

CHROM. 17,010

## CALCULATION OF THE PEAK CAPACITY IN CAPILLARY GAS CHROMATOGRAPHY\*

J. KRUPČÍK\* and J. GARAJ

*Slovak Technical University, Chemical Faculty, Department of Analytical Chemistry, Janska 1, 812 37 Bratislava (Czechoslovakia)*

P. ČELLÁR

*Slovnaft n.p., AV-VVZ, 824 12 Bratislava (Czechoslovakia)*  
and

G. GUIOCHON

*École Polytechnique, Laboratoire de Chimie Analytique Physique, 91120 Palaiseau (France)*

(Received June 29th, 1984)

---

### SUMMARY

The peak capacity of open-tubular columns was calculated using the Golay equation to relate the plate number to the column capacity factor. A general relationship was obtained that permits the prediction of the peak capacity between any pair of peaks. A comparison with experimental data showed that the results of this calculation are much more accurate than those obtained from conventional relationships. In agreement with the experimental results, the equation used provided larger values of the peak capacity of capillary columns at low  $k'$  values. This is explained by the very rapid increase in the plate height with increasing capacity factors at low  $k'$ . Accordingly, the peak capacity is large in this range, a fact the conventional relationships cannot take into account. The plate number varies significantly from one chemical group to another group, which could provide for qualitative analysis.

---

### INTRODUCTION

The separation power of a chromatographic column is best characterized by the extent of spreading of solute zones during their migration through the column. A column that elutes narrower zones permits the achievement of better separations. Accordingly, the most useful criteria in practice are those based on the number of compounds separated under given conditions.

The peak capacity ( $PC$ ) over a certain retention range is one such promising criteria as it gives the number of peaks separable with a resolution of unity between two given compounds<sup>1</sup>. Although most often used to determine the number of peaks

---

\* Paper presented at the *IVth Danube Symposium on Chromatography, August 28th-September 2nd, 1983, Bratislava, Czechoslovakia*. Dedicated to Dr. J. Janák on his 60th birthday.

separated between the gas hold-up time ( $t_m$ ) and a given retention time ( $t_R$ ), the peak capacity can also give the number of peaks separable between two compounds with retention times  $t_{R,1}$  and  $t_{R,2}$ . Most of the properties of the peak capacity have been studied in detail by Grushka<sup>1</sup>. It has been shown that it can be calculated using the following equation:

$$PC = 1 + \int_{t_m}^{t_R} \frac{\sqrt{n}}{4t} \cdot dt \quad (1)$$

where  $n$  is the number of theoretical plates of the column for a compound with retention time  $t$ . For packed columns,  $n$  usually varies slowly if at all with increasing retention and eqn. 1 can be easily integrated to

$$PC = 1 + \frac{\sqrt{\bar{n}}}{4} \cdot \log \left( \frac{t_R}{t_m} \right) \quad (2)$$

where  $\bar{n}$  is an average number of theoretical plates, which takes into account the slow variation of  $n$  with the capacity factor,  $k'$ , when the plate number is not constant<sup>2,3</sup>. Similarly, the peak capacity between two components with retention times  $t_{R,1}$  and  $t_{R,2}$  is given by

$$PC = 1 + \frac{\sqrt{\bar{n}}}{4} \cdot \log \left( \frac{t_{R,2}}{t_{R,1}} \right) \quad (2a)$$

For a capillary column, however, the variation of plate number with increasing retention is too important, especially in the early range, and it is not possible to derive simply the proper average plate number, so this approach had to be abandoned.

In this paper we consider the possibility of the direct integration of eqn. 1 for capillary columns and compare the results with those derived from experimental data.

## THEORETICAL

Combination of eqn. 1 with the basic equation for retention time:

$$t_R = t_m (1 + k') \quad (3)$$

where  $k'$  is the column capacity factor, gives

$$PC = 1 + \frac{1}{4} \int_0^{k'} \frac{n^{\frac{1}{2}}}{1 + k'} \cdot dk' \quad (4)$$

In this equation  $n$  is a function of  $k'$ , which can be made explicit using the Golay equation<sup>4</sup>, which relates the height equivalent to a theoretical plate,  $h$ , to the column characteristics, the gas velocity,  $u$ , and  $k'$ :

$$h = \frac{2D_m}{u} + \frac{1 + 6k' + 11k'^2}{24(1 + k')^2} \cdot \frac{r^2}{D_m} \quad (5)$$

where  $D_m$  is the diffusion coefficient of the solute vapour in the gas phase and  $r$  is the column radius. We may assume in practice that the resistance to mass transfer in the stationary phase is negligible. There is an optimum velocity at which the two contributions in the right-hand side of eqn. 5 are equal, but analyses are usually carried out at a velocity larger than this optimum. The plate number is related to the plate height by

$$n = \frac{L}{h} \quad (6)$$

where  $L$  is the column length. Combination of eqns. 4–6 gives a complex function of  $k'$ . Further,  $D_m$  (in eqn. 5) is also related to  $k'$ , as it decreases with increasing molecular weight of the solute, while heavier compounds tend to have larger  $k'$ . An approximate, adjustable relationship between  $n$  and  $k'$  that takes into account the correlation between  $D_m$  and  $k'$  is necessary.

Eqns. 5 and 6 show that the plate height increases from a minimum value achieved for  $k' = 0$ :

$$h = \frac{2D_m}{u} + \frac{r^2}{24 D_m} \cdot u \quad (7)$$

to a maximum value, reached for infinite  $k'$ :

$$h = \frac{2D_m}{u} + \frac{11 r^2}{24 D_m} \cdot u \quad (8)$$

It is thus possible to relate  $n$  to  $k'$  by a series expansion of the powers of  $1/k'$  (ref. 5). The coefficients of this series depend on the flow velocity and take into account the variation of  $D_m$  with  $k'$ :

$$n = N_\infty + \frac{b}{k'} + \frac{c}{k'^2} + \dots \quad (9)$$

In many instances, the first two terms of the expansion are sufficient<sup>5</sup>. Combination of eqns. 4 and 9 now gives

$$PC = 1 + \frac{1}{4} \int_0^{k'} \frac{(N_\infty + b/k' + c/k'^2 + \dots)^{\frac{1}{2}}}{1 + k'} \cdot dk' \quad (10)$$

In the general case, eqn. 10 cannot be integrated. In most instances, however, this equation can be simplified by limiting the expansion to the first two terms and writing the integrand as

$$\frac{(N_\infty k'^2 + bk')^{\frac{1}{2}}}{k' (1 + k')} \quad (11)$$

decomposing it into the difference between two fractions with  $k'$  and  $1 + k'$  in their denominators, and using conventional integral equations<sup>9</sup>. The result is extremely complicated, however, involving the logarithm of a complex expression of  $k'$  and two arcsines. Accordingly, it has been found easier to calculate the numerical integrals when necessary. In such a case it is not much more difficult to use a longer expansion, which proves to be much more precise.

## EXPERIMENTAL

A Fractovap 2350 gas chromatograph (Carlo Erba, Milan, Italy), equipped with a flame-ionization detector and an all-glass inlet splitter was used. The velocity of the nitrogen used as the carrier gas was between 6.7 and 9.3 cm/sec in all the experiments. This is slightly above the optimum velocity or close to it. Glass capillary columns were made of soft glass, the inner wall being etched prior to phase coating, using gaseous HCl, following a procedure described elsewhere<sup>4</sup>. The columns were coated dynamically using 0.3 ml of a squalane solution (3 g in 10 ml of pentane) followed by a 3–5 cm mercury plug, at a velocity of 2 cm/sec. The main characteristics of the three glass capillary columns used are given in Table I. Single columns were coupled in series using shrinkable PTFE tubings. Retention times were measured either using a stop-watch or from the distances of the peaks on chromatogram and the chart speed of the recorder. Peak widths were measured on the chromatograms using a calibrated magnifying glass with a resolution of  $\pm 0.1$  mm. Two model mixtures of hydrocarbons were analysed. The peaks on the chromatograms were identified by running single standards. The compositions of the two mixtures used are given in Tables II and III and typical analysis of these mixtures are shown in Figs. 1 and 2. Sample volumes of  $0.1 \mu\text{l}$  were injected, with a splitting ratio of 1:200.

TABLE I  
BASIC CHARACTERISTICS OF SINGLE COLUMNS

Column	Length (m)	I.D. (mm)	$L/d_c$
L-4	103	0.30	$3.4 \cdot 10^5$
L-5	90	0.25	$3.6 \cdot 10^5$
L-6	101	0.30	$3.4 \cdot 10^5$

## RESULTS AND DISCUSSION

As shown in Fig. 3, the dependence of the plate number on the capacity ratio is important. This is in agreement with the prediction of the Golay eqn.<sup>4</sup> and with the experimental results. This precludes the use of eqn. 2 to calculate the peak capacity, but requires the use of a relationship between  $n$  and  $k'$  for the integration of eqn. 4.

TABLE II  
CHARACTERIZATION OF PEAKS IN MODEL MIXTURE NO. 1

Peak No.	Compound	$k'$ (58°C), L-5 + L-6	Peak No.	Compound	$k'$ (58°C) L-5 + L-
1	<i>n</i> -Pentane	0.25	22	Methylcyclohexane	1.97
2	2,2-Dimethylbutane	0.34	23	2,5-Dimethylhexane	2.00
3	1,2,3-Trimethylcyclopropane	0.38	24	2,4-Dimethylhexane	2.08
4	Cyclopentane	0.45	25	Ethylcyclopentane	2.12
5	2,3-Dimethylbutane	0.46	26	3,3-Dimethylhexane	2.32
6	2-Methylpentane	0.47	27	Toluene	2.34
7	3-Methylpentane	0.54	28	2,3-Dimethylhexane	2.70
8	<i>n</i> -Hexane	0.61	29	2,3,3-Trimethylpentane	2.70
9	2,2-Dimethylpentane	0.77	30	3,4-Dimethylhexane	2.97
10	2,4-Dimethylpentane	0.79	31	<i>cis</i> -1,3-Dimethylcyclohexane	3.43
11	Methylcyclopentane	0.80	31a	<i>trans</i> -1,4-Dimethylcyclohexane	3.45
12	Benzene	0.85	32	<i>trans</i> -1-Methyl-3-ethylcyclopentane	3.64
13	3,3-Dimethylpentane	1.03	33	<i>n</i> -Octane	3.92
14	2,-Methylhexane	1.11	34	<i>trans</i> -1,2-Dimethylcyclohexane	4.02
15	2,3-Dimethylpentane	1.17	35	<i>trans</i> -1,3-Dimethylcyclohexane	4.17
16	1,1-Dimethylcyclopentane	1.19	36	<i>cis</i> -1,2-Dimethylcyclohexane	5.13
17	<i>cis</i> -1,3-Dimethylcyclopentane	1.30	37	Ethylbenzene	5.35
18	3-Ethylpentane	1.34	38	1,4-Dimethylbenzene	6.15
19	<i>trans</i> -1,2-Dimethylcyclopentane	1.38	39	1,3-Dimethylbenzene	6.29
20	<i>n</i> -Heptane	1.52	40	1,2-Dimethylbenzene	7.55
21	2,2-Dimethylhexane	1.84			

TABLE III  
CHARACTERIZATION OF PEAKS IN MODEL MIXTURE NO. 2

Peak No.	Compound	$k'$ (69°C), L-5 + L-6	Peak No.	Compound	$k'$ (69°C), L-5 + L-6
1	2,3,4-Trimethylpentane	2.14	17	2,6-Dimethyloctane	9.63
2	2,3,5-Trimethylhexane	2.58	18	3,3-Dimethyloctane	9.76
3	<i>n</i> -Octane	3.11	19	3,4-Diethylhexane	9.83
4	2,3,5-Trimethylhexane	3.48	20	3-Ethyl-2-methylheptane	10.01
5	2,4-Dimethylheptane	3.71	21	1,3,5-Trimethylbenzene	12.22
6	4,4-Dimethylheptane	3.97	22	1,2,4-Trimethylbenzene	14.00
7	3,5-Dimethylheptane ( $\alpha,\beta$ )	4.14	23	<i>tert.</i> -Butylbenzene	15.18
8	3,3-Dimethylheptane	4.27	24	1,2,4-Trimethylbenzene	17.06
9	2,3-Dimethylheptane	4.97	25	<i>n</i> -Decane	17.17
10	3,4-Dimethylheptane ( $\alpha$ )	5.12	26	<i>sec.</i> -Butylcyclohexane	19.93
11	3,4-Dimethylheptane ( $\beta$ )	5.14	27	1,3-Diethylbenzene	20.25
12	3,3-Diethylpentane	6.22	28	<i>n</i> -Butylbenzene	20.80
13	Isopropylbenzene	7.13	29	<i>n</i> -Butylcyclohexane	21.31
14	<i>n</i> -Nonane	7.31	30	1,4-Diethylbenzene	21.39
15	4,4-Dimethyloctane	8.68	31	1,2-Diethylbenzene	21.58
16	<i>n</i> -Propylbenzene	9.13			

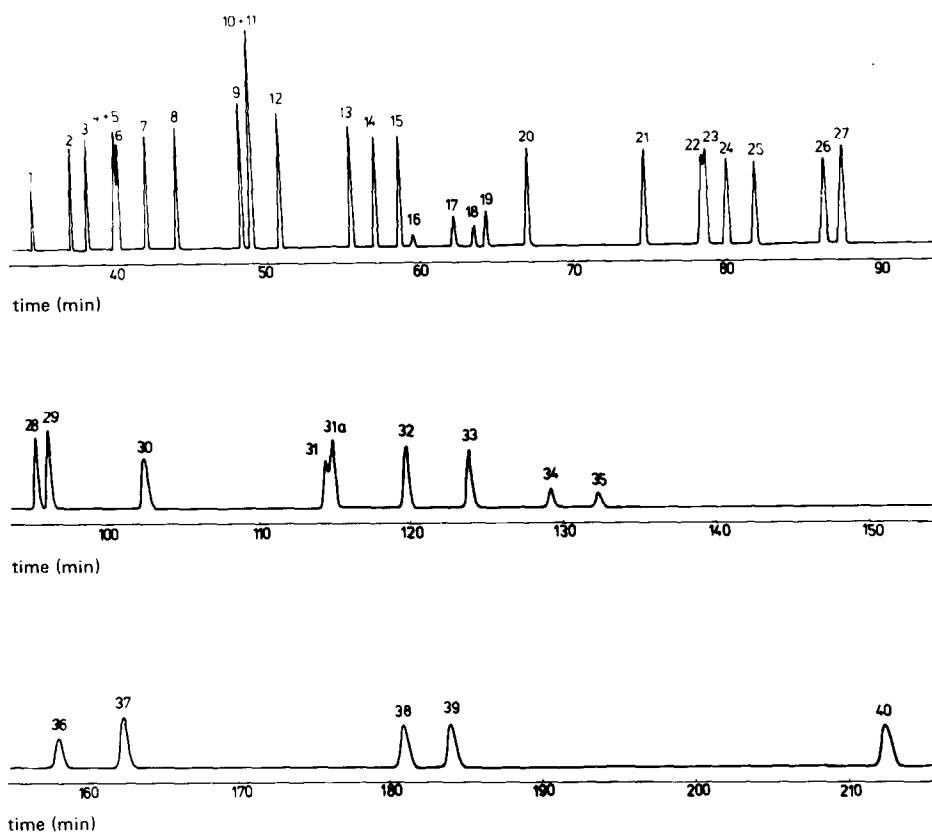


Fig. 1. Separation of hydrocarbon mixture No. 1 on column L-5 + L-6 at 58°C (for peak identification see Table II).

#### *Relationship between plate number and capacity factor*

The correlation of eqn. 9 was studied using the data collected as explained above. The fits of  $n$  versus  $1/k'$  were analyzed, and the results are reported in Table IV for a two-term expansion and in Table V for three- and four-term expansions.

The correlation coefficients, also given in these tables, show that the correlation offered by a two-term expansion is only fair at best. This is essentially because all data have been used, including those for which  $k'$  is markedly below unity, and for which it can be expected that important deviations occur, as  $n$  does not tend towards infinity when  $k'$  tends towards zero. Attempts to eliminate outlying points using conventional statistical methods<sup>7</sup> failed, as the deviation from a linear relationship was not random, but systematic, as expected, and as explained above. This is further illustrated by the fact that much better correlation coefficients are obtained with longer expansions (*cf.*, Table V).

If only the points corresponding to values of  $k'$  larger than unity are included, on the other hand, and if the data corresponding to the three groups of compounds present in our test mixtures, namely normal alkanes, branched alkanes and aromatic hydrocarbons, are treated separately, excellent values of the correlation coefficients

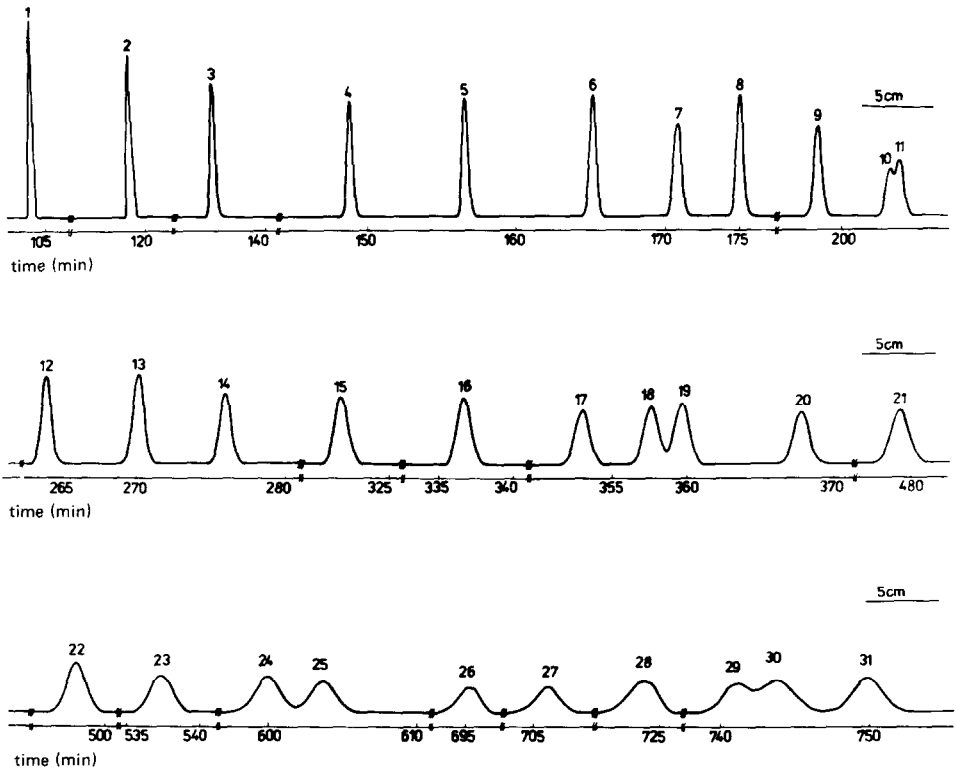


Fig. 2. Separation of the hydrocarbon mixture No. 2 on column L-5 + L-6 at 58°C (for peak identification see Table III).

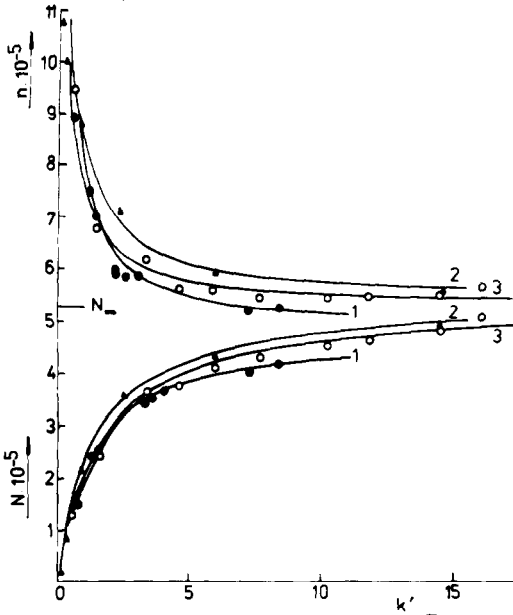


Fig. 3. Dependence of the theoretical ( $n$ ) and effective ( $N$ ) plate numbers on the capacity ratio ( $k'$ ) found for branched alkanes (1), normal alkanes (2) and aromatics (3). Open-tubular column L-5 + L-6 at 58°C.

TABLE IV  
COEFFICIENTS OF EQN. 9 OBTAINED FROM THE ANALYSIS OF HYDROCARBONS

Column	$T$ ( $^{\circ}\text{C}$ )	$N_{\infty}$	$b$	$r_{xy}^*$
L-4	58	279,000	91,000	0.880
L-5	58	258,000	288,000	0.890
L-4	70	275,000	165,000	0.930
L-5	70	300,000	133,000	0.940

\*  $r_{xy}$  is a correlation coefficient

TABLE V  
COEFFICIENTS OF EQN. 9 OBTAINED FOR DIFFERENT EXPANSIONS

Conditions: columns L-5 + L-6 at  $70^{\circ}\text{C}$ , hydrocarbons listed in Tables I and II.

Equation	$N_{\infty}$	$b$	$c$	$d$	$r_{xy}^*$
$n = N_{\infty} + b/k'$	$6.72 \cdot 10^5$	$7.75 \cdot 10^4$	—	—	0.845
$n = N_{\infty} + b/k' + c/k'^2$	$5.78 \cdot 10^5$	$2.63 \cdot 10^5$	$-2.93 \cdot 10^4$	—	0.975
$n = N_{\infty} + b/k' + c/k'^2 + d/k'^3$	$5.18 \cdot 10^5$	$5.36 \cdot 10^5$	$-1.79 \cdot 10^5$	$1.73 \cdot 10^4$	0.999

\*  $r_{xy}$  is a correlation coefficient.

TABLE VI  
COEFFICIENTS OF EQN. 9 FOUND FOR A TWO-TERM EXPANSION USING COMPOUNDS WITH  $k' > 1$

Compounds	Column	$T$ ( $^{\circ}\text{C}$ )	$N_{\infty}$	$b$	$r_{xy}^*$
C <sub>7</sub> -C <sub>10</sub> <i>n</i> -alkanes	L-4	58	287,000	112,000	0.99
	L-5	70	330,000	40,000	0.99
	L-6	70	352,000	55,000	0.98
	L-5 + L-6	70	545,000	340,000	0.99
Branched alkanes (9)	L-4	58	279,000	87,000	0.99
	L-6	70	344,000	62,000	0.98
	L-5 + L-6	70	481,000	352,000	0.99
Aromatics (12)	L-4	58	282,000	99,000	0.99
	L-5	58	262,000	227,000	0.97
	L-6	58	341,000	98,000	0.97
	L-5 + L-6	58	497,000	233,000	0.99

\*  $r_{xy}$  is a correlation coefficient.

TABLE VII  
COEFFICIENTS OF EQN. 9 OBTAINED FOR BRANCHED ALKANES ELUTED WITH  $k' > 1$  ON DIFFERENT COLUMNS (9 POINTS) USING THE METHOD OF LEAST SQUARES

Column	$T$ ( $^{\circ}\text{C}$ )	$N_{\infty}$	$b$	$r_{xy}^*$
L-4	58	279,000	87,000	0.99
L-6	70	344,000	62,000	0.98
L-5 + L-6	70	481,000	352,000	0.99

\*  $r_{xy}$  is a correlation coefficient.



are obtained (Tables VI and VII). This is also illustrated by the significant difference between the three curves in Fig. 3. Accordingly, the columns will have slightly but significantly different peak capacities, depending upon which class of compounds is considered.

It is remarkable under such conditions that, on the other hand, the limiting efficiency is independent of the temperature, in excellent agreement with the prediction of the Golay equation: eqn. 5 predicts that around the optimum flow velocity, the limiting plate height will be

$$h = 2 \sqrt{\frac{22}{24}} \cdot r = 1.91 r \quad (12)$$

This value, practically equal to the column diameter, is independent of temperature. This result has not been investigated further, but a comparison of the data given in Tables I and VIII shows that columns L5 and L5 + L6 give a limiting plate number,  $N$ , about 25% lower than predicted by eqn. 12, and column L6 about the right number.

TABLE VIII  
LIMITING NUMBER OF EFFECTIVE PLATES FOR AROMATIC HYDROCARBONS

Column	$T$ ( $^{\circ}C$ )	$N_{\infty} \pm st_{\alpha}^*$	$\bar{u}$ (cm/sec)
L-5	58	262,000 $\pm$ 16,000	8.00
L-5	70	291,000 $\pm$ 13,000	7.83
L-6	58	341,000 $\pm$ 8,000	7.28
L-6	70	343,000 $\pm$ 13,000	7.83
L-5 + L-6	58	497,000 $\pm$ 19,000	8.55
L-5 + L-6	70	531,000 $\pm$ 18,000	8.20

\*  $s$  = Standard deviation of  $N_{\infty}$ ;  $t_{\alpha}$  = Student's coefficient ( $t$  = distribution; significance level  $\alpha$  = 0.01).

#### Peak capacity

Eqn. 10 was integrated using either a two- or a four-term expansion, as well as the corresponding coefficients given in Table V. The results are reported in Table IX. They can be compared with those obtained by two classical approximations. The first approximation is the direct use of eqn. 2, assuming constancy of the plate number over the range of retention studied. The second approximation is the use of the separation number (Trennzahl,  $TZ$ )<sup>8</sup>. The separation number is the ratio of the difference in the retention times of the two compounds considered, usually successive normal alkanes, to the sum of their peak widths at half-height, this ratio being further decreased by one unit. As shown previously<sup>9</sup>, the separation number found between two consecutive normal alkanes is related to the peak capacity by the following equation:

$$PC = 1.18 (TZ + 1) \quad (13)$$

TABLE IX

COMPARISON BETWEEN VALUES OF THE PEAK CAPACITY CALCULATED FROM EQNS. 2, 10 AND 13 BETWEEN NORMAL ALKANES FOR COLUMN L-5 + L-6

Normal alkanes*	Calculated PC			
	Eqn. 2	Eqn. 10 (2 terms)	Eqn. 10 (4 terms)	Eqn. 13
C <sub>5</sub> -C <sub>6</sub> (0.22-0.58)	49.1	90.2	93.2	47.7
C <sub>6</sub> -C <sub>7</sub> (0.58-1.46)	86.4	97.2	99.1	83.7
C <sub>7</sub> -C <sub>8</sub> (1.46-3.81)	128.4	128.6	127.7	126.1
C <sub>8</sub> -C <sub>9</sub> (3.81-10.30)	142.8	140.4	142.2	137.9
C <sub>9</sub> -C <sub>10</sub> (10.30-25.41)	148.8	150.3	149.2	143.1

\* Values in parentheses are the  $k'$  values at 580°C for the  $n$ -alkanes. The differences from the values in Table II are due to phase bleeding between the series of measurements.

Comparison of the four series of data in Table IX shows marked differences at small retentions, becoming smaller and smaller as the retention increases. For example, between pentane and hexane the actual peak capacity is about twice as large as predicted by the equations that take the plate number as the average between those of the two compounds considered, or use the separation number, which is practically equivalent. This, of course, is related to the value of  $k'$  for pentane (0.5). The difference becomes negligible for compounds eluted after  $n$ -heptane.

## CONCLUSION

There are two main conclusions. First, the use of conventional equations, such as eqn. 2, or the separation number does not provide a correct estimate of column performance when applied to capillary columns and data taken at values of  $k'$  below about 2. Second, in many instances the plate number of a column changes measurably from one family of compounds to another, as shown in Fig. 3. Although this result has been known for a long time it has not previously been investigated in detail.

## REFERENCES

- 1 E. Grushka, *Anal. Chem.*, 42 (1970) 1142.
- 2 H. Colin and G. Guiochon, *J. Chromatogr. Sci.*, 18 (1980) 54.
- 3 A. S. Said, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 637.
- 4 M. J. E. Golay, in D. H. Desty (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958.
- 5 J. Krupčík, M. Kristín, M. Valachovičová and Š. Janiga, *J. Chromatogr.*, 126 (1976) 147.
- 6 R. C. Weast (Editor), *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., Cleveland, OH, 1980.
- 7 P. Moritz, in G. Svehla (Editor), *Wilson and Wilson's Comprehensive Analytical Chemistry*, Elsevier, Amsterdam, 1981, p. 31.
- 8 R. E. Kaiser, *Z. Anal. Chem.*, 189 (1962) 1.
- 9 J. Krupčík, J. Garaj, G. Guiochon and J. M. Schmitter, *Chromatographia*, 14 (1981) 501.