

## A GRAPHICAL AND NUMERICAL METHOD FOR PREDICTING GAS CHROMATOGRAPHIC RETENTION VOLUMES OF HOMOLOGOUS HYDROCARBONS

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(Received March 21st, 1966)

The comparison of retention volumes measured on polar and non-polar columns is a well known method for the gas chromatographic identification of hydrocarbons. SMITH, OHLSON AND LARSON<sup>1</sup> have measured the retention volumes of the homologous series of different types of hydrocarbons using a number of liquid phases of different polarity, and plotted the logarithms of the retention volumes obtained with liquid phases of opposite polarity against each other. The points pertaining to the different homologous series formed parallel straight lines in these diagrams.

If the retention volume of an unknown hydrocarbon is determined first on a polar and then on a non-polar column and the logarithms of these values are then plotted on such a diagram as described above, it will be possible to determine the homologous series to which the unknown compound may belong from the position of the points corresponding to the two values on the diagram.

On the straight line corresponding to a given homologous series—especially if this is plotted only from a few known points—it is, however, not easy to state with any certainty which member of this series our unknown might be while, on the other hand, it is practically impossible to predict on the diagram the position of members which have not been measured.

KALLEN<sup>2</sup> who had to identify widely different C<sub>6</sub> to C<sub>7</sub> hydrocarbons found that in diagrams of the type described the distance between the neighbouring members of a homologous series is the same in every series.

Our experiments, however, indicated that this rule is valid but for a very narrow range of carbon numbers as actually the points lie nearer together as the number of carbon atoms increases. This is due to the fact that within a homologous series the logarithm of the retention volume is not a linear function of the carbon number.

EVANS AND SMITH<sup>3,4</sup> have introduced another graphical method in which the logarithm of the adjusted retention volumes is proportional to the carbon number. This so-called "log plot" method has, however, the disadvantage that not the gas hold-up but a smaller value has to be subtracted from the retention volume and this corrected gas hold-up must be determined either by trial and error or by some complicated, increasingly exact calculation till the desired linear correlation is approached. Thus the results may depend on certain individual requirements of the person who performs these operations, the more so as it is impossible to find in this way a correction valid for a wide range of carbon numbers: a given "log plot" may

either be convenient for low numbers of carbon atoms but deviate at higher numbers or the other way round.

The calculation method for retention volumes by BEREZKIN *et al.*<sup>5</sup> based on increments of the retention volumes referring to each structural element in the molecules is of great theoretical importance. For practical applications, however, it is too complicated since many relationships between the increments and the polarity, or the structural characteristics of the various liquid phases have to be considered.

In the work presented here we have aimed at finding a simple, generally valid correction which may be applied in practice to a wide range of carbon numbers, with the help of which a linear correlation between retention volume and carbon number should be obtained, *i.e.* in the comparative diagrams of the polar and non-polar columns the members of the homologous series should indeed be positioned at equal distances.

#### EXPERIMENTAL

Squalane (Sq) was used as the non-polar and  $\beta,\beta'$ -oxydipropionitrile (ODP) as the polar liquid phase. Retention volumes were measured with nitrogen carrier gas in a "Chrom I" type gas chromatograph (Laboratory Equipment, N.E., Prague, Czechoslovakia). When set at the highest sensitivity, the flame ionization detector signalled the emergence of air with a low negative peak so that gas hold-up could be measured.

Columns of 1.7 m length and 6 mm I.D. were used. The percentage of the liquid phase on the firebrick solid support was 15 %.

In most cases the reference materials were highly purified. When hydrocarbons of commercial grade were used they contained only such contaminants which under the experimental conditions could be separated perfectly from the main component so that the determinations of the retention volumes were not affected.

#### RESULTS AND DISCUSSION

To ensure a general validity for our results we started from the *specific* retention volume for which an additive correction applicable without any time-consuming and tiresome calculation was necessary. As indicated in the foregoing discussion a constant value fails to fulfil this requirement, the correction had to increase with increasing carbon number. We attempted the introduction of a correction which bears a simple relationship with the number of carbon atoms.

With the aim of determining the suitable correction we have measured the retention volume of *n*-paraffins and *n*- $\alpha$ -olefins on both columns at several temperatures. By using the least squares method the experimental results led to the equations given in Table I.

The corrections in the equations are extremely simple and in the given range are independent of the temperature and the type of hydrocarbon.

The measured and calculated specific retention volumes are compared in Table II. As may be seen the agreements are good with conspicuous differences only at low temperatures with high carbon numbers: the measured values are considerably higher than the calculated ones probably because of the slow evaporation.

TABLE I

RELATIONSHIPS BETWEEN SPECIFIC RETENTION VOLUMES AND CARBON NUMBERS

 $V_g$  is the specific retention volume, and  $n$  is the carbon number.

Liquid phase	Temperature (°C)	<i>n</i> -Paraffins	<i>n</i> - $\alpha$ -Olefins
Sq	70	$\log (V_g + n/2) = 0.380 n - 0.390$	$\log (V_g + n/2) = 0.389 n - 0.511$
Sq	150	$\log (V_g + n/2) = 0.234 n - 0.250$	$\log (V_g + n/2) = 0.241 n - 0.335$
ODP	30	$\log (V_g + n/6) = 0.336 n - 0.653$	$\log (V_g + n/6) = 0.260 n - 0.015$
ODP	70	$\log (V_g + n/6) = 0.260 n - 0.813$	$\log (V_g + n/6) = 0.246 n - 0.540$

TABLE II

COMPARISON OF THE MEASURED AND CALCULATED SPECIFIC RETENTION VOLUMES (in ml)

Hydrocarbon	Sq				ODP			
	70°		150°		30°		70°	
	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated
<i>n</i> -Paraffins								
Pentane	30	30	5.8	5.8	10.3	9.8	2.27	2.24
Hexane	71	75	11.3	11.3	21.1	22.1	4.63	4.60
Heptane	184	183	20.8	20.9	46.6	48.8	9.05	9.02
Octane	443	443	37.5	37.9	112	107	17.2	17.2
Nonane	—	1070	—	67	—	230	—	32.2
Decane	2462	2565	118	118	650	508	54.7	59.7
Undecane	—	—	210	205	—	—	118	110
Dodecane	—	—	365	355	—	—	227	202
<i>n</i> - $\alpha$ -Olefins								
Ethene	0.77	0.85	0.27	0.40	3.35	2.87	0.41	0.56
Propene	3.11	3.03	0.91	0.94	5.49	5.30	1.07	1.08
Butene	9.37	9.10	2.24	2.25	9.37	9.87	2.15	2.11
Pentene	—	24.7	—	4.90	—	18.4	—	4.06
Hexene	65.2	63.5	10.41	9.90	34.5	34.1	7.69	7.63
Heptene	—	159	—	18.97	—	62.4	—	14.0
Octene	382	395	34.24	35.13	159.5	115.0	26.1	25.5

TABLE III

COMPARISON OF THE SPECIFIC RETENTION VOLUMES CALCULATED FROM THE EQUATIONS WITH THOSE MEASURED BY EVERED AND POLLARD<sup>6</sup> ON SQUALANE

Hydrocarbon	80°		111°		139°	
	Measured	Calculated	Measured	Calculated	Measured	Calculated
<i>n</i> -Pentane	24	25	—	—	—	—
<i>n</i> -Hexane	62	60	27	30	14	15
<i>n</i> -Heptane	145	142	55	62	27	29
<i>n</i> -Octane	330	332	115	128	50	54
<i>n</i> -Nonane	750	768	253	262	99	99

TABLE IV

COMPARISON OF RELATIVE RETENTIONS CALCULATED BY US AND MEASURED BY VARIOUS AUTHORS FOR SQUALANE

<i>n-Paraffin</i>	$25^{01}$		$64.7^{04}$		$80^{06}$		$100^{04}$		$111^{06}$		$138^{04}$		$139^{06}$	
	<i>Meas- ured</i>	<i>Calcu- lated</i>	<i>Meas- ured</i>	<i>Calcu- lated</i>	<i>Meas- ured</i>	<i>Calcu- lated</i>	<i>Meas- ured</i>	<i>Calcu- lated</i>	<i>Meas- ured</i>	<i>Calcu- lated</i>	<i>Meas- ured</i>	<i>Calcu- lated</i>	<i>Meas- ured</i>	<i>Calcu- lated</i>
Propane	0.009	0.012												
Butane	0.030	0.038												
Pentane	0.100	0.116	0.164	0.157	0.166	0.176	0.223	0.203						
Hexane	0.320	0.343	0.406	0.400	0.431	0.424	0.469	0.456	0.486	0.476			0.52	0.52
Heptane	1.000		1.000		1.000		1.000		1.000		1.000		1.000	
Octane			2.47	2.48	2.276	2.33	2.116	2.155	2.110	2.07	1.80	1.88	1.83	1.87
Nonane			6.06	6.12	5.17	5.39	4.464	4.60	4.275	4.24	3.28	3.49	3.67	3.45
Decane			14.9	15.05			9.42	9.78			6.03	6.38		
Undecane							19.85	20.7			11.1	11.6		
Dodecane							42.0	43.9			20.43	21.1		
Tridecane											37.6	38.1		
Tetradecane											69.6	69.0		

These equations were also checked against literature data, our calculated values being compared with the specific retention volumes of some *n*-paraffins measured by EVERED AND POLLARD<sup>6</sup>. As, however, these data refer to 80°, 111° and 139° we have determined the assumed constants for these temperatures by linear interpolation from the constants for 70 and 150° on the right side of the equations. The specific retention volumes of EVERED AND POLLARD are compared with our calculated values in Table III which shows that with the exception of the values for 111° the agreement is excellent. This seems to indicate that the differences must be attributed essentially to the error in linear interpolation.

As the literature quotes mainly relative retentions the calculated specific retention volumes need to be converted into relative retentions in order to be compared with more data. Table IV shows such a comparison with *n*-heptane as reference compound. The differences are not great, indeed not greater than the general scattering of data of the various authors, in spite of the fact that the constants of the equations for different temperatures were obtained by interpolation and in some cases even by extrapolation.

It follows from these results that if the  $\log(V_g + n/6)$  values measured on ODP are plotted against  $\log(V_g + n/2)$  obtained on Sq the points corresponding to the different members of a given homologous series will be on a straight line and at equal distance from each other (Fig. 1).

The diagram was plotted from data obtained at 70° as this is the highest temperature at which ODP can still be used while at lower temperatures the upper limit of the range of carbon numbers which can still be measured is very low. At 70° specific retention volumes could be determined up to C<sub>10</sub>. The distance between the neighbouring points is the same on both lines, the numerical value of this distance in the logarithmic scale is 0.46. As only the measured and not the calculated values are shown, points corresponding to certain members are missing from the graph.

To make the method applicable to widely different hydrocarbon homologues

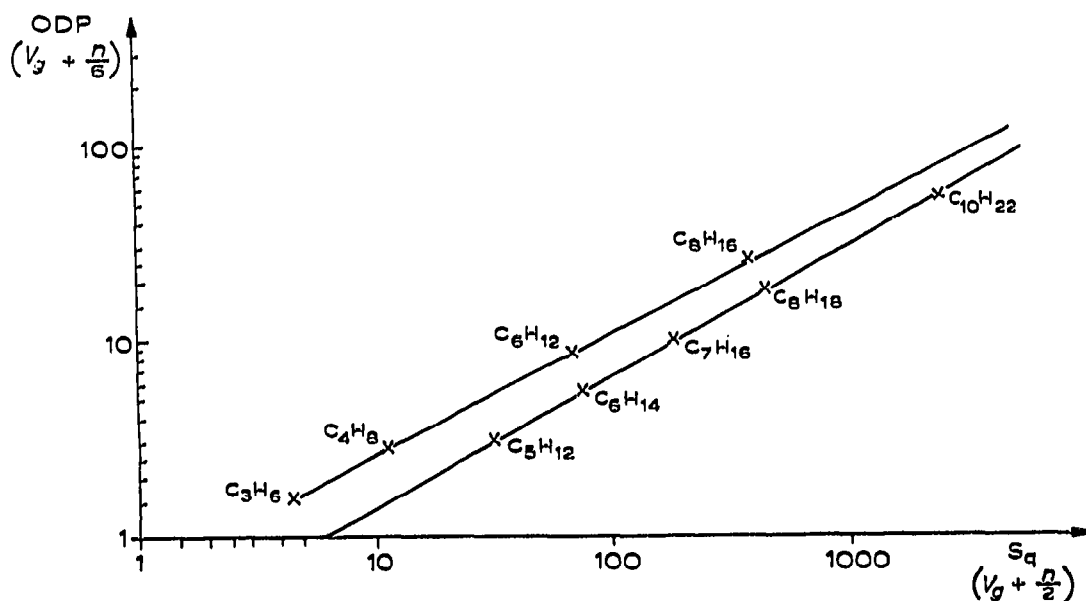


Fig. 1. Corrected specific retention volumes measured on ODP vs. those measured on Sq (log scale).

these corrections were applied to the data of SMITH, OHLSON AND LARSON<sup>1</sup> (Table V). The data refer to 25°, thus the highest carbon number was C<sub>7</sub>.

Our corrections can, therefore, be applied to other temperatures and to other types of hydrocarbons resulting in a linear correlation between the number of carbon atoms and retention volume. There is a considerable difference between measured

TABLE V

APPLICATION OF THE CALCULATIONS TO THE MEASUREMENTS OF SMITH, OHLSON AND LARSON<sup>1</sup> FOR VARIOUS TYPES OF HYDROCARBONS

Series	Sq		ODP	
	Meas- ured	Calcu- lated	Meas- ured	Calcu- lated
<i>n-Alkanes</i>				
Ethane	3.4	2.6	0.74	0.75
Propane	10.0	10.0	1.82	1.91
Butane	34.0	34.4	5.11	4.71
Pentane	114	113	11.36	11.10
Hexane	365	362	24.4	25.5
Heptane	1140	1150	57.7	57.8
<i>2-Methyl-alkanes</i>				
2-Methyl-propane	21.7*	25.9	3.52*	4.13
2-Methyl-butane	83.2	83.1	9.43	9.20
2-Methyl-pentane	258	259	19.1	20.0
2-Methyl-hexane	801	801	43.7	42.7
<i>Cycloalkanes</i>				
Cyclobutane			17.8	17.9
Cyclopentane			36.7	36.4
Cyclohexane			73.3	73.6
<i>n-α-Alkenes</i>				
Ethene	3.4*	2.4	5.00*	2.57
Propene	10.3	9.1	5.45	5.40
Butene-1	31.9	31.3	11.9	11.3
Pentene-1	99	102	21.7	23.5
Hexene-1	323	324	47.2	48.5
Heptene-1	1035	1025	104.5	99.5
<i>n-cis-β-Alkenes</i>				
cis-Butene-2	47*	44	18.6*	14.4
cis-Pentene-2	137	137	30.0*	29.8
cis-Hexene-2	424	421	60.5	61.3
cis-Heptene-2	1277	1282	126.1	125.4
<i>n-trans-β-Alkenes</i>				
trans-Butene-2	41*	41	15.1*	12.0
trans-Pentene-2	129	129	25.6	25.2
trans-Hexene-2	400	398	51.1	52.6
trans-Heptene-2	1220	1223	110.6	109.0
<i>n-α-Alkynes</i>				
Acetylene	4.0*	4.2		
Propyne-1	20.5	14.8		
Butyne-1	49.0	49.2		
Pentyne-1	154	158		
Hexyne-1	500	502		

and calculated values only in the case of the symmetric members of homologous series consisting of asymmetric molecules. These are marked with an asterisk in the Table.

The values obtained on the two different columns are compared in Fig. 2. To make this figure clearer for surveying homologous series with very closely adjacent lines are not shown. An example of closely adjacent series is given by the paraffin isomers which are separately shown in Fig. 3. The points of the branched chain

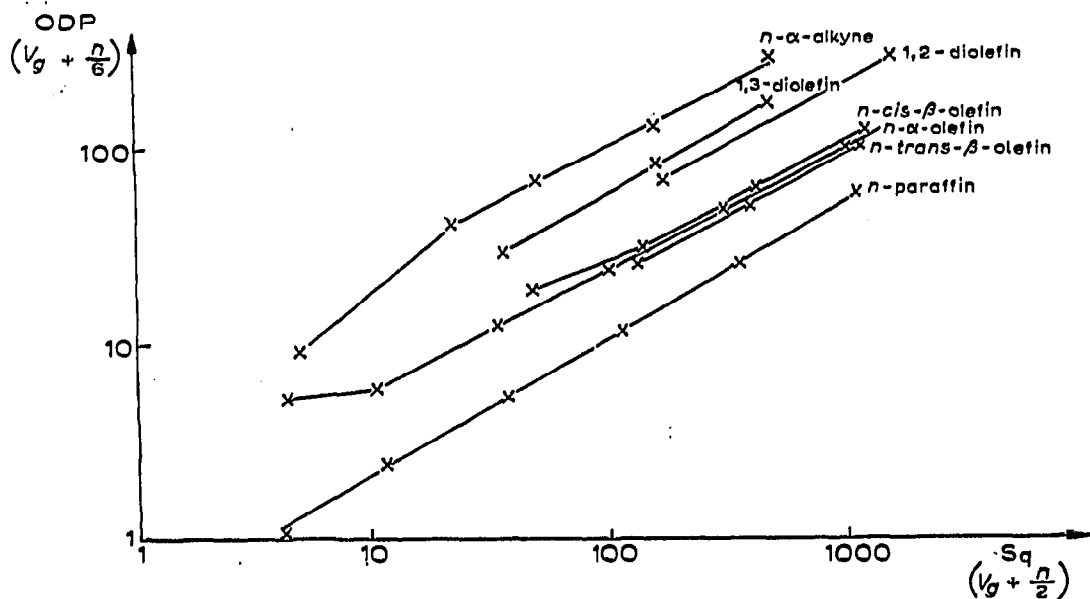


Fig. 2. The corrected values of the specific retention volumes of SMITH, OHLSON AND LARSON<sup>1</sup> (log scale).

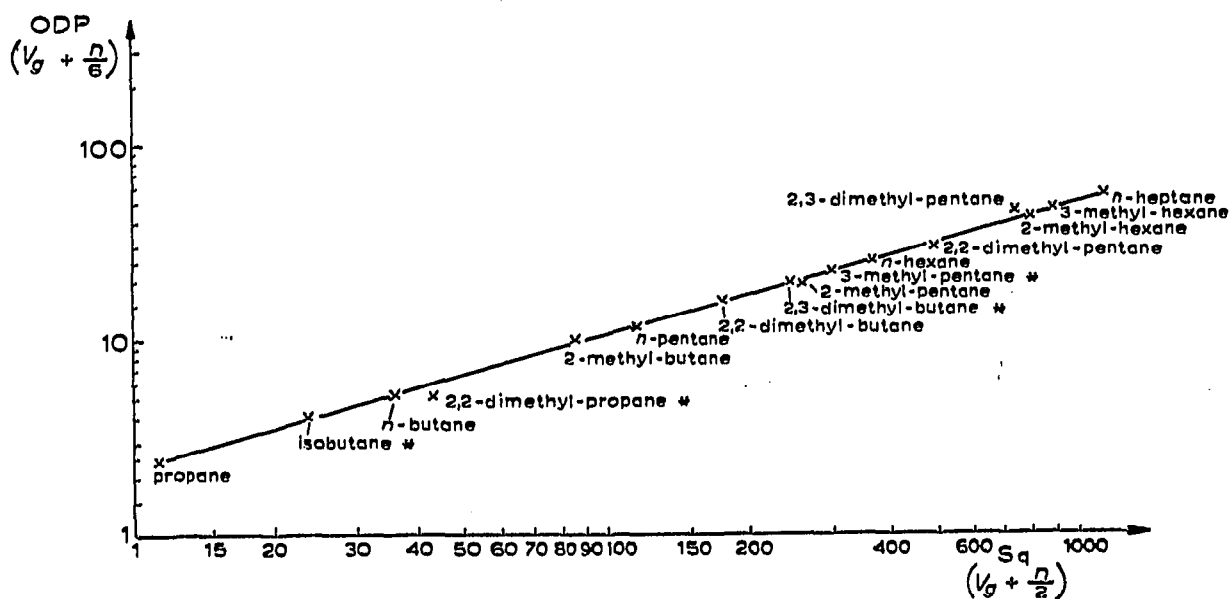


Fig. 3. The corrected values of the specific retention volumes of several paraffins measured by SMITH, OHLSON AND LARSON<sup>1</sup> (log scale).

paraffins essentially coincide with the line for the  $n$ -paraffins but are shifted in a way which is characteristic of their structure. These shifts can apparently not be accounted for by the differences in polarity because of the colinearity. It suggests more the role of the compactness of the molecules which was observed by LITTLEWOOD<sup>7,8</sup>.

Since structural differences between the homologous series have a greater effect on retention volume at lower temperatures, the distances between the points vary in accordance with the structures: thus it is 0.60 for alkanes, 0.59 for cycloalkanes, 0.575 for alkenes, and 0.50 for alkynes.

#### CONCLUSIONS

Once the retention volumes of a few members of a homologous series have been measured it will be possible with the help of the procedure outlined here to predict the retention volumes of the other members. The method is also useful in the identification of unknown compounds.

If the retention volume of an unknown hydrocarbon is measured on both Sq and ODP, and on the basis of the known boiling point estimation\*, the probable carbon number can be estimated from the measurement on Sq; by plotting the corrected values not only can it be determined whether this point lies on one of the straight lines of a homologous series but also whether this point coincides with one of the points representing a member of this homologous series even if we have no such hydrocarbon reference material at our disposal.

If, on the other hand, on the basis of the retention data a point lies on one of the homologous series but its position does not coincide with any of the points representing members of this series, it is highly probable that the unknown material is not a member of this homologous series.

#### ACKNOWLEDGEMENT

The author is greatly indebted to Dr. J. H. PURNELL for the helpful discussions and suggestions.

#### SUMMARY

If the logarithms of retention volumes on a polar column are plotted against the values obtained on a non-polar column, the points representing members of the homologous series will lie on straight lines but at unequal distances. This is an obstacle when trying to decide the position of missing points.

If, however, the  $\log (V_g + n/6)$  values measured on  $\beta, \beta'$ -oxydipropionitrile are plotted against  $\log (V_g + n/2)$  measured on squalane, the points corresponding to the individual members of the homologous series will be located at equal distances. ( $V_g$  is the specific retention volume,  $n$  is the carbon number).

Comparisons of the retention data calculated from these linear correlations with measured ones and those published in the literature are given.

\* It should be noted that an error certainly not greater than  $\pm 1$  is involved here; an error of this order cannot be excluded in the measurement of retention volumes either.



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