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Note

Linearity of the retention time versus carbon number plot for *n*-alkanes

M. S. WAINWRIGHT, J. K. HAKEN and D. SRISUKH

Department of Industrial Chemistry and Polymer Science, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

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The increasing use of computer processors for reporting retention data has focused attention on the mathematical computation of dead time, which has been described by us¹⁻³ and other workers (see ref. 4). All of these studies assumed a linear plot of retention time *versus* carbon number for *n*-alkanes, although several conflicting reports have appeared concerning this matter.

Groenendijk and Van Kemenade⁵ reported linearity of the semi-logarithmic plot over a wide carbon number range, *viz.*, C₁₉-C₃₂ and C₁-C₈, on an SE-30 capillary column and suggested that the curvature has often been observed owing to the assumption that methane is not retarded. They showed retention of methane, a conclusion recently further demonstrated³, but indicated that the retention was small and only slightly different from the calculated dead time in many instances.

Rohrschneider⁶ subsequently reported a deviation from linearity of the *n*-alkane retention line up to at least *n*-nonane and suggested that the linearity or curvature of the plot depended on the dead time. Three methods of analysis were employed, the first a graphical treatment, which is of restricted accuracy, the second a different procedure that calculates the slopes of the retention of pairs of *n*-alkanes and requires a constant value between all pairs as an indication of linearity, a procedure of limited value as some experimental error will occur with all data. The third procedure considers retention index values where increments of 100 are required between homologues to indicate linearity, as reported by Groenendijk and Van Kemenade⁵. Rohrschneider showed the dependence of the slope of the *n*-alkane retention line on the choice of the dead time. Using retention figures calculated to produce a linear semi-logarithmic relationship with one particular dead time, it was shown that with variation of this dead time the slope values calculated between neighbouring *n*-alkanes were variant. The work of Rohrschneider⁶ indicates that a unique solution of the calculated data is achieved, however with experimental data treatment of all of the data points is desirable rather than individual pairs of data points.

In two recent papers^{7,8}, Sevčik and co-workers described the accurate calculation of adjusted retention time by using the ratio, *A*, of the time differences for neighbouring *n*-alkanes in a homologous series. They claimed that the procedures used to indicate the time of injection have a marked effect on gross retention times and this causes errors in the dead time, *t_m*, either measured or calculated, in spite of

the gas chromatographic conditions remaining unchanged. The value of A is the ratio of the antilogarithms of the slopes the lines between successive pairs of n -alkanes and hence gives a measure of constancy of the slope of the n -alkane line. They showed that the value of A is essentially constant for n -alkanes higher than C_9 by injection of a mixture of C_9 - C_{20} n -alkanes. Separate experiments with narrower ranges of n -alkanes (C_5 - C_8 , C_7 - C_{12} , C_{10} - C_{13} and C_{12} - C_{20}) were also carried out but the A values were not reported.

In this work the retention of n -alkanes is considered on non-polar stationary phases, as in earlier work, and also on stationary phases of increasing polarity. With calculation of the dead times the complete data are considered and the deviation of each data point from the calculated line is demonstrated. Further, it is shown that the calculation of the ratio, A , of the differences in retention times of successive n -alkanes provides a sensitive test of the linearity of the n -alkane line.

EXPERIMENTAL

The equipment used consisted of a Hewlett-Packard 5750 research chromatograph interfaced to a 16K PDP, 11/40 digital computer. Interfacing was achieved by the use of an LPS 11 Laboratory Peripheral System comprising a 12-bit analogue-to-digital converter, a programmable real-time clock with two Schmitt triggers and a display controller with two 12-bit digital-to-analogue converters. All on-line programming was written in CAPS II Basic with LPS options. The sampling rate was 0.5 sec.

A mixture of n -alkanes from methane to n -heptane in nitrogen was obtained from Commonwealth Industrial Gases (Alexandria, Australia). Liquid samples for use on more polar columns were mixtures of C_5 - C_{12} n -alkanes.

The retention times measured for the n -alkanes were used to calculate the dead times using the method of Grobler and Balizs⁹. This method has been proved to be simple and accurate¹. The dead time, t_m , the slope, b , and intercept, C , were then used in the following equation to estimate the uncorrected retention times, t_r , of the n -alkanes and methane of carbon number Z :

$$\log(t_r - t_m) = bZ + C \quad (1)$$

The ratio, A , of the differences in retention times was calculated as an alternative method for assessing the linearity of the n -alkane line.

RESULTS AND DISCUSSION

The results in Tables I-IV were obtained from six injections of n -alkane mixtures on to columns of low, moderate and high polarity. It can be seen from the low values of the standard deviations that the data are of high accuracy and consistency. The columns headed \bar{i} , \bar{i}_{calc} and \bar{i}' refer to the means of the experimental uncorrected retention times, calculated uncorrected retention times and corrected retention times calculated using the mathematical dead time t_m .

The data in Table I are for the non-polar SE-30 stationary phase. The significant features are the large net retention of methane and the large differences between the

TABLE I

RETENTION TIME DATA FOR *n*-ALKANES ON SE-30

Column temperature, 30°; carrier gas (helium) flow-rate, 30 ml/min; column, 10% SE-30 on Chromosorb W, aluminium, 22 ft. \times $\frac{1}{8}$ in. O.D. $\bar{t}_m = 189.0$ sec; S.D. = 0.73 sec.

<i>n</i> -Alkane	\bar{t} (sec)	S.D. (sec)	\bar{t}_{calc} (sec)	S.D. (sec)	\bar{t}' (sec)	\bar{A}	S.D.
Methane	200.6	0.408	200.2	0.459	11.6		
Ethane	212.6	0.345	211.8	0.304	23.6	1.744	0.348
<i>n</i> -Propane	233.6	0.342	235.4	0.309	44.6	2.284	0.026
<i>n</i> -Butane	281.5	0.641	283.5	0.465	92.6	2.051	0.012
<i>n</i> -Pentane	379.9	0.917	381.5	0.880	190.9	2.064	0.008
<i>n</i> -Hexane	582.9	2.090	581.0	2.870	393.9	2.070	0.014
<i>n</i> -Heptane	1003.0	2.678	987.3	9.653	814.1		

TABLE II

RETENTION TIME DATA FOR *n*-ALKANES ON OV-25

Column temperature, 30°; carrier gas (helium) flow-rate, 35 ml/min; column, 10% OV-25 on Chromosorb W, aluminium, 36 ft. \times $\frac{1}{8}$ in. O.D. $\bar{t}_m = 208.3$ sec; S.D. = 0.78 sec.

<i>n</i> -Alkane	\bar{t} (sec)	S.D. (sec)	\bar{t}_{calc} (sec)	S.D. (sec)	\bar{t}' (sec)	\bar{A}	S.D.
Ethane	214.5	0.256	215.2	0.592	6.2		
<i>n</i> -Propane	226.6	0.189	227.3	0.300	18.3	3.092	0.144
<i>n</i> -Butane	263.9	0.927	260.6	0.556	55.6	2.564	0.052
<i>n</i> -Pentane	359.6	1.379	359.6	2.364	151.3	2.729	0.029
<i>n</i> -Hexane	620.8	1.270	609.2	5.980	412.5	2.648	0.019
<i>n</i> -Heptane	1312.5	3.688	1310.4	15.491	1104.3		

A values calculated for $C_1-C_2-C_3$ and $C_2-C_3-C_4$ *n*-alkanes and the values obtained for higher *n*-alkanes. Similar results are shown in Table II for the moderately polar OV-25 stationary phase, for which the A value for $C_2-C_3-C_4$ *n*-alkanes is considerably greater than that for the higher *n*-alkanes.

The results in Tables III and IV for the retention of higher *n*-alkanes on the moderately polar OV-25 and highly polar SILAR-7CP stationary phases show constant

TABLE III

RETENTION TIME DATA FOR *n*-ALKANES ON OV-25

Column temperature, 25°; carrier gas (helium) flow-rate, 25 ml/min; column, 10% OV-25 on Chromosorb W, aluminium, 12 ft. \times $\frac{1}{8}$ in. O.D. $\bar{t}_m = 48.8$ sec; S.D. = 1.68 sec.

<i>n</i> -Alkane	\bar{t} (sec)	S.D. (sec)	\bar{t}_{calc} (sec)	S.D. (sec)	\bar{t}' (sec)	\bar{A}	S.D.
<i>n</i> -Hexane	69.0	0.386	69.0	0.378	20.2		
<i>n</i> -Heptane	90.5	1.279	90.5	0.845	41.7	2.098	0.113
<i>n</i> -Octane	135.2	1.383	134.9	2.035	86.4	2.040	0.039
<i>n</i> -Nonane	226.5	1.429	226.8	3.148	177.7	2.076	0.027
<i>n</i> -Decane	416.0	2.749	416.5	3.676	367.2	2.072	0.052
<i>n</i> -Undecane	808.7	13.054	808.9	10.740	759.9	2.081	0.023
<i>n</i> -Dodecane	1625.9	34.761	1620.2	42.857	1577.1		

TABLE IV

RETENTION TIME DATA FOR *n*-ALKANES ON SILAR-7CP

Column temperature, 60°; carrier gas (helium) flow-rate, 25 ml/min; column, 10% SILAR-7CP on Chromosorb W, aluminium, 12 ft. \times $\frac{1}{8}$ in. O.D. $\bar{t}_m = 111.9$ sec; S.D. = 0.29 sec.

<i>n</i> -Alkane	\bar{t} (sec)	S.D. (sec)	\bar{t}_{calc} (sec)	S.D. (sec)	\bar{t}' (sec)	\bar{A}	S.D.
<i>n</i> -Pentane	124.5	0.0	124.4	0.1472	12.6		
<i>n</i> -Hexane	135.4	0.2092	135.2	0.2608	23.5	1.833	0.0374
<i>n</i> -Heptane	155.3	0.5164	155.4	0.4930	43.5	1.867	0.0242
<i>n</i> -Octane	192.6	0.9704	192.0	0.9432	80.7	1.868	0.0138
<i>n</i> -Nonane	262.2	2.2286	263.25	1.9547	150.3	1.892	0.0216
<i>n</i> -Decane	393.3	3.8330	394.3	3.4126	282.0	1.847	0.0476
<i>n</i> -Undecane	637.25	7.6256	638.7	7.1203	525.4		

values of A for all *n*-alkanes, indicating complete linearity of plot of logarithm of retention time versus carbon number.

The values of the calculated and experimental retention times of the *n*-alkanes on all four columns show excellent agreement, indicating that the *n*-alkane lines are essentially linear. Similarly, the plots of corrected retention time in Fig. 1 show complete linearity, even for methane, ethane and *n*-propane. However, the low A

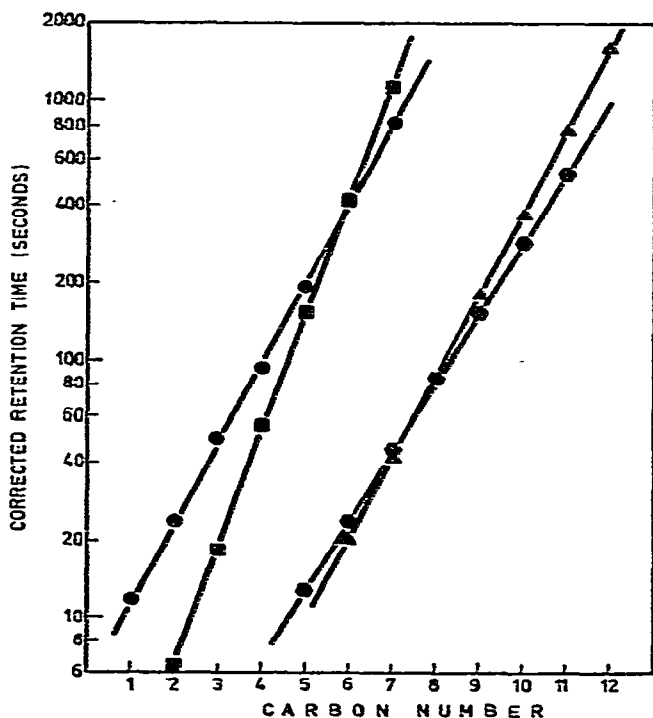


Fig. 1. Plots showing corrected retention times of *n*-alkanes. ●, SE-30 at 30° (data in Table I); ■, OV-25 at 30° (data in Table II); ▲, OV-25 at 25° (data in Table III); ◆, SILAR-7CP at 60° (data in Table IV).

values for $C_1-C_2-C_3$ and high A values for $C_2-C_3-C_4$ n -alkanes indicate some curvature in the n -alkane plot for the gaseous species. It therefore appears that the method is more sensitive in determining the linearity of the n -alkane line as it uses only the differences between experimentally measured retention times. The graphical method of plotting corrected retention times *versus* carbon number is insensitive as logarithms are taken. Further, some method of dead time estimation, mathematical or otherwise, must be used.

The inconsistent values of A calculated for the gaseous n -alkanes may be thought to arise from the fact that the differences in the retention times of these species are small, thereby resulting in inaccurate measurement. However, this is not so, as can be seen from the data presented in Tables I and IV, in which the differences for $C_1-C_2-C_3$ and $C_5-C_6-C_7$ n -alkanes are of the same order. It should also be noted that the A values calculated for six injections showed little variation.

The reason for the non-linearity of the n -alkane line in the region of C_1-C_4 n -alkanes is not readily explained. However, Rohrschneider⁶ has made some attempt to explain the behaviour on the basis of thermodynamics using vapour pressure ratios. There is now experimental evidence to show some non-linearity in the line below n -pentane. These new data and the sensitive test for linearity show that the choice of sufficient n -alkanes (four or more), with carbon number 5 or greater, provides for an accurate estimate of dead-time, as indicated previously⁴. The considerable retention of methane on SE-30 shows that it is undesirable to use this as a method of estimating dead times for non-polar columns.

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REFERENCES

- 1 J. K. Haken, M. S. Wainwright and R. J. Smith, *J. Chromatogr.*, 133 (1977) 1.
- 2 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 147 (1978) 65.
- 3 M. S. Wainwright, J. K. Haken and D. Srisukh, *J. Chromatogr.*, 179 (1979) 160.
- 4 M. S. Wainwright and J. K. Haken, *J. Chromatogr.*, 184 (1980) in press.
- 5 H. Groenendijk and A. W. C. van Kemenade, *Chromatographia*, 1 (1968) 472.
- 6 L. Rohrschneider, *Chromatographia*, 2 (1969) 437.
- 7 J. Ševčík, *J. Chromatogr.*, 135 (1977) 183.
- 8 J. Ševčík and N. S. H. Löwentap, *J. Chromatogr.*, 147 (1978) 75.
- 9 A. Grobler and G. Balizs, *J. Chromatogr. Sci.*, 12 (1974) 57.