

CHROM. 12,750

## GAS CHROMATOGRAPHIC RETENTION CHARACTERISTICS OF DIFFERENT COATING THICKNESSES ON A GLASS CAPILLARY COLUMN

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(First received August 6th, 1979; revised manuscript received February 7th, 1980)

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### SUMMARY

The influences of coating thickness on Kováts' index was investigated. Five different thicknesses of Carbowax 20M were applied to glass capillary columns (50 m × 0.28 mm i.d.; coating film thickness, 0.041–0.45 μm) by the static coating method. The Kováts indices of alcohols (C<sub>5</sub>–C<sub>9</sub>), aldehydes (C<sub>7</sub>–C<sub>10</sub>) and ethyl esters (C<sub>6</sub>–C<sub>9</sub>) were measured on the five columns at 80°C and at 120°C. More variation in Kováts' index was observed for columns having thinner coating films measured at the lower temperature. Hydrocarbons were less influenced by differences in coating thickness than were alcohols, aldehydes and ethyl esters. The partition ratio of the tested solutes increased in proportion to the coating thickness.

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### INTRODUCTION

One of the major problems which the analytical chemist faces is the reproducibility of gas chromatographic (GC) retentions. In 1958, Kováts<sup>1</sup> introduced the retention index system, which describes the retention behaviour of a compound as equivalent to that of a hypothetical *n*-paraffin hydrocarbon, in order to minimize errors in reporting retention data obtained under different conditions (columns, instruments, temperatures, samples sizes, etc.). Many investigators have subsequently advanced other GC retention index systems<sup>2–6</sup>. The Kováts index is, however, the most widely accepted system.

Nevertheless, retention data from different sources still exhibit variations owing to sample size effects, variations in polymeric distributions in the stationary phases and temperature-related effects<sup>4</sup>. Van Lenten *et al.*<sup>7</sup> pointed out seven factors which promote variation in the retention index: the variability of the composition of the stationary phase with column age<sup>3</sup>, differences in supports<sup>8,9</sup>, sample size effects<sup>7</sup>, accuracy of the measurement of column temperature<sup>10,11</sup>, differences in flow-rates<sup>12</sup> and accurate timing during data acquisition<sup>13</sup>.

These variations have been characterized by many workers<sup>3,4,7,9-12,14</sup>, but there are, however, few reports concerning the variation in retention indices caused by variation in the coating thickness of liquid phases. Mathiasson *et al.*<sup>22</sup> studied variation in retention indices using *n*-octadecane and 3,3'-oxydipropionitrile as stationary phases on Supasorb as the support. They reported that a variation of 5-10 retention index units was observed for the samples tested (acetonitrile, toluene, ethyl methyl ketone, ethanol, benzene, trifluorobenzene, di-*n*-butyl ether, 1-chlorobutane) when the liquid phase loading was varied between 10 and 25% (w/w). Fritz *et al.*<sup>16</sup> studied various liquid phase loadings and concluded that retention indices of *n*-alkanes are strongly influenced by the column loading. These data were obtained using packed columns. The present study reports the variation of Kováts' index with different coating thicknesses on a glass capillary column.

#### EXPERIMENTAL

The capillary columns were prepared from Pyrex glass (Iwaki Code 7740) purchased from Iwaki Glass Co. (Tokyo, Japan). After cleaning with several solvents, the tubing was drawn into 50-m lengths (0.28 mm I.D.; coil diameter, 13 cm) by a Shimadzu Glass Drawing Machine, Model GDM-1. Prior to coating, the surface of all columns was deactivated by the method reported by Blomberg and Wännman<sup>15</sup>. The columns were coated by the static method described by Jennings *et al.*<sup>17</sup>, then filled with Carbowax 20M solutions (1, 2, 4, 8, 12 mg/ml in CH<sub>2</sub>Cl<sub>2</sub>) and one end was flame-sealed. They were then introduced into the coiled tube-form reactor (250°C) from the other, open end. After passage through the reactor, the columns were driven into the oven (170-180°C) attached to the reactor, over a 2-h period. All columns possessed over 100,000 theoretical plates at  $k = 3$  (Table I).

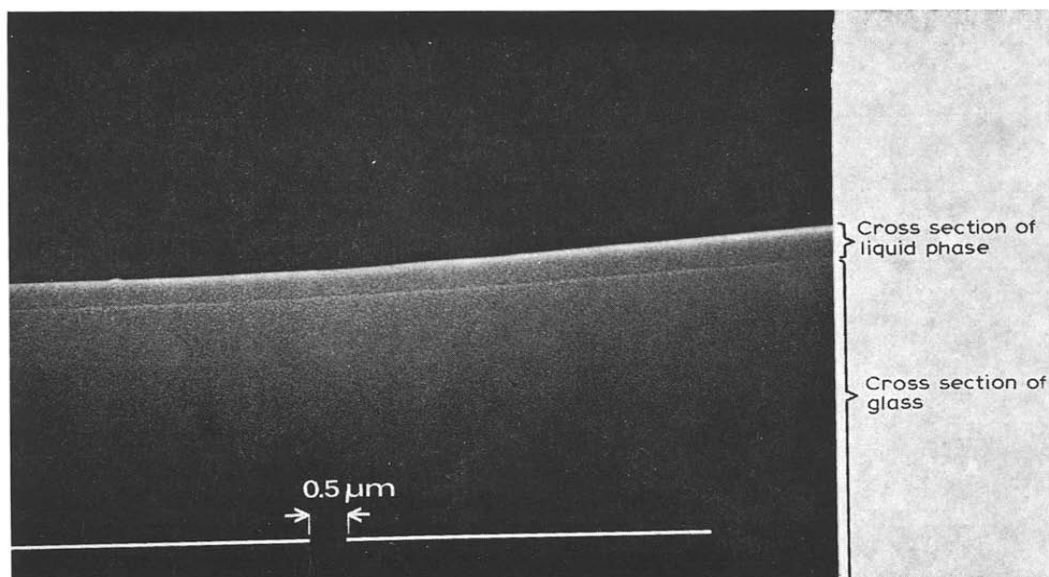


Fig. 1. Electron microscopic photograph of the cross section of a column.

A Hewlett-Packard Model 5710A gas chromatograph equipped with a flame ionization detector was used. Two isothermal oven temperatures were applied (80°C and 120°C). The nitrogen carrier gas flow-rate was 13 cm/sec (ca. 0.68 ml/min); injector and detector temperatures were 250°C, and the injector splitting ratio was 1:100. Fig. 1 shows a photograph ( $\times 10,000$ ) of the coated surface of a glass capillary column (12 mg/ml Carbowax 20M in  $\text{CH}_2\text{Cl}_2$ ) taken by a scanning electron microscope (Hitachi Model MSM-101). The coating thicknesses and number of theoretical plates of the columns used are listed in Table I.

TABLE I  
CHARACTERISTICS OF COLUMNS USED FOR THE EXPERIMENTS

Column No.	Concentration of liquid phase (mg/ml in $\text{CH}_2\text{Cl}_2$ )	$d_f$ ( $\mu\text{m}$ )		$k_{120}$ ***	No. of theoretical plates	
		Measured*	Calculated**		at 80°C	at 120°C
1	1	0.041	0.058	0.51	130,000	230,000
2	2	0.089	0.116	0.90	116,000	176,000
3	4	0.200	0.232	1.66	107,000	145,000
4	8	0.320	0.464	2.78	103,000	125,000
5	12	0.450	0.696	4.11	100,000	116,000

\* By scanning electron microscopy.

\*\* Using the equation  $d_f = 5cr/p$ , where  $d_f$  = thickness of the liquid phase film in  $\mu\text{m}$ ,  $r$  = inner radius of the tube in cm,  $p$  = density of the liquid phase, and  $c$  = concentration of liquid phase (mg/ml) in the coating solution.

\*\*\* The partition ratio measured at 120°C for  $\text{C}_{14}$  *n*-paraffin hydrocarbon.

## RESULTS AND DISCUSSION

The variations in Kováts' retention index ( $I$ ) of alcohols, aldehydes and ethyl esters observed with differences in coated film thickness ( $d_f$ ) of Carbowax 20M are shown in Fig. 2. The Kováts index of substance A was calculated from<sup>18</sup>

$$I_A = 100N + 100n \cdot \frac{\log V'_{R(A)} - \log V'_{R(N)}}{\log V'_{R(N+n)} - \log V'_{R(N)}} \quad (1)$$

where  $V'_{R(N+n)}$  and  $V'_{R(N)}$  are the adjusted retention volumes of *n*-paraffin hydrocarbons of carbon number  $N$  and  $(N+n)$  that are, respectively, smaller and larger than  $V'_{R(A)}$ , the adjusted retention volume of A. The variation of  $I_A$  is due to changes in the relative proportions of  $V'_{R(A)}$ ,  $V'_{R(N)}$  and  $V'_{R(N+n)}$  caused by certain phenomena. For example,  $I_A$  changes with oven temperature, owing to the change of phase ratio  $\beta$  with temperature change<sup>2</sup>.  $\beta$  is expressed<sup>19</sup> as

$$\beta = V_G/V_L \quad (2)$$

where  $V_G$  is the gas volume of the column and  $V_L$  is the liquid phase volume of the column. The relation between  $\beta$  and film thickness ( $d_f$ ) is expressed by

$$\beta = r_0/d_f \quad (3)$$

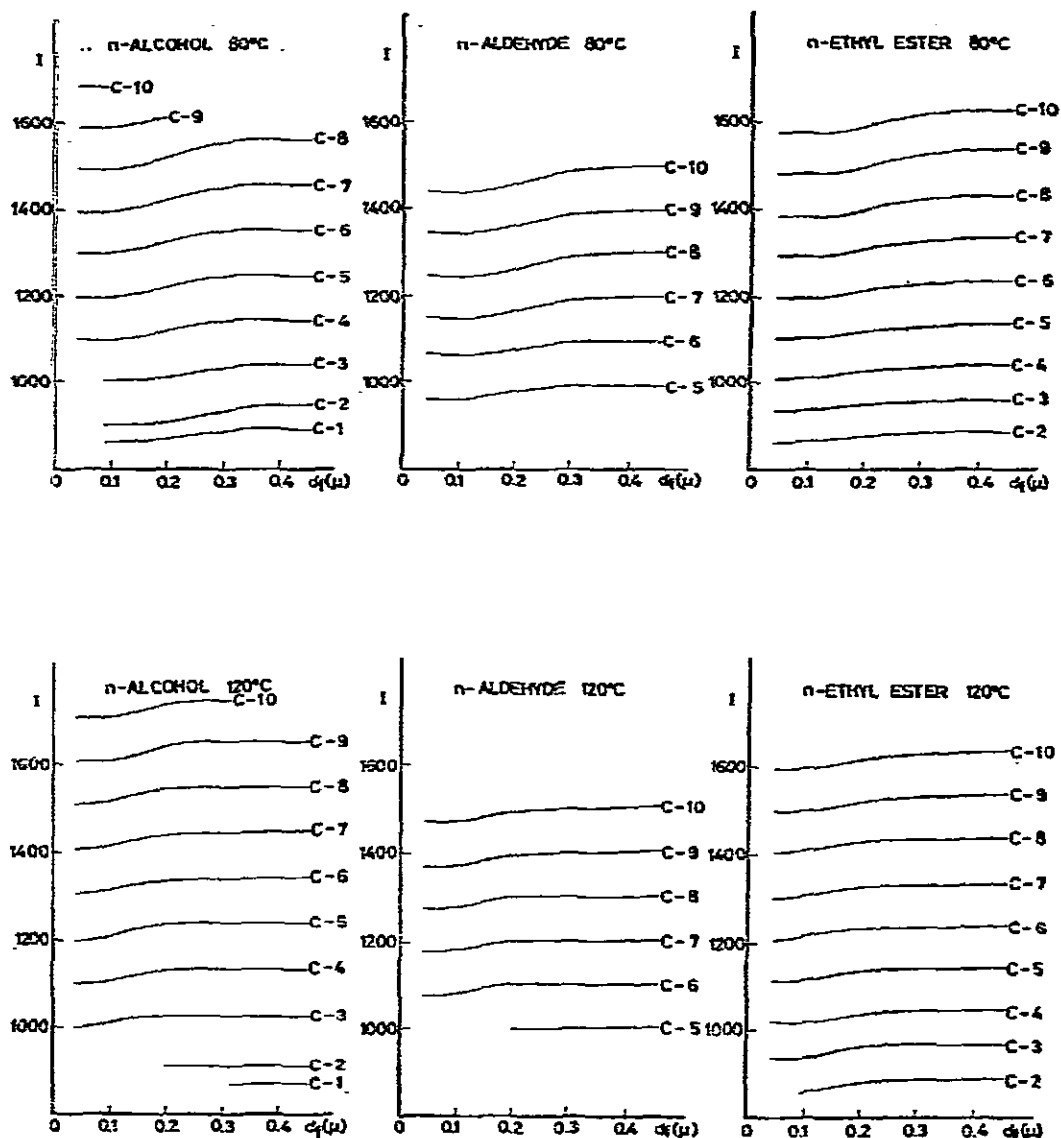


Fig. 2. Kováts' index versus coating film thickness.

where  $r_0$  is the radius of the column. From eqns. 2 and 3, it can be seen the  $V_L$  is dependent on  $d_f$ . Although  $d_f$  and  $V_L$  change, however, if  $V'_{R(A)}$ ,  $V'_{R(N)}$  and  $V'_{R(N+S)}$  change in the same proportion,  $I_A$  should not vary.

We can write

$$K_D = \beta k \quad (4)$$

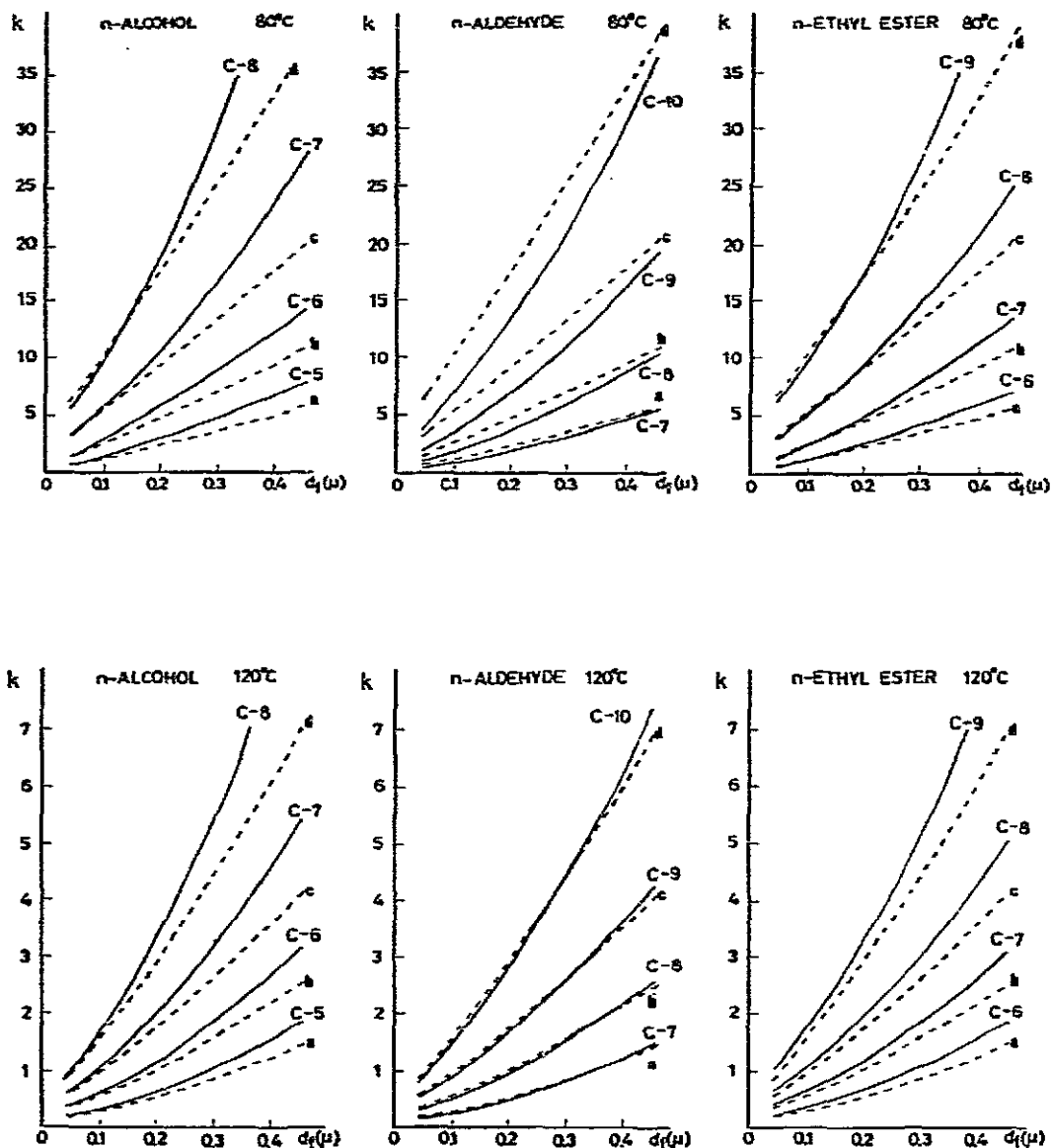


Fig. 3. Partition ratio versus coating film thickness. a = Dodecane; b = tridecane; c = tetradecane; d = pentadecane.

where  $K_D$  is the distribution coefficient and  $k$  is the partition ratio. Then, from eqns. 3 and 4, we obtain:

$$k = \frac{K_D}{r_0} - d_f \quad (5)$$

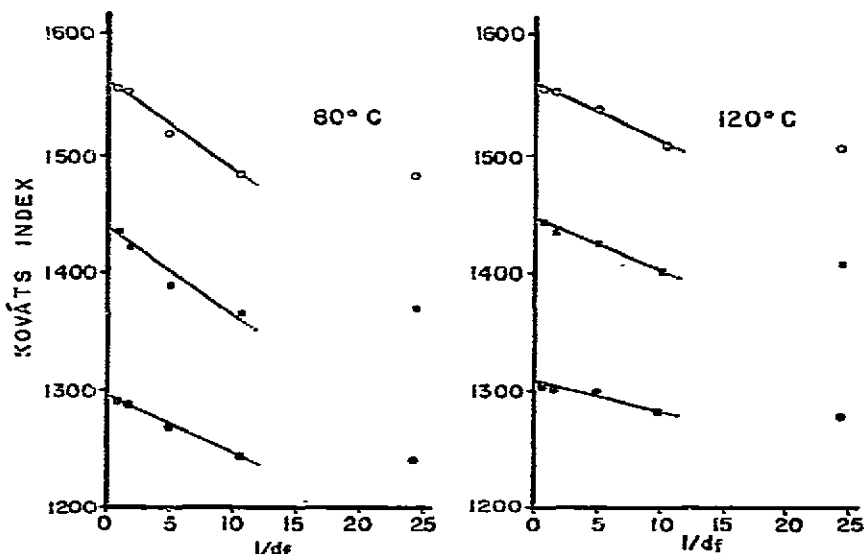
$K_D$  is constant when it is measured at constant column temperature, solute and liquid

TABLE II

*I* DIFFERENCES ( $\Delta I$ ) MEASURED ON COLUMNS 2 AND 5 AT 80°C AND 120°C

Compound	$\Delta I$ at 80°C	$\Delta I$ at 120°C
<i>Alcohols</i>		
<i>n</i> -Pentanol (C <sub>5</sub> )	50	34
<i>n</i> -Hexanol (C <sub>6</sub> )	54	34
<i>n</i> -Heptanol (C <sub>7</sub> )	57	38
<i>n</i> -Octanol (C <sub>8</sub> )	65	42
<i>Aldehydes</i>		
<i>n</i> -Heptanal (C <sub>7</sub> )	42	26
<i>n</i> -Octanal (C <sub>8</sub> )	46	30
<i>n</i> -Nonanal (C <sub>9</sub> )	53	36
<i>n</i> -Decanal (C <sub>10</sub> )	59	40
<i>Ethyl esters</i>		
Ethyl <i>n</i> -hexanoate (C <sub>8</sub> )	37	33
Ethyl <i>n</i> -heptanoate (C <sub>7</sub> )	46	37
Ethyl <i>n</i> -octanoate (C <sub>8</sub> )	52	43
Ethyl <i>n</i> -nonanoate (C <sub>9</sub> )	57	46

phase, so that  $k$  depends only upon  $d_f$ . Fig. 3 shows the relations between  $d_f$  and  $k$  for *n*-paraffin hydrocarbons (C<sub>12</sub>-C<sub>15</sub>), alcohols, aldehydes and ethyl esters. If  $I_A$  varies with  $d_f$ , the lines of a hydrocarbon and a solute will intersect. In other words, a large angle between the lines of hydrocarbon and a solute indicates that the magnitude of the change in  $V'_{R(A)}$  is different from those in  $V'_{R(N)}$  and  $V'_{R(N+S)}$ . One can see that the larger is  $d_f$ , the smaller is the difference in  $I_A$ . The variation in  $I_A$  measured at 120°C is smaller than that at 80°C (Fig. 2). The  $I$  differences ( $\Delta I$ ) for alcohols, aldehydes and ethyl esters measured on columns 2 and 5 at 80°C and

Fig. 4. Kováts' index against  $1/d_f$  plotted for C<sub>8</sub> alcohol (O), C<sub>8</sub> ethyl ester (■) and C<sub>8</sub> aldehyde (●).

120°C are summarized in Table II. The results indicate that  $\Delta I$  is larger at 80°C than at 120°C for all solutes tested.

Fig. 4 shows the relationship between Kováts indices and  $1/d_f$ . A linear relationship was observed in the higher loading range.

The index  $I_E$  is obtained using ethyl esters as standards<sup>20</sup>. The  $I_E$  differences ( $\Delta I_E$ ) were obtained by the same method, and are shown in Table III.  $\Delta I_E$  is clearly much smaller than  $\Delta I$ , except in the case of hydrocarbons. This is due to the polarity of Carbowax 20M and the solutes.  $d_f$  influences the  $k$  values of the aldehydes, alcohols and ethyl esters more than that of hydrocarbons. Referring to Fig. 2, it is seen that  $k$  for aldehydes, alcohols and ethyl esters increases proportionately with an increase in film thickness. The rate of increase of  $k$  in the case of hydrocarbons is, however, different from that in the case of alcohols, aldehydes and ethyl esters. It is, therefore, desirable to use ethyl esters as standard for obtaining the retention indices of alcohols, aldehydes or other polar compounds when a polar column such as Carbowax 20M is employed.

TABLE III

$I_E$  DIFFERENCES ( $\Delta I_E$ ) MEASURED ON COLUMNS 2 AND 5 AT 80°C AND 120°C

Compound	$\Delta I_E$ at 80°C	$\Delta I_E$ at 120°C
<i>Alcohols</i>		
<i>n</i> -Pentanol (C <sub>5</sub> )	12	7
<i>n</i> -Hexanol (C <sub>6</sub> )	16	7
<i>n</i> -Heptanol (C <sub>7</sub> )	14	7
<i>n</i> -Octanol (C <sub>8</sub> )	13	11
<i>Aldehydes</i>		
<i>n</i> -Heptanal (C <sub>7</sub> )	3	8
<i>n</i> -Octanal (C <sub>8</sub> )	2	7
<i>n</i> -Nonanal (C <sub>9</sub> )	2	10
<i>n</i> -Decanal (C <sub>10</sub> )	2	13
<i>Hydrocarbons</i>		
Dodecane (C <sub>12</sub> )	62	35
Tridecane (C <sub>13</sub> )	50	39
Tetradecane (C <sub>14</sub> )	45	43
Pentadecane (C <sub>15</sub> )	37	46

## CONCLUSIONS

The Kováts index system has been used in many studies. It is recognized that a more polar liquid phase leads to more variation in the Kováts indices obtained. This was usually thought to be due to the influence of temperature, and the glass column surface<sup>21</sup>. We found in this study that the thickness,  $d_f$ , of film coating also influenced the Kováts index system. In order to minimize  $\Delta I$ , one should use a column of large  $d_f$  at high temperature. Ethyl esters are superior to hydrocarbons as standards for alcohols, aldehydes and esters on a Carbowax 20M column. It is further desirable to give the thickness of the film coating when a gas chromatographic analysis is reported, although measuring column coating thickness is difficult under

any circumstances, and impossible when porous-layer open-tubular or support-coated open-tubular columns are used. From eqns. 2 and 4, we obtain:

$$V_L = \frac{V_G}{K_D} k \quad (6)$$

An approximate  $d_f$  value can be estimated from eqn. 6. If the value obtained at 120°C using tetradecane ( $C_{14}$ , *n*-paraffin hydrocarbon) is reported along with the Kováts indices, one can determine the nature of  $\Delta I$  for that column. Moreover, if the value of  $k_{120}$  is close to the reported one, the Kováts indices given will be sufficiently accurate to use as references for identification of unknowns. We therefore suggest that the  $k_{120}$  value for  $C_{14}$  be stated in addition to the gas chromatographic retention indices to enable readers to utilize fully the reported data.

#### REFERENCES

- 1 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 2 L. S. Ettre, *Anal. Chem.*, 36 (1964) 31A.
- 3 R. Kaiser, *Chromatographia*, 3 (1970) 127.
- 4 L. J. Lorenz and L. B. Rogers, *Anal. Chem.*, 43 (1971) 1593.
- 5 A. Göbler, *J. Chromatogr. Sci.*, 10 (1972) 128.
- 6 E. P. Woodford and C. M. van Gent, *J. Lipid Res.*, 1 (1960) 88.
- 7 F. J. van Lenten, J. E. Conaway and L. B. Rogers, *Separ. Sci.*, 1 (1977) 12.
- 8 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 36 (1968) 489.
- 9 L. S. Ettre, *Chromatographia*, 4 (1971) 286.
- 10 J. F. K. Huber and R. G. Gerritse, *J. Chromatogr.*, 80 (1973) 25.
- 11 H. Groenendijk and A. W. C. van Kemanade, *Chromatographia*, 4 (1971) 286.
- 12 L. S. Ettre and K. Billeb, *J. Chromatogr.*, 30 (1967) 1.
- 13 M. Goedert and G. Guiochon, *Anal. Chem.*, 42 (1970) 969.
- 14 G. Schomburg, *Chromatographia*, 4 (1971) 286.
- 15 L. Blomberg and T. Wännman, *J. Chromatogr.*, 148 (1978) 379.
- 16 D. F. Fritz, A. Sahil and E. sz. Kováts, *J. Chromatogr.*, 186 (1979) 63.
- 17 W. G. Jennings, K. Yabumoto and R. H. Wohleb, *J. Chromatogr. Sci.*, 12 (1974) 346.
- 18 E. Kováts, *Advan. Chromatogr.*, 1 (1966) 229.
- 19 W. G. Jennings, *Gas Chromatography with Glass Capillary Columns*, Academic Press, New York, 1978 p. 9.
- 20 H. van den Dool and P. D. Kratz, *J. Chromatogr.*, 11 (1963) 463.
- 21 T. Sarff, G. Redant and P. Sandra, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, (1979) 75.
- 22 L. Mathiasson, J. Å. Jönsson, A. M. Olsson and L. Haraldson, *J. Chromatogr.*, 152 (1978) 11.