The Relationship of Kováts Retention Indices and Equivalent Chain Lengths of Fatty Acid Methyl Esters on a Methyl Silicone Capillary Column

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Abstract

The Kováts retention indices of normal paraffins, fatty acid methyl esters (FAMEs), and fatty alcohols separated on a 15 m × 0.25-mm i.d. OV-101 capillary column are calculated directly from their retention data. Also, the described equations are used to convert the equivalent chain length value of FAMEs to retention indices or vice versa. All the calculated retention indices are in good agreement with those reported in the literature.

Introduction

Gas chromatographic (GC) identification of organic compounds can be performed by several methods (1–5). Among these, the retention index system proposed by Kováts (1) has been widely accepted as a general identification system. However, Gobler (6) pointed out that the Kováts retention index system requires *n*-paraffins as references which are not suitable for analysis of polar compounds; thus, a second retention index system was required. Consequently, the equivalent chain length (ECL) (4) and carbon number (5) systems, which use fatty acid methyl esters (FAMEs) as references, were proposed specifically for the identification of FAMEs. Though the Kováts retention index, ECL, and carbon number systems are very closely related, there is no direct method of conversion from ECL values to the more general system of Kováts retention index, or vice versa. Recent advances in chromatography have extensively exploited basic thermodynamics theory to predict the retention times or retention factors of homologues (7–11). Also, it has been demonstrated that the retention factors of FAMEs are related to their carbon number by the following equation:

$$\ln k' = a + bn + \frac{c}{T} + \frac{dn}{T} \qquad \text{Eq 1}$$

where k' is the retention factor, n is the carbon number or ECL, T is the absolute temperature, and a, b, c, and d are constants related to thermodynamic parameters.

$$a = \frac{\Delta S^0}{R} + \ln\beta \qquad \text{Eq 2}$$

$$b = \frac{\delta S}{R} \qquad \text{Eq 3}$$

$$c = \frac{\Delta H^0}{R} + \ln\beta \qquad \text{Eq 4}$$

$$d = \frac{\delta S}{R} \qquad \text{Eq 3}$$

R is the gas constant, β is the phase ratio of the column, ΔH^0 is standard molar enthalpy, ΔS^0 is standard molar entropy, and δH and δS are the increment in enthalpy and entropy, respectively.

In this paper, we describe an easy method of conversion of ECL to Kováts retention index using a methyl silicone column.

Experimental

FAMEs and *n*-paraffins of various chain lengths were purchased from Sigma Chemical (St. Louis, MO). GC analysis was performed on a Shimadzu model 14A GC equipped with a flame ionization detector, split/splitless injector, and a C-R4A data processor (Shimadzu, Kyoto, Japan). An OV-101 (15 m × 0.25-mm i.d., 0.2-µm film thickness) capillary column (Supelco, Bellefonte, PA) was used with nitrogen as the carrier gas at flow rates of 0.5–1 mL/min. Oven temperatures were held isothermally at intervals between 140 and 170°C for the hydrocarbons and 170 and 200°C for FAMEs.

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Results and Discussion

The four constants *a, b, c,* and *d* for *n*-paraffins and FAMEs were determined according to Krisnangkura et al. (12). Normal paraffins with carbon numbers 15–20 were chromatographed in the range of 140–170°C at 5° intervals. The natural logarithm of the retention factors, as well as the slopes, intercepts, and the four constants of Equation 1, are tabulated in Table I. Rewriting Equation 1 with the numerical values of the four constants resulted in the following equation:

$$\ln k' = -6.37 - 0.517n + \frac{214.43}{T} + \frac{421.91n}{T} \qquad \text{Eq 6}$$

or

$$\ln k' = -6.37 - 0.00517I + \frac{214.43}{T} + \frac{4.2191I}{T} \qquad \text{Eq 7}$$

where

$$I = 100n \qquad \text{Eq 8}$$

Equation 7 can be used to estimate the Kováts retention indices of organic compounds (including FAMEs) from their retention factors or retention times.

The constants *a, b, c,* and *d* for FAMEs are similarly determined; here, FAMEs with carbon numbers (of the acid) 16–20 are used as references and the temperatures are set between 170 and 200°C. The results are summarized in Table II. Rewriting Equation 1 with the numerical values of the four constants gives:

Table I. Natural Logarithms of Retention Factors of *n*–Paraffins at Various Temperatures and the Constants *a, b, c,* and *d*

Carbon numbers	140°C	145°C	150°C	155°C	160°C	165°C	170°C	Intercept	Slope
15	1.730	1.519	1.338	1.160	0.985	0.812	0.644	–14.18	6566.6
16	2.233	2.011	1.820	1.631	1.445	1.262	1.085	–14.62	6955.1
17	2.739	2.506	2.302	2.102	1.904	1.711	1.523	–15.10	7365.7
18	3.246	3.002	2.786	2.572	2.363	2.159	1.960	–15.65	7799.1
19	3.749	3.494	3.265	3.038	2.816	2.603	2.393	–16.20	8235.8
20	4.248	3.981	3.740	3.500	3.268	3.043	2.821	–16.74	8664.8
Intercept	–5.832	–5.876	–5.870	–5.862	–5.865	–5.881	–5.885	–6.37 (*a*)	214.43 (*c*)
Slope	0.504	0.493	0.481	0.468	0.457	0.446	0.436	–0.517 (*b*)	421.91 (*d*)

Table II. Natural Logarithms of Retention Factors of FAMEs at Various Temperatures and the Constants *a, b, c,* and *d*

Carbon numbers	170°C	175°C	180°C	185°C	190°C	195°C	200°C	Intercept	Slope
16	2.414	2.203	2.000	1.814	1.629	1.439	1.259	–15.76	8048.7
17	2.848	2.625	2.412	2.215	2.019	1.821	1.634	–16.27	8468.9
18	3.274	3.042	2.819	2.611	2.405	2.197	2.001	–16.79	8887.6
19	3.702	3.459	3.224	3.007	2.790	2.575	2.370	–17.30	9300.0
20	4.121	3.869	3.623	3.396	3.170	2.944	2.732	–17.81	9711.4
Intercept	–4.413	–4.458	–4.490	–4.514	–4.532	–4.581	–4.628	–7.58 (*a*)	1401.76 (*c*)
Slope	0.427	0.417	0.406	0.396	0.385	0.376	0.368	–0.512 (*b*)	415.64 (*d*)

Table III. Kovats Retention Indices of Saturated FAMEs Calculated from the Retention Factors in Table II using Equation 3*

Carbon numbers	170°C	175°C	180°C	185°C	190°C	195°C	200°C
16	1904.1 (1908.8)	1905.2 (1908.9)	1906.4 (1908.9)	1907.6 (1908.9)	1908.9 (1909.0)	1910.2 (1909.0)	1911.5 (1909.1)
17	2001.9	2003.1	2004.2	2005.5	2006.7	2008.0	2009.3
18	2099.8 (2109.4)	2101.0 (2109.6)	2102.1 (2109.7)	2103.3 (2109.8)	2104.5 (2109.8)	2105.8 (2110.0)	2107.1 (2110.2)
19	2197.7	2198.8	2200.0	2201.2	2202.4	2203.6	2204.9
20	2295.6 (2309.7)	2296.7 (2309.8)	2297.8 (2310.0)	2299.0 (2310.1)	2300.2 (2310.2)	2301.4 (2310.3)	2302.7 (2311.0)
22	2491.4 (2510.6)	2492.5 (2510.8)	2493.6 (2510.9)	2494.7 (2511.0)	2495.9 (2511.2)	2497.1 (2511.3)	2498.3 (2511.5)

* Values in parentheses were obtained from Krop et al. (7).

$$\ln k' = -7.58 - 0.512n + \frac{1401.76}{T} + \frac{415.64n}{T} \quad \text{Eq 9}$$

or

$$\ln k' = -7.58 - 0.512(ECL) + \frac{1401.76}{T} + \frac{415.64(ECL)}{T} \quad \text{Eq 10}$$

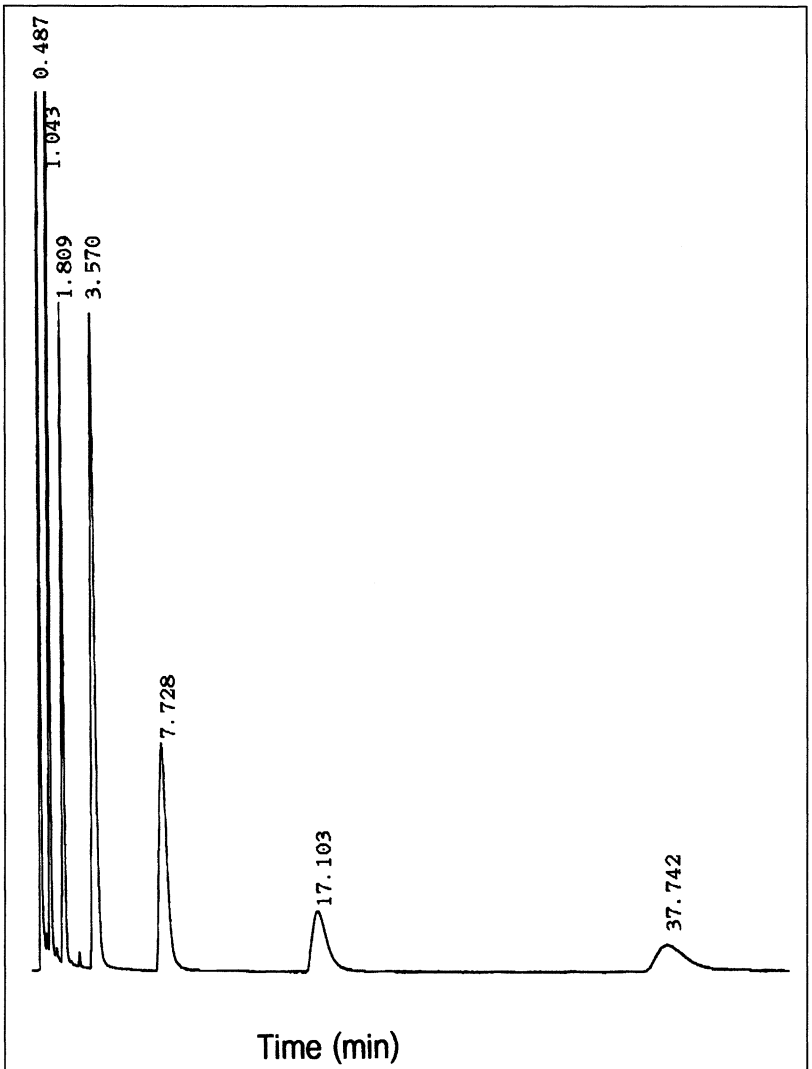

Figure 1. GC of fatty alcohols with carbon numbers 12–22 separated on a 15 m x 0.25-mm i.d. OV-101 capillary column at 200°C. The values over the peak are the retention times in min. Hexane eluted at 0.487 min.

Because Equation 7 and Equation 10 are derived using the same column, it is expected that the retention factors of FAMEs or any other organic compounds obtained on this column can be substituted into either equation, depending on whether retention index or ECL is needed. Thus, with substitution of the retention factors of the FAMEs in Table II into Equation 7, the Kováts retention indices of FAMEs at different temperatures were generated, and the results are summarized in Table III. The values in parentheses were taken from the publication of Krop et al. (13). The retention indices obtained by Krop et al. show a very slight effect of temperature: the calculated values shift about 3.4 units/10°C. The calculated value is close to that reported by Ettre (14) who reported a change of 3.7 units/10°C. Methyl erucate analyzed at 170°C shows the greatest difference with 19.2 units, which is 0.76%.

We demonstrated that Kováts retention indices of FAMEs could be calculated from their retention factors. However, Equation 10 provides a convenient method for calculating retention factors of FAME using their ECL. Therefore, the Kováts retention indices of FAMEs can be directly calculated from their ECL. Table IV lists some common FAMEs whose Kováts retention indices (13) and ECL (15) were reported in the literature. Substitution of ECL (column 2 of Table IV) into Equation 10 with $T = 473$ generated a series of retention factor logarithms (column 3). Substitution of these logarithms into Equation 7 at the same temperature produced Kováts retention index values which are summarized in column 4. The values reported by Krop et al. (13) are included for comparison. The greatest difference is 1.04% for methyl decanoate. Kováts retention indices were also calculated at other temperatures, but the results are not reported. The retention indices of FAMEs in Table IV increased about 2.4 units/10°C as the temperature increased.

Although Equation 1 can be used to calculate the Kováts retention indices and ECL of FAMEs,

Table IV. Kovats Retention Indices of Some Common FAMEs Calculated from ECL

FAMEs	ECL*	lnk'	I_{200} (OV-101)†	I_{200} (DB-1)‡	% Difference
Methyl decanoate	10.00	–0.428	1319.2	1305.6	–1.04
Methyl dodecanoate	12.00	0.384	1514.9	1506.9	–0.53
Methyl tetradecanoate	14.00	1.195	1710.6	1708.0	–0.15
Methyl oleate	17.72	2.705	2074.7	2076.4	0.08
Methyl linoleate	17.64	2.672	2066.9	2066.4	–0.02
Methyl linolenate (alpha)	17.69	2.693	2071.8	2069.6	–0.11
Methyl erucate	21.66	4.315	2460.3	2482.6	0.90

* Values obtained from Dorris et al. (15).
† Values obtained using Equation 3.
‡ Values obtained from Calvalli et al. (7).

Table V. Kovats Retention Indices of Fatty Alcohols

Fatty alcohols	ln*k'*	I_{180} (OV-101)*	I_{180} (SE-30)†	% Difference
Dodecanol	0.133	1455.1	1471	1.08
Tetradecanol	0.999	1664.1	1669	0.29
Hexadecanol	1.845	1868.3	1864	-0.23
Octadecanol	2.699	2074.4	2060	-0.70
Eicosanol	3.536	2276.4	n/a‡	-
Docosanol	4.340	2470.4	n/a‡	-

* Values obtained using Equation 3.
† Values obtained from Ettre (14).
‡ n/a, data not available.

it is expected that it can be used for other organic compounds as well. Because the four constants in Equation 1 are thermodynamic parameters, they probably dictate the way that a molecule migrates through the chromatographic column. Figure 1 is a chromatogram of fatty alcohols at 180°C. Substitution of these retention data into Equation 7 provided the retention indices of the alcohols which are listed in Table V. The calculated retention indices for alcohols with carbon numbers 12–16 are similar to those reported in the literature (16). The greatest different is about 1%.

Because the constants *a, b, c,* and *d* are thermodynamic parameters, we speculated that any changes in the stationary phase properties (e.g., oxidation or aging) would cause the values of these four constants to change simultaneously. Also, because constant a is associated with the column phase ratio, it is expected that column size and stationary phase film thickness would undoubtedly affect the value of this constant. Therefore, the four constants in Equation 1 are very column specific. They may change with time and the purity of the samples being analyzed. However, the changes can be easily monitored by injecting a sample with a known retention index or ECL onto the column and comparing the calculated values with those reported in the literature.

Conclusion

This work demonstrates that Kováts retention indices of hydrocarbons, FAMEs, and fatty alcohols can be calculated using Equation 1. Also, the ECL of FAMEs can be conveniently converted to the more general system of Kováts retention index.

Acknowledgments

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