CONTRIBUTION TO THE CONCEPT AND METHOD OF ROHRSCHNEIDER. II

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SUMMARY

During the last few years, the retention index system developed by KovÁts[1] has been further developed into a method suitable for use in analytical practice. In this field, ROHRSCHNEIDER's concept[2] seems to be the most suitable for investigating the connection between retention index and molecular structure. In the present paper, we show that the gas chromatographic interaction (between a substance and the stationary phase) can be characterized not only by the difference in the retention indices, but also by quotients of their indices. This mathematical interpretation of ROHRSCHNEIDER's concept gives better and more significant relations among the substance-specific factors than the original concept.

INTRODUCTION

The retention index system developed by KovÁts[1] has been further developed during the last few years into a method suitable for use in analytical practice. However many complicated questions still remain to be resolved, for example the connection between retention index and molecular structure.

In this field, many researchers have obtained significant results, *e.g.*, SCHOMBURG[2], JONAS *et al.*[3], ROHRSCHNEIDER[4], ZARAZIR *et al.*[5], CHOVIN[6], WALRAVEN *et al.*[7], GRENIER AND BONASTRE[8], GOLOVNYA *et al.*[9], WALRAVEN[10], MCREYNOLDS[11] and SUPINA AND ROSE[12].

Having critically evaluated the published papers, we have concluded that the method of ROHRSCHNEIDER seems to be the most suitable for investigating the connection between retention index and molecular structure. This method was rendered more complete by the theoretical work of KovÁts[13].

ROHRSCHNEIDER's original method was discussed in our earlier paper[14]. Be-

cause of some deviations in the widespread use of the method in some cases, we thought it necessary to deal with the mathematical interpretation of ROHRSCHNEIDER's concept in detail. During this work it was shown that the theory is faultless, but approximation based on the formation of differences is not suitable enough to follow some of the more complicated process because of error compensation possibilities. Therefore we have developed an approximation based on the formation of quotients in agreement with ROHRSCHNEIDER's concept.

THEORY

On the basis of ROHRSCHNEIDER's concept, we supposed that the gas chromatographic interaction between a substance and stationary phase could be characterized not only by the difference in the retention indices[15], but also by the quotients of their indices, so we derived the following equation for any constant temperature:

$$I_x^p(T) = I_x^s(T) \cdot \sum_{i=1}^{5} f_i s_i \tag{1}$$

where I = retention index under isothermal conditions; p = polar stationary phase; s = squalane stationary phase; x = substance; T = column temperature; f_i = i-th polarity factor, determined as $f_i = \left(\frac{I^p}{I^s}\right)_i$; i = serial number of standard substance; and s_1–s_5 = substance-specific factors, characterizing the molecular structure of substance x and the interaction forces and relations formed.

As a general case:

$$\sum_{i=1}^{5} s_i = 1.000 \tag{2}$$

There is a direct connection between the original ROHRSCHNEIDER equation and eqn. 1. Any ROHRSCHNEIDER index difference can be represented by:

$$x = \left[\frac{\Delta I}{100}\right]_{\text{benzene}} = \frac{I^p - I^s}{100} = \frac{I^s}{100}\left[\left(\frac{I^p}{I^s}\right) - 1\right]_{\text{benzene}} \tag{3}$$

Since

$$f_i = \left(\frac{I^p}{I^s}\right)_i$$

eqn. 3 can be written as follows:

$$x = \frac{I^s}{100}(f_1 - 1)_{\text{benzene}} \tag{4}$$

Similarly:

$$y = \frac{I^s}{100}(f_2 - 1)_{\text{ethanol}}$$

and so on.

x, y, etc. from eqns. 4, 5, etc. are substituted into the original ROHRSCHNEIDER equation:

$$\Delta I = ax + by + cz + du + es = \frac{aI_1^s}{100}(f_1 - 1) + \frac{bI_2^s}{100}(f_2 - 1) +$$

$$+ \frac{cI_3^s}{100}(f_3 - 1) + \frac{dI_4^s}{100}(f_4 - 1) + \frac{eI_5^s}{100}(f_5 - 1) \tag{6}$$

Multiplying eqn. 6 by $\left(\frac{1}{I_x^s}\right)$, we obtain:

$$\frac{\Delta I}{I_x^s} = \frac{I_x^p - I_x^s}{I_x^s} = \frac{I_x^p}{I_x^s} - 1 = \frac{a}{100}\frac{I_1^s}{I_x^s}(f_1 - 1) + \frac{b}{100}\frac{I_2^s}{I_x^s}(f_2 - 1) +$$

$$+ \frac{c}{100}\frac{I_3^s}{I_x^s}(f_3 - 1) + \frac{d}{100}\frac{I_4^s}{I_x^s}(f_4 - 1) + \frac{e}{100}\frac{I_5^s}{I_x^s}(f_5 - 1) \tag{7}$$

On introducing the following terms:

$$\frac{a}{100} \cdot \frac{I_1^s}{I_x^s} = s_1 \tag{8}$$

$$\frac{b}{100} \cdot \frac{I_2^s}{I_x^s} = s_2 \tag{9}$$

and so on, eqn. 7 can be written as follows:

$$\frac{I_x^p}{I_x^s} - 1 = s_1(f_1 - 1) + s_2(f_2 - 1) + s_3(f_3 - 1) + s_4(f_4 - 1) + s_5(f_5 - 1) =$$

$$\sum_{i=1}^{5} f_i s_i - \sum_{i=1}^{5} s_i \tag{10}$$

Eqns. 1 and 10 are the same if $\sum_{i=1}^{5} s_i = 1.000$. This mathematical interpretation of ROHRSCHNEIDER's concept gives a higher degree of precision than the original one. The relation among the substance-specific factors is significant.

ROHRSCHNEIDER's concept enables us to construct the following equations:

$$\frac{I_x^{p,1}}{I_x^{p,2}} = \sum_{i=1}^{5} F_i S_i \tag{11}$$

where $F_i = i$-th polarity factor for any two stationary phases, neither of which may be squalane; and $S_i = i$-th substance-specific factor, $F_i = \left(\frac{I^{p,1}}{I^{p,2}}\right)_i$ for a system based on a non-squalane stationary phase.

The other equation is of greater importance, as it enables the "theoretical squalane index" to be determined in cases when for any reason the substance cannot be analyzed adequately on squalane or the index cannot be determined experimentally.

$$\frac{I_x^s}{I_x^p} = \sum_{i=1}^{5} \frac{1}{f_i} \cdot S_i \tag{12}$$

Eqn. 12 is of importance when interactions and molecular structure are to be

studied, since in these calculations knowledge of the data for the stationary phase of squalane is essential. It should be mentioned, however, that the temperature dependence of substance-specific factors has not yet been studied.

So far we have used in our experiments the five standard substances recommended by ROHRSCHNEIDER, but taking into account the work of MCREYNOLDS[11] and practical experience, it seems more suitable to change the quality of the standard substances rather than the number used, as MCREYNOLDS did in some cases. Our investigations in this field have shown that ROHRSCHNEIDER's concept makes possible the selection of the five standards from a wide variety of substances and it is not absolutely necessary to use the original standards.

On the basis of the well known error-calculating method, the value of the error during the determination of $I_x^p(T)$ can be obtained by forming the partial derivatives of eqn. 1 according to the parameters effecting the dermination, i.e., in our case the error (E_R) during the determination of $I_x{}^p(T)$:

$$E_R \leqslant \left| \frac{\partial I_x^p}{\partial I_x^s} \right| \Delta I_x^s + \left| \frac{\partial I_x^p}{\partial I_1^p} \right| \Delta I_1^p + \left| \frac{\partial I_x^p}{\partial I_1^s} \right| \Delta I_1^s + \left| \frac{\partial I_x^p}{\partial I_2^p} \right| \Delta I_2^p +$$

$$+ \left| \frac{\partial I_x^p}{\partial I_2^s} \right| \Delta I_2^s + \left| \frac{\partial I_x^p}{\partial I_3^p} \right| \Delta I_3^p + \left| \frac{\partial I_x^p}{\partial I_3^s} \right| \Delta I_3^s + \left| \frac{\partial I_x^p}{\partial I_4^p} \right| \Delta I_4^p +$$

$$+ \left| \frac{\partial I_x^p}{\partial I_4^s} \right| \Delta I_4^s + \left| \frac{\partial I_x^p}{\partial I_5^p} \right| \Delta I_5^p + \left| \frac{\partial I_x^p}{\partial I_5^s} \right| \Delta I_5^s \tag{13}$$

Substituting the values of the partial derivatives obtained into eqn. 13:

$$E_R \leqslant \left| s_1 \cdot \frac{I_1^p}{I_1^s} + s_2 \cdot \frac{I_2^p}{I_2^s} + s_3 \cdot \frac{I_3^p}{I_3^s} + s_4 \cdot \frac{I_4^p}{I_4^s} + s_5 \cdot \frac{I_5^p}{I_5^s} \right| \cdot \Delta I_x^s +$$

$$+ \left| s_1 \cdot \frac{I_x^s}{I_1^s} \right| \cdot \Delta I_1^p + \left| - s_1 \cdot \frac{I_x^s \cdot I_1^p}{I_1^{s^2}} \right| \cdot \Delta I_1^s + \left| s_2 \cdot \frac{I_x^s}{I_2^s} \right| \cdot \Delta I_2^p +$$

$$+ \left| - s_2 \cdot \frac{I_x^s \cdot I_2^p}{I_2^{s^2}} \right| \cdot \Delta I_2^s + \left| s_3 \cdot \frac{I_x^s}{I_3^s} \right| \cdot \Delta I_3^p + \left| s_4 \cdot \frac{I_x^s}{I_4^s} \right| \cdot \Delta I_4^p +$$

$$+ \left| - s_3 \cdot \frac{I_x^s \cdot I_3^p}{I_3^{s^2}} \right| \cdot \Delta I_3^s + \left| - s_4 \cdot \frac{I_x^s \cdot I_4^p}{I_4^{s^2}} \right| \cdot \Delta I_4^s +$$

$$+ \left| s_5 \cdot \frac{I_x^s}{I_5^s} \right| \cdot \Delta I_5^p + \left| - s_5 \cdot \frac{I_x^s \cdot I_5^p}{I_5^{s^2}} \right| \cdot \Delta I_5^s \tag{14}$$

EXPERIMENTAL

The first part of our experiments was aimed at studying and completing the data in the literature. Our measurements were made with Carlo Erba Fractovap

Models C, D, GV and GI-452. In all cases flame-ionisation detection, nitrogen as carrier gas and oxygen and hydrogen as auxiliary gases were used. The introduction of mixtures was made with a Hamilton syringe. A recorder Speedomax G and W, 2.5 mV full-scale deflection, functioning with 5.08 cm/min paper-speed to diminish the error in the evaluation was used.

After having confirmed the suitability of the original ROHRSCHNEIDER equation, extensive investigations were started in connection with the new equation. As an example of the results for the new equation, the case of *iso*-propanol is given, as we had available most of the retention index data on different stationary phases for this substance.

TABLE I

SUBSTANCE-SPECIFIC FACTORS OF CYCLOHEXANE

Calculated using the following standards: *m*-diethylbenzene, *n*-hexanol, 2-hexanone, benzene and butyl butyrate at 100°.

s_1	s_2	s_3	s_4	s_5	$\sum\limits_{i=1}^{5} s_i$
1.339	−0.108	−0.635	−0.085	0.508	1.019

TABLE II

COMPARISON OF MEASURED AND CALCULATED DATA

Stationary phase	Retention index of cyclohexane (index units)		
	Measured[a]	Calculated	Deviation
Isooctyl decyl adipate	681.0	682.0	−1.0
Acetyl tributyl citrate	690.0	699.2	−9.2
PEG-1540	753.0	757.9	−4.9

[a] By McREYNOLDS[11].

TABLE III

SUBSTANCE-SPECIFIC FACTORS AND RETENTION INDEX OF BENZENE AT 120°

Substance-specific factors on DEGS						Retention index on DC-710 (index units)	
s_1	s_2	s_3	s_4	s_5	$\sum\limits_{i=1}^{5} s_i$	Measured[a]	Calculated
−0.295	0.992	0.424	−0.130	−0.013	0.978	760.0	761.2

[a] By McREYNOLDS[11].

TABLE IV

SUBSTANCE-SPECIFIC FACTORS OF *tert.*-BUTANOL AT 100°

Five standards recommended by ROHRSCHNEIDER.

s_1	s_2	s_3	s_4	s_5	$\sum_{i=1}^{5} s_i$
1.619	0.465	0.376	0.318	−1.769	1.009

TABLE V

MEASURED INDEX VALUES (INDEX UNITS)

$I^s_1 = 649.2$ $I^p_1 = 664.8$

$I^s_2 = 384.0$ $I^p_2 = 441.1$

$I^s_3 = 531.8$ $I^p_3 = 578.5$

$I^s_4 = 457.5$ $I^p_4 = 535.6$

$I^s_5 = 695.6$ $I^p_5 = 739.1$ $I^s_x = 471.3$

$\Delta I^s_1 = 0.45, \Delta I^s_2 = 1.06,$ $\Delta I^s_3 = 1.45, \Delta I^s_4 = 1.45,$ $\Delta I^s_5 = 0.82$

$\Delta I^p_1 = 0.82, \Delta I^p_2 = 1.21,$ $\Delta I^p_3 = 0.55, \Delta I^p_4 = 1.43,$ $\Delta I^p_5 = 0.39$

$\Delta I^s_x = 1.13$

To determine the substance-specific factors, data were obtained on the following stationary phases: squalane, DC-200, Apiezon L, neopentyl glycol succinate, PEG-4000 and diethylene glycol succinate.

With the help of the data obtained, five equations could be satisfied. Having solved this equation system, the following substance-specific factors were obtained: $s_1 = -0.152$, $s_2 = -0.078$, $s_3 = 0.542$, $s_4 = 0.503$ and $s_5 = 0.182$. The sum of these five substance-specific factors was calculated as 0.997.

As an example of a calculation using the new equation, the calculation of the retention index of *iso*-propanol on PEG-400 stationary phase is given:

$$I^{\text{PEG-400}}_{iso\text{-propanol}} (100°) = 431 [1.496 \times (-0.152) + 2.422 \times (-0.078) +$$
$$+ (1.727 \times 0.542) + (2.565 \times 0.503) + (1.725 \times 0.182)]$$
$$= 915.4 \text{ index units} \tag{15}$$

The value as measured by ROHRSCHNEIDER was 916.0 index units. We used in our experiment the five standard substances recommended by ROHRSCHNEIDER.

Table I demonstrates that the nature of the five standards can be altered. Some of the calculated values were compared with experimental data in Table II. From the data summarized in Table III we wished to demonstrate the usefulness of a non-squalane-based calculation system. Relying on the data of MCREYNOLDS[11] the following substances were used as standards: *cis*-hydrindane, 1-iodobutane, 2-methyl-2-pentanol, 2-pentanone and nitropropane.

From our calculations, the error during the determination of the retention index of *tert.*-butanol on DC-200 stationary phase was determined with the help of the data in Tables IV and V.

$$E_R \leqslant [(1.023 \times 1.619) + (1.146 \times 0.465) + (1.089 \times 0.376) +$$
$$+ (1.171 \times 0.318) - (1.063 \times 1.769)] \times 1.13 + [0.726 \times 1.619] \times 0.82 +$$
$$+ [0.743 \times 1.619] \times 0.45 + [1.227 \times 0.465] \times 1.21 +$$
$$+ [1.405 \times 0.465] \times 1.06 + [1.031 \times 0.318] \times 1.43 +$$
$$+ [0.965 \times 0.376] \times 1.16 + [0.887 \times 0.376] \times 0.55 +$$
$$+ [1.207 \times 0.318] \times 1.45 + [0.678 \times 1.769] \times 0.39 +$$
$$+ [0.721 \times 1.769] \times 0.82 = 7.3 \text{ index units.} \tag{16}$$

Summarizing the above, on the examples shown, the suitability of ROHR-SCHNEIDER's concept seems to be very good. But since for the determination of five substance-specific factors for a substance, 36 index values must be determined with the help of 144 experimentally measured values, it is clear that relatively exact factors can be obtained only from exact experimental results. Knowing that from 144 values, 120 can be used in the case of any substance (data for standard substances) and that the number of phases often used in practice is about 20, it would be worthwhile to determine these values in the most exact manner possible. Of course, this work could be carried out only after the further selection of the five standard substances.

Having carried out this work, the effectiveness of chromatogram planning could be greatly increased on the basis of ROHRSCHNEIDER's concept, and also the great advantages of using a computer for calculating techniques could be made possible in this field.

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