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Note

Linearity of retention data plots for *n*-alkanes on porous polymers in gas chromatography

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In a recent publication[1] we have shown that the method of Ševčík[2,3] provides a sensitive test of the linearity of plots of retention time *versus* carbon number for the *n*-alkanes. For the accurate calculation of the adjusted retention time the ratio[4] of the time differences for neighbouring *n*-alkanes in a homologous series was used. The ratio, *A*, of the antilogarithms of the slopes of the lines between successive pairs of *n*-alkanes gives a measure of constancy of the slope of the *n*-alkane line. Ševčík 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 the previous investigation[1] we employed stationary phases of increasing polarity from SE-30 through OV-25 to Silar 7CP and the deviation of each data point from the calculated values was determined for the lower *n*-alkanes. Thus, while we considered only gas–liquid chromatography, gas–solid chromatography is also of importance.

Since the mid-1960s and the pioneering work of Hollis and co-workers[4,5] the use of porous polymers for gas chromatographic separations has become widespread. These polymer beads are considered to have separating powers normally associated with both gas–solid and gas–liquid chromatography[6]. Hollis[4] considered the solubility of the compound in the polymer to be the most important factor in determining retention behaviour, whereas Smith and Waddington[7] reported that a linear relationship exists between the logarithm of retention time and boiling point of compounds in an homologous series. The work of Johnson and Barrall[8] shows that the surface characteristics such as pore-size distribution, pore volume and surface area are important in determining the separating power of the polymer.

In this paper we have investigated the linearity of the plot of retention time *versus* carbon number for a series of *n*-alkanes using a range of porous polymers.

EXPERIMENTAL

The equipment used consisted of a Hewlett-Packard 5750 research chromatograph interfaced to a 16K P.D.P. 11/40 digital computer. Interfacing was achieved by

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the use of an LPS 11 Laboratory Peripheral System comprising a 12-bit analog-to-digital converter, a programmable real-time clock with two Schmitt triggers and a display controller with two 12-bit digital-to-analog converters. All on-line programming was written in CAPS II Basic with LPS options. The sampling rate was 0.5 sec.

The retention times measured for the alkanes were used to calculate the dead times using the method of Grobler and Balizs[9]. This method has been proven to be simple and accurate[10]. The dead time t_m, the slope b and intercept C were then used in eqn. 1 to estimate the uncorrected retention times t_R of the alkanes and methane

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

where t_R is the uncorrected retention time of the *n*-alkane with carbon number Z.

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

Samples of Porapak (N, P, PS, Q, QS, R, S and T) polymer beads (80–100 mesh) were obtained from Waters Assoc. (Milford, MA, U.S.A.). They were packed in PTFE columns (6 ft. × 1/8 in. O.D.). A mixture of *n*-alkanes from methane to heptane in nitrogen was obtained from Commonwealth Industrial Gases (Alexandria, Australia). Higher alkanes were injected as liquids.

The column oven was operated isothermally at temperatures below the temperature limits recommended by the manufacturer.

RESULTS AND DISCUSSION

The results presented in Table I are for the injection of a mixture of C_1–C_7 *n*-alkanes in nitrogen onto the columns using a gas sampling valve. This technique was shown previously[11] to have high precision for determining the retention times of lower *n*-alkanes. The retention data for the C_5–C_9 *n*-alkanes are presented in Table II. The uncorrected retention data of the C_5–C_{12} *n*-alkanes reported by Dave[6] have been used to calculate dead times and A values presented in Table III.

It is apparent from the data in Table I that the plot of retention time *versus* carbon number is non-linear for the lower alkanes. This is evident from the values of A calculated for the C_1–C_3 and C_2–C_4 *n*-alkanes. Values of A calculated for higher alkanes are essentially constant. On all porous polymers the A value is lower for the C_1–C_3 *n*-alkanes and higher for the C_2–C_4 *n*-alkanes than the constant value observed

TABLE I

RETENTION TIME DATA FOR C_1–C_7 *n*-ALKANES

Column conditions	*Alkane*	*t(sec)*	$t_{calc.}$*(sec)*	*t'(sec)*	*A*
Porapak N	Methane	39.9	39.0	13.7	
Temperature, 100°C	Ethane	60.0	59.3	33.8	2.49
Carrier gas (helium)	*n*-Propane	110.0	111.3	83.8	2.64
Flow-rate, 52 ml/min	*n*-Butane	242.0	244.9	215.8	2.54
Dead time (t_m), 26.2 sec	*n*-Pentane	577.0	588.6	550.8	2.59
	n-Hexane	1443.8	1472.0	1417.6	2.58
	n-Heptane	3680.0	3743.3	3653.8	

(Continued on p. 158)

TABLE I *(continued)*

Column conditions	*Alkane*	*t(sec)*	$t_{calc.}$*(sec)*	*t'(sec)*	*A*
Porapak P	Methane	78.4	79.6	12.0	
Temperature, 110°C	Ethane	95.8	95.8	29.4	1.88
Carrier gas (helium)	*n*-Propane	128.5	131.7	62.1	2.46
Flow-rate, 48 ml/min	*n*-Butane	209.1	211.6	142.7	2.20
Dead time (t_m), 66.4 sec	*n*-Pentane	382.0	389.2	315.6	2.23
	n-Hexane	767.5	784.3	701.1	2.32
	n-Heptane	1660.5	1662.9	1594.1	
Porapak PS	Methane	61.5	61.8	8.2	
Temperature, 110°C	Ethane	72.5	72.2	19.2	1.95
Carrier gas (helium)	*n*-Propane	94.0	95.3	40.7	2.47
Flow-rate, 50 ml/min	*n*-Butane	147.0	146.5	93.7	2.20
Dead time (t_m), 53.3 sec	*n*-Pentane	263.8	260.0	210.5	2.19
	n-Hexane	519.5	511.6	466.2	2.19
	n-Heptane	1080.3	1070.8	1027.0	
Porapak Q	Methane	71.5	70.1	25.0	
Temperature, 220°C	Ethane	90.5	87.7	44.0	1.42
Carrier gas (helium)	*n*-Propane	117.5	118.4	71.0	1.88
Flow-rate, 48 ml/min	*n*-Butane	168.3	172.2	121.8	1.77
Dead time (t_m), 46.5 sec	*n*-Pentane	258.0	266.1	211.5	1.79
	n-Hexane	419.0	430.3	372.5	1.79
	n-Heptane	707.9	717.1	661.4	
Porapak QS	Methane	58.2	58.3	15.7	
Temperature, 230°C	Ethane	69.5	69.4	27.0	1.64
Carrier gas (helium)	*n*-Propane	88.0	88.5	45.5	1.81
Flow-rate, 44 ml/min	*n*-Butane	121.5	121.1	79.0	1.69
Dead time (t_m), 42.5 sec	*n*-Pentane	177.5	177.0	135.0	1.70
	n-Hexane	272.8	272.4	230.2	1.71
	n-Heptane	436.0	435.7	393.5	
Porapak R	Methane	44.5	43.4	12.8	
Temperature, 180°C	Ethane	55.3	53.3	23.6	1.45
Carrier gas (helium)	*n*-Propane	71.0	71.8	39.3	2.01
Flow-rate 40 ml/min	*n*-Butane	102.5	105.9	70.8	1.90
Dead time (t_m), 31.7 sec	*n*-Pentane	162.5	169.0	130.8	1.89
	n-Hexane	275.8	285.8	244.1	1.90
	n-Heptane	491.0	502.0	459.3	
Porapak S	Methane	58.5	57.7	15.4	
Temperature, 180°C	Ethane	72.3	70.7	29.2	1.59
Carrier gas (helium)	*n*-Propane	94.3	95.4	51.2	2.05
Flow-rate, 40 ml/min	*n*-Butane	139.5	142.0	96.4	1.91
Dead time (t_m), 43.1 sec	*n*-Pentane	225.8	230.3	182.7	1.90
	n-Hexane	389.8	397.1	346.7	1.91
	n-Heptane	703.3	712.7	660.2	
Porapak T	Methane	43.0	40.4	15.4	
Temperature, 120°C	Ethane	56.5	53.0	28.9	1.60
Carrier gas (helium)	*n*-Propane	76.5	77.9	48.9	2.20
Flow-rate, 38 ml/min	*n*-Butane	120.5	127.1	92.9	2.00
Dead time (t_m), 27.6 sec	*n*-Pentane	208.25	224.4	180.7	2.04
	n-Hexane	387.0	417.0	359.4	2.09
	n-Heptane	761.0	797.7	733.4	

TABLE II

RETENTION TIME DATA FOR C_5–C_9 *n*-ALKANES

Column conditions	*Alkane*	*t(sec)*	$t_{calc.}$*(sec)*	*t'(sec)*	*A*
Porapak N	*n*-Pentane	55.4	55.4	38.5	
Temperature, 180°C	*n*-Hexane	90.9	91.7	74.0	2.12
Carrier gas (helium)	*n*-Heptane	166.3	165.4	149.4	1.70
Flow-rate, 40 ml/min	*n*-Octane	294.3	298.4	277.4	2 11
Dead time (t_m), 16.9 sec	*n*-Nonane	564.1	562.8	547.2	
Porapak P	*n*-Pentane	96.3	96.4	50.0	
Temperature, 180°C	*n*-Hexane	127.5	127.8	81.2	1.67
Carrier gas (helium)	*n*-Heptane	179.4	179.0	133.1	1.61
Flow-rate, 43 ml/min	*n*-Octane	262.75	262.3	216.4	1.62
Dead time (t_m), 46.3 sec	*n*-Nonane	397.8	397.9	351.5	
Porapak PS	*n*-Pentane	39.0	39.0	18.8	
Temperature, 180°C	*n*-Hexane	49.9	50.1	29.7	1.69
Carrier gas (helium)	*n*-Heptane	68.25	67.7	48.0	1.50
Flow-rate, 34 ml/min	*n*-Octane	95.75	95.7	75.5	1.61
Dead time (t_m), 13.7 sec	*n*-Nonane	140.25	140.2	120.0	
Porapak Q	*n*-Pentane	52.5	52.4	37.5	
Temperature, 230°C	*n*-Hexane	80.25	79.9	65.2	1.73
Carrier gas (helium)	*n*-Heptane	128.2	127.7	113.2	1.66
Flow-rate, 38 ml/min	*n*-Octane	297.9	210.8	192.9	1.85
Dead time (t_m), 15.0 sec	*n*-Nonane	355.6	355.2	340.6	
Porapak QS	*n*-Pentane	38.6	38.8	27.6	
Temperature, 240°C	*n*-Hexane	58.0	57.6	46.8	1.65
Carrier gas (helium)	*n*-Heptane	89.2	89.7	78.0	1.64
Flow-rate, 40 ml/min	*n*-Octane	140.7	142.1	129.5	1.79
Dead time (t_m), 11.2 sec	*n*-Nonane	232.8	232.5	221.3	
Porapak R	*n*-Pentane	53.1	53.3	43.7	
Temperature, 200°C	*n*-Hexane	87.1	87.6	77.7	1.84
Carrier gas (helium)	*n*-Heptane	149.6	148.8	140.2	1.78
Flow-rate, 43 ml/min					
Dead time (t_m), 9.4 sec	*n*-Nonane	452.6	452.4	443.2	
Porapak S	*n*-Pentane	99.3	99.5	79.8	
Temperature, 230°C	*n*-Hexane	164.8	165.2	145.3	1.84
Carrier gas (helium)	*n*-Heptane	285.5	285.1	265.9	1.82
Flow-rate, 39 ml/min	*n*-Octane	504.8	503.6	485.3	1.81
Dead time (t_m), 19.6 sec	*n*-Nonane	902.0	901.9	882.4	
Porapak T	*n*-Pentane	21.6	21.6	12.6	
Temperature, 190°C	*n*-Hexane	29.2	29.0	20.2	1.56
Carrier gas (helium)	*n*-Heptane	40.9	40.8	31.9	1.55
Flow-rate, 48 ml/min	*n*-Octane	59.1	59.7	50.1	1.69
Dead time (t_m), 9.0 sec	*n*-Nonane	89.9	89.7	80.9	

for the series of *n*-alkanes of carbon number 4 and greater. These results indicate that the retention times for methane and ethane are different from the values for *n*-alkanes having carbon numbers of one and two respectively. This suggests that there is curvature in the plot of corrected retention time *versus* carbon number for *n*-alkanes.

The results in Tables II and III indicate no apparent curvature in the plots of retention time *versus* carbon number for *n*-alkanes of carbon number from C_5 to C_{12}.

TABLE III

RETENTION TIME DATA FOR C_5–C_{12} *n*-ALKANES

Column conditions	*Alkane*	*t(sec)*	$t_{calc.}$*(sec)*	*t'(sec)*	*A*
Porapak N	*n*-Pentane	142.2	142.3	140.1	
Temperature, 175°C	*n*-Hexane	303.6	303.9	301.5	2.16
Carrier gas (helium)	*n*-Heptane	652.8	651.7	650.7	2.14
Flow-rate, 58 ml/min	*n*-Octane	1400.4	1400.2	1398.3	
Dead time (t_m), 2.1 sec					
Porapak P	*n*-Pentane	37.2	37.1	20.1	
Temperature, 200°C	*n*-Hexane	49.2	48.9	32.1	1.50
Carrier gas (helium)	*n*-Heptane	67.2	67.6	50.1	1.67
Flow-rate, 58 ml/min	*n*-Octane	97.2	97.2	80.1	1.56
Dead time (t_m), 17.1 sec	*n*-Nonane	144.0	144.4	126.9	1.59
	n-Decane	218.4	219.2	201.3	1.61
	n-Undecane	338.4	338.1	321.3	1.57
	n-Dodecane	526.2	527.0	509.1	
Porapak Q	*n*-Pentane	67.2	67.2	57.3	
Temperature, 200°C	*n*-Hexane	112.8	112.6	102.9	1.78
Carrier gas (helium)	*n*-Heptane	193.8	194.2	183.9	1.82
Flow-rate, 58 ml/min	*n*-Octane	340.8	340.5	330.9	1.78
Dead time (t_m), 9.9 sec	*n*-Nonane	602.4	603.1	592.5	1.80
	n-Decane	1974.0	1074.1	1064.1	
Porapak QS	*n*-Pentane	100.8	100.8	90.0	
Temperature, 200°C	*n*-Hexane	185.4	186.7	174.6	2.05
Carrier gas (helium)	*n*-Heptane	358.8	354.3	348.0	1.85
Flow-rate, 58 ml/min	*n*-Octane	679.2	681.7	668.4	2.00
Dead time (t_m), 10.8 sec	*n*-Nonane	1318.8	1321.3	1308.0	1.96
	n-Decane	2571.0	2570.4	2560.2	
Porapak R	*n*-Pentane	79.8	78.7	66.5	
Temperature, 200°C	*n*-Hexane	144.0	142.4	130.7	1.93
Carrier gas (helium)	*n*-Heptane	267.6	268.0	254.3	1.91
Flow-rate, 58 ml/min	*n*-Octane	503.4	575.7	490.1	2.12
Dead time (t_m), 13.3 sec	*n*-Nonane	1002.0	1004.5	988.7	
Porapak S	*n*-Pentane	55.2	55.4	44.6	
Temperature, 225°C	*n*-Hexane	90.0	89.3	77.4	1.74
Carrier gas (helium)	*n*-Heptane	147.0	150.2	134.4	2.03
Flow-rate, 58 ml/min	*n*-Octane	262.8	259.4	250.2	1.68
Dead time (t_m), 12.6 sec	*n*-Nonane	457.2	455.1	444.6	1.80
	n-Decane	806.4	806.0	793.8	
Porapak T	*n*-Pentane	76.8	77.1	67.7	
Temperature, 200°C	*n*-Hexane	139.9	139.9	130.1	1.96
Carrier gas (helium)	*n*-Heptane	261.6	260.6	252.5	1.90
Flow-rate, 58 ml/min	*n*-Octane	494.4	492.8	485.3	1.92
Dead time (t_m), 9.1 sec	*n*-Nonane	940.8	939.2	931.7	1.93
	n-Decane	1800.0	1797.6	1790.9	

Any variations in the values of *A* for the higher alkanes on a given column appear to be random and not related to carbon number. Therefore the lack of constancy of the values of *A* may be attributed to experimental error.

In this comprehensive study of the retention behaviour of *n*-alkanes on porous polymer packings we have shown the same lack of linearity of the plot of retention

time *versus* carbon number that we observed for the retention of *n*-alkanes on stationary phases of varying polarity[1]. This suggests that the use of methane retention as a method of estimating dead times for columns packed with porous polymers will lead to the same type of errors as those encountered in gas–liquid chromatography[11,12]. We therefore suggest the use of four *n*-alkanes of carbon number C_4 and above (when suitably separated) to determine dead times of columns employing both supported liquid phase and porous polymer packings.

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REFERENCES

1 M. S. Wainwright, J. K. Haken and D. Srisukh, *J. Chromatogr.*, 188 (1980) 246.
2 J. Ševčík, *J. Chromatogr.*, 135 (1977) 183.
3 J. Ševčík, *J. Chromatogr.*, 147 (1978) 75.
4 O. L. Hollis, in A. Zlatkis and L. S. Ettre (Editors), *Advances in Gas Chromatography 1965*, Preston, Niles, IL, 1966, p. 56.
5 O. L. Hollis and W. V. Hayes, *J. Gas Chromatogr.*, 4 (1966) 235.
6 S. B. Dave, *J. Chromatogr. Sci.*, 7 (1969) 389.
7 J. R. Lindsay Smith and D. J. Waddington, *J. Chromatogr.*, 36 (1968) 145.
8 J. F. Johnson and E. M. Barrall, II, *J. Chromatogr.*, 31 (1967) 547.
9 A. Grobler and G. Balizs, *J. Chromatogr. Sci.*, 12 (1974) 57.
10 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 147 (1978) 65.
11 M. S. Wainwright, J. K. Haken and D. Srisukh, *J. Chromatogr.*, 179 (1979) 160.
12 M. S. Wainwright and J. K. Haken, *J. Chromatogr.*, 184 (1980) 1.