces (measured by the behaviour of the alkane series), and of hydrogen bonding (by the behaviour of 1-alkanol series), and columns whose action mainly depends on the dipole interaction (measured by the behaviour of methyl ketones, methyl esters and 1-nitroalkanes). The correlation plots between McReynolds' values of 1-butanol, 2-pentanone, and 1-nitropropane and the result of the alcohol series, methyl ketones series, and 1-nitroalkanes series in the new method as shown in Tables 3 and 4 (Figs. 5 and 6), for all phases, gives correlation coefficients 0.954, 0.928 and 0.914 (with 7 points). These correspond to less than 1% significant level as shown in Table-2. So, this method
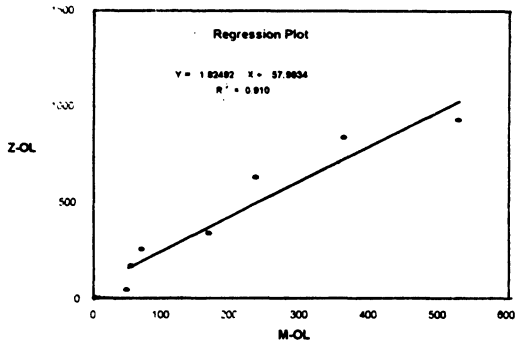
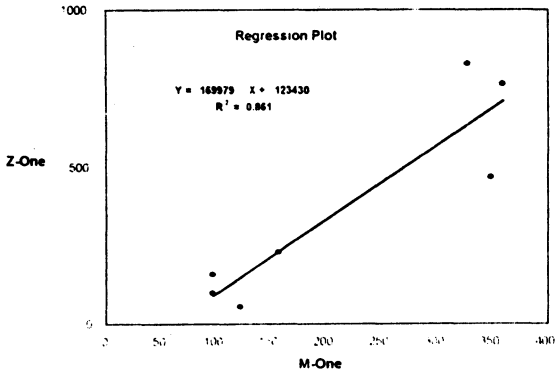Fig. 4.   Regression plot of Z-OL upon M-OL
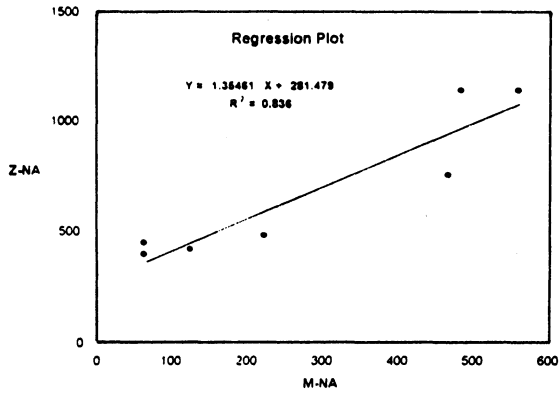

Fig. 5.   Regression plot of Z-one upon M-one

Fig. 6.   Regression plot of Z-NA upon M-NA

can be used to determine the selectivity of the columns with respect to a class of compounds by comparing the values of respective homologous series to all stationary phases. The stationary phase that has a higher value will be more suitable for separating the classes of these compounds.

TABLE-3
NEW INDEX VALUES FOR THE ALCOHOL, METHYL KETONES AND
METHYL ESTERS HOMOLOGOUS SERIES

Column	Alcohol Series	Methyl ketones	Methyl esters
OV-1	147.0	918.0	397.0
SE-54	250.4	50.5	409.8
OV-1701	326.0	245.4	422.3
OV-215	618.0	618.0	740.0
OV-225	851.6	740.5	1114.3
CW 20 M	918.7	682.9	1246.0

TABLE-4
McREYNOLDS' VALUES FOR 1-BUTANOL, 2-PENTANONE AND 1-NITROPROPANE

Column	1-Butanol	2-Pentanone	1-Nitropropane
OV-1	55	44	65
SE-54	72	66	99
OV-1701	170	153	228
OV-215	240	363	478
OV-225	369	338	492
CW 20 M	536	368	572

The advantage of this method is that it can be used as absolute method without using a reference column. This method can be used up to the maximum allowable temperature of the column, but McReynold's cannot be used over 120°C. The member of the homologous series used can be selected in order to give suitable and well measurable retention times at any temperature.

Another advantage of this method is that it can detect any differences between the stationary phases probably caused by the different recipes of the suppliers in preparing their columns[23, 25]. For example, this method can differentiate between the OV-I and CP-Sil 5, which have the same stationary phase polydimethylsiloxane, but supplied by different manufacturers. Even the McReynolds' cannot differentiate clearly between the two stationary phases (gives approximately one value), but this method can differentiate clearly between OV-1 and CP-Sil 5 (gives two different values) as shown in Fig. 3.

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