

A method for the prediction of retention indices of hydrocarbons on squalan

At present, the retention indices (I) are the means most widely used for identification of chromatographic peaks. These indices, like the boiling temperature, density and other physicochemical characteristics of substances, are experimentally determined. Even for one and the same substance, these values depend on the conditions of the analysis. Due to the great number of variables in GC, a long time is required for the experimental determination of I .

In this paper we develop a new method for the calculation of I in which no experimental chromatographic data are necessary. This allows a very precise prediction of the retention of the isoparaffins and naphthenes on squalan.

In the analysis of natural products and especially of oil cuts, which contain components similar in their properties, there are two problems to be solved. Firstly, the most complete resolution and exact identification is required in order to make the second step—quantitative analysis. There are different techniques for the determination of the degree of resolution, which are not the subject of the present paper. KOVATS' indices¹⁻³ are the most popular and successful means for the identification of the peaks in a chromatogram. They are calculated from the experimentally-determined V_N of the components of the mixture and the V_N of the reference n -paraffins added.

There are several methods^{1,4,5} for the determination of I , based on the indices obtained for similar substances on the same stationary phase. In one of these methods¹, the difference between the indices of two substances is determined by the empirical relationship:

$$\Delta I \approx 5\Delta t_b^\circ \quad (1)$$

According to this relationship, the indices do not depend on the temperature of the analysis, which is not true. Apart from this, it is only valid for paraffin isomers.

Another method for the determination of I has been developed by SCHOMBURG^{4,5}. He uses the experimentally-determined indices of different isomeric hydrocarbons in order to obtain what he calls the "homomorphic" factor. By means of this factor, he calculates ΔI between an n -paraffin and the corresponding isoparaffin using the formula:

$$I_i^A = I_z^A + \Sigma H_i^A \quad (2)$$

where I_i^A is the retention index of an isomer on a nonpolar stationary phase; I_z^A the index of the corresponding n -paraffin, and H_i^A is the "homomorphic" factor. This method also does not allow another way of determining the influence of the temperature of the analysis on the resolution except an experimental one.

The other methods for calculating ΔI concern the differences in I with the change in the stationary phases.

The new method for calculating the retention indices of hydrocarbons on squalan requires knowledge of the vapour pressures of the substances analysed at the temperature of the analysis, their molecular weights and densities. The method is based on the fact that squalan is a non-specific medium with respect to the solution of paraffins and naphthenes⁶. This means that the non-ideality of the solution is

compensated in sign and magnitude by the ratios of the molecular volumes of the solutes mentioned. According to an earlier paper⁶ on a phase for which

$$\log \gamma' \leq 0.0 \pm 0.03 \text{ units} \quad (3)$$

where γ' is the deviation from ideality of the solution after correction with $V_{\text{mol},i,s}$, the relative retention of two solutes, $r_{i,s}$, can be expressed by the relation:

$$r_{i,s} = \frac{p_s^\circ \cdot V_{\text{mol}}}{p_i^\circ \cdot V_{\text{mol},i}} \quad (4)$$

In this equation, p° is the vapour pressure for the substances i and s at the temperature of the analysis, and V_{mol} are their molecular volumes. In analogy with the KOVATS' formula, we can write the following equation for $I_{\text{theor.}}$:

I
ON INDICES OF ISOPARAFFINS AND NAPHTHENES

hydrocarbon	$I_{\text{theor.}} - I_{\text{exp.}}$	$I_{p^\circ} - I_{\text{exp.}}$	$I_{(8)} - I_{(0)}$	$I_{(4)} - I_{\text{exp.}}$	$I_{(1)} - I_{\text{exp.}}$
2-Dimethylbutane	-6	—	4.5	—	30
cyclopentane	0.5	—	3.5	—	—
3-Dimethylbutane	-7	—	2	-15	20
Methylpentane	-1	—	1	0	—
Methylpentane	-4	—	1	0	11
2-Dimethylpentane	-4.5	7	2	11.5	20
ethylcyclopentane	-3	-16.5	2.5	—	—
4-Dimethylpentane	-3	7	0	—	—
2,3-Trimethylbutane	-12	-4	1.5	-8	25
3-Dimethylpentane	-10.5	-5	0	-4	18
cyclohexane	-1	-21	2.5	—	—
Methylhexane	-1	3	0	-4	18
1-Dimethylcyclopentane	-7	-10.5	—	—	—
3-Dimethylpentane	-7	-4	2	-20	13
Methylhexane	-3.5	-1	0	7	9
cis-3-Dimethylcyclopentane	-2.5	-7.5	—	—	—
trans-3-Dimethylcyclopentane	-10	-15	—	—	—
Ethylpentane	-5.5	-5	0.5	—	10
trans-2-Dimethylcyclopentane	-7	-14	—	—	—
cis-2-Dimethylcyclopentane	-7	-19	—	—	—
2-Dimethylhexane	-3.5	7	—	8	12
1,3-Trimethylcyclopentane	-10.5	-8	—	—	—
ethylcyclohexane	-9	-21	2.5	—	—
5-Dimethylhexane	-2.5	6.5	1.5	-1	—
ethylcyclopentane	-4.5	-17.5	—	—	—
4-Dimethylhexane	-4	4	2	3	—
2,3-Trimethylpentane	-9	-2.5	1.5	—	20
3-Dimethylhexane	-7	0	0	0	9
3,4-Trimethylpentane	-8.5	-4	—	—	—
3,3-Trimethylpentane	-13	-10	—	-37	—
3-Dimethylhexane	-5.5	-2	—	-25	10
Methyl-3-ethylpentane	-7	-3.5	—	—	—
Methylheptane	-1	4	—	1	3
Methylheptane	-2	1.5	—	—	—
4-Dimethylhexane	-7	-4.5	—	-28	13
cis-2-trans-4-Trimethylcyclopentane	-11	-14.5	—	—	—
Methyl-3-ethylpentane	-12.5	-10	—	—	—
Ethylhexane	-4	0	—	—	—
Methylheptane	-2.5	0	—	0	5

$$I_{\text{theor.}} = 100 \cdot z + 100 \frac{\log (p_{z-1}^{\circ} \cdot V_{\text{mol}_{z-1}} / p_i^{\circ} \cdot V_{\text{mol}_i})}{(p_{z-1}^{\circ} \cdot V_{\text{mol}_{z-1}} / p_z^{\circ} \cdot V_{\text{mol}_z})} \quad (5)$$

where z and $z - 1$ are the carbon numbers of the standard n -paraffins and i , the corresponding hydrocarbons.

Using this formula, the retention indices of many isoparaffins and naphthenes were calculated using tabulated data for p° and d^4 taken from ref. 7. The calculated values of $I_{\text{theor.}}$ were compared with those obtained experimentally or listed in the literature⁸. In order to assess the accuracy of the new method, we give, instead of the indices themselves, several differences (δ) in their values. The first column of Table I gives the difference between $I_{\text{theor.}}$ calculated by eqn. (5) and I obtained experimentally, with an accuracy of 0.5 index units. In the second column is given the difference between I calculated only from the values of p° and $I_{\text{exp.}}$. The third column shows the differences between $I_{\text{exp.}}$ obtained by two different authors^{8,9}. The fourth column gives the differences between the results of SCHOMBURG's method and $I_{\text{exp.}}$; the last column shows the differences between the indices from eqn. (1) and $I_{\text{exp.}}$.

The results in Table I show an extremely good agreement between the theoretically and experimentally obtained values for the retention indices. Compared to the methods described in refs. 1, 4 and 5, where experimental data are used, the new method is more accurate. The calculation of I based only on the values of p° , assuming that $\gamma_{i,s}^{\circ} = 1$, is not precise; the values obtained show deviations in different directions. Another advantage of the new method is that it allows the calculation of the indices of the naphthenes.

The newly-developed method has the advantage that, for the calculation of I , physicochemical characteristics of the analysed hydrocarbons which are precisely determined, are used. Besides this, $I_{\text{theor.}}$ accurately shows the effect of the temperature of the analysis on the relative resolution. The deviations, when present, are always negative. This means the absence of random error.

The advantages of the new method would allow the planning of the conditions of an analysis and the prediction of the resolution at different temperatures. All these factors will considerably shorten the time for the preliminary analysis and the time for the identification of the peaks of hydrocarbons separated on squalan.

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