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CONTRIBUTION TO THE THEORY OF THE RETENTION INDEX SYSTEM

I, RETENTION INDICES USING PROGRAMMED-TEMPERATURE GAS CHROMATOGRAPHY

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SUMMARY

After examining the relationship between retention index and column temperature under isothermal conditions, we have shown in a recent publication that the temperature-dependence of the retention index may generally be determined by an Antoine-type equation:

$$I^{\text{stationary phase}}_{\text{substance}}(T) = A + \frac{B}{T + C}$$

After further investigation, we have established that the retention indices can be exactly calculated from programmed-temperature gas chromatography data with the following equation:

$$\frac{\int_{T_0}^{T_r}\left(A + \frac{B}{T+C}\right)\mathrm{d}T}{T_r - T_0} = A + \left[\frac{2.3 \cdot B \cdot \log\frac{(T_r + C)}{(T_0 + C)}}{T_r - T_0}\right]$$

A great advantage of this equation is that the data from normal hydrocarbons are not included in it.

INTRODUCTION

It is generally known that working without pure standard substances, the retention index system worked out by KOVÁTS[1] is the most important one among the qualitative evaluation methods of gas chromatography. The retention indices give a suitable foundation—beyond the application mentioned—for other investigations[2,3], and as a result of this recognition increasing interest has been manifested in recent years in some problems of the retention index system. Among these questions, the application of the retention index system is most prominent in programmed-temperature gas chromatography (PTGC). Although in this field the appropriate equations of VAN DEN DOOL AND KRATZ[4], GUIOCHON[5], HABGOOD AND HARRIS[6] and GIDDINGS[7], among others, are available the differences in index experienced in some cases have stimulated the researchers working in this field to undertake further investigations. Also GOLOVNYA AND URALETZ[8], in addition to suggesting a new equation for using isothermal retention indices under PTGC conditions, are dealing with index-influencing factors and also are comparing different methods of index conversion.

In examining the relationship between retention index and column temperature under isothermal conditions, we recently demonstrated[9] that the temperature dependence of the retention index may generally be determined by an Antoine-type equation:

$$I^{\text{st. ph.}}_{\text{substance}}(T) = A + \frac{B}{T + C} \tag{1}$$

where

I = the symbol for the retention index

T = column temperature in °K

A, B and C = constants of the Antoine-type eqn. (1).

The three constants of the equation depend only on the quality of the substance and of the stationary phase and can easily be determined from experimental results[9]. Considering this information, we supposed that relying on eqn. (1), the index values in PTGC may be exactly described. In this paper we report on the results reached so far, based on data in the literature[4–8] and on our measurements.

THEORY

In our investigations we have been concerned only with cases in which the continuous temperature programming started simultaneously with the introduction of the sample and terminated only after the elution of the component examined; it may be described by a constant heating rate, β (°C/min). In the case examined, the following relationship is applicable, using the average value of integration:

$$I^{\text{st. ph.}}_{\text{substance}}(\text{PTGC}) = \frac{\int_{T_0}^{T_r} \left(A + \frac{B}{T + C}\right) \mathrm{d}T}{T_r - T_0} \tag{2}$$

where

T_r = retention temperature in °K

T_0 = initial temperature in °K.

Solution of the integral calculus in the numerator on the right-hand side of eqn. (2) yields:

$$\int_{T_0}^{T_r} \left(A + \frac{B}{T + C}\right) \mathrm{d}T = [AT + B\cdot\ln\ (T + C)]_{T_0}^{T_r} =$$

$$AT_r + B\cdot\ln(T_r + C) - AT_0 - B\cdot\ln(T_0 + C) = A\ (T_r - T_0) +$$

$$[\ln(T_r + C) - \ln(T_0 + C)]\cdot B = A\ (T_r - T_0) + B\cdot\ln\left(\frac{T_r + C}{T_0 + C}\right) =$$

$$A\ (T_r - T_0) + 2.3\cdot B\cdot\log\left(\frac{T_r + C}{T_0 + C}\right) \tag{3}$$

Thus for eqn. (2) we may write:

$$I^{\text{st. ph.}}_{\text{substance}}(\text{PTGC}) = \frac{A\,(T_r - T_0) + 2.3 \cdot B \cdot \log\left(\dfrac{T_r + C}{T_0 + C}\right)}{T_r - T_0} =$$

$$A + \frac{2.3 \cdot B \cdot \log\left(\dfrac{T_r + C}{T_0 + C}\right)}{T_r - T_0} \qquad (4)$$

Eqn. (4) is suitable for the exact calculation of retention indices in PTGC.

EXPERIMENTAL

Our measurements were made using gas chromatographs (Carlo Erba Model C, D, GV and GI-452) with flame ionisation detectors in all cases. Carrier gas was N_2, while auxiliary gases were H_2 and O_2. Stationary phases were squalane; the silicone oils, SE-30, DC-200, DC-550, DC-702; Apiezon L; di-ethyleneglycol adipate; di-ethyleneglycol succinate; polyethylene glycol 1500 (PEG-1500); and polyethylene glycol 20 M.

As an example we present the calculation of benzene using PEG-1500 as stationary phase. The retention index of benzene on PEG-1500 under isothermal conditions is dependent on column temperature according to the following equation:

$$I^{\text{PEG-1500}}_{\text{Benzene}}(T) = 1\,718 - \frac{1\,032\,240}{T + 967} \qquad (5)$$

When the initial temperature, T_0 was 84°C, the retention temperature, T_r was 99°C. [$\beta = 4.5$°C/min]. The corresponding data are substituted into eqn. (4) and the following calculations are made.

$$I^{\text{PEG-1500}}_{\text{Benzene}}(\text{PTGC}) = 1\,718 + \frac{2.3 \cdot (-\,1\,032\,240) \cdot \log\left(\dfrac{372 + 967}{357 + 967}\right)}{372 - 357} =$$

$$1\,718 + \frac{2.3 \cdot (-\,1\,032\,240) \cdot \log\left(\dfrac{1\,339}{1\,324}\right)}{15} =$$

$$1\,718 + \frac{2.3 \cdot (-\,1\,032\,240) \cdot \log 1.0113}{15} =$$

$$1\,718 - \frac{2.3 \cdot 1\,032\,240 \cdot 0.0049}{15} =$$

$$1\,718 - 776 = 942 \qquad (6)$$

We compared data in the literature with that calculated by eqn. (6). The results are shown in Table I.

TABLE I

COMPARISON OF RETENTION INDEX DATA

Index units		
Literature data	*Calculated by eqn. (6)*	*Divergence from calculated value*
944[a]	942	+2
943[b]	942	+1
943[c]	942	+1

[a] VAN DEN DOOL AND KRATZ (ref. 4).
[b] GIDDINGS (ref. 7).
[c] GOLOVNYA AND URALETZ (ref. 8).

SYMBOLS

I = retention index
T = column temperature
T_0 = initial temperature
T_r = retention temperature
A, B and C = constants of Antoine-type equation
β = heating rate
st. ph. = stationary phase

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