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Retention Index in Programmed Temperature Gas Chromatography

Isao TAKEMURA

Quality Control Laboratory, Max Factor Co., Ltd., Nishi-Gotanda, Shinagawa-ku, Tokyo

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Linear programmed temperature gas chromatography (PTGC) can be applied to simultaneous analysis of mixtures consisting of many ingredients with a wide range of boiling points. However, fundamental data of ingredients under the same conditions, such as retention temperature and relative retention values, should be collected prior to qualitative or quantitative analysis of unknown samples. Recently the data on ingredients of many stationary liquids in isothermal gas chromatography (IGC) have been summarized systematically by many workers. If the data in IGC could be applied to PTGC, the complexity in PTGC would be reduced considerable.

For a linear PTGC with constant flow rate, the author has presented the following linear relationship between logarithmic relative retention value (α^{IT}) of IGC and relative retention value (α^{PT}) of PTGC.[1)]

$$\log \alpha^{IT} = m(\alpha^{PT} - 1) \tag{1}$$

where m is a constant dependent upon the column temperature in IGC, the evaporation potential of internal standard material, the program rate, the flow rate of carrier gas, the initial temperature and the column length in PTGC.[2)] If the operating conditions do not change, Eq. (1) holds in different homologous series on both polar and nonpolar columns.[3)]

The Kovats index system[4)] is widely accepted in IGC. In this system, the relative retention is referred to the series of normal paraffin hydrocarbons as standard substances. Retention indices I_{IT} are calculated by means of the relation

$$I_{IT} = 100\frac{\log \alpha_{X,N}}{\log \alpha_{N+1,N}} + 100N \tag{2}$$

where $\alpha_{X,N}$ is the relative retention value of unknown compound X compared to the n-paraffin with N carbon atoms, and $\alpha_{N+1,N}$ the relative retention value of the two n-paraffins with $N+1$ and N carbon atoms. Van den Dool and Kratz[5)] and also Kaiser[6)] have shown that for PTGC the retention indices can be calculated by means of the following relation and that the values are equal to those calculated by Eq. (2) for IGC provided that the indices measured are independent of temperature.

$$I_{PT} = 100\frac{T_r(X) - T_r(N)}{T_r(N+1) - T_r(N)} + 100N \tag{3}$$

where $T_r(X)$, $T_r(N)$, $T_r(N+1)$ are retention temperatures of unknown compound and n-paraffins of carbon number N and $N+1$, and $T_r(N) \leq T_r(X) \leq T_r(N+1)$. Guiochon[7)] realized that, when the column temperature in IGC was 0.92 times the retention temperature of unknown compound X in PTGC, the retention index for IGC was approximately the same as that for PTGC.

In this paper, it is shown that Eq. (3) can be obtained from Eqs. (1) and (2).

The retention index for IGC gives the relative retention values for PTGC obtained from Eqs. (1) and (2):

$$I_{IT} = 100\frac{\alpha^{PT}_{X,N} - 1}{\alpha^{PT}_{N+1,N} - 1} + 100N \tag{4}$$

The relative retention value of n-paraffin of carbon number $N+1$ in PTGC is given by

$$\alpha^{PT}_{N+1,N} = \frac{\{T_r(N+1) - T_0\}/r - t_0}{\{T_r(N) - T_0\}/r - t_0} \tag{5}$$

It follows that

$$\alpha^{PT}_{N+1,N} - 1 = \frac{T_r(N+1) - T_r(N)}{T_r(N) - (T_0 + rt_0)} \tag{6}$$

where T_0 is the initial temperature, r is the program rate and t_0 is the time of air peak from the starting point. Similarly, for unknown compound X, we get

$$\alpha^{PT}_{X,N} - 1 = \frac{T_r(X) - T_r(N)}{T_r(N) - (T_0 + rt_0)} \tag{7}$$

Substituting Eqs. (6) and (7) into Eq. (4), the same equation as Eq. (3) is obtained:

$$I_{IT} = 100\frac{T_r(X) - T_r(N)}{T_r(N+1) - T_r(N)} + 100N \tag{8}$$

This is the equation of retention index for IGC related with retention temperature in PTGC. It may indicate that retention index for PTGC is the same as that for IGC.

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