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CONTRIBUTION TO THE CONCEPT AND METHOD OF  
ROHRSCHNEIDER. I

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## SUMMARY

In the present paper we deal with ROHRSCHNEIDER's concept and method. ROHRSCHNEIDER has given a simple interpretation to the interactions between a substance and the stationary phase. McREYNOLDS<sup>2</sup>, in one of his latest papers, recommends for the characterization of the liquid phases the use of the retention index differences of ten standard substances. Without discussing this proposal in detail, some remarks must be made. Using ROHRSCHNEIDER's concept we can follow the change in the interactions from stationary phase to stationary phase.

## INTRODUCTION

Among the works dealing with this problem, the retention index system of KOVÁTS<sup>3</sup>, further developed over the last few years, has great importance and it seems to be suitable as a general method in gas chromatography.

Although some researchers in this field, *e.g.*, PIEROTTI *et al.*<sup>4</sup>, TENNEY<sup>5</sup>, WEHRLI AND KOVÁTS<sup>6</sup>, CHOVIN<sup>7</sup> and MARTIRE<sup>8</sup>, obtained remarkable results, in our opinion it was ROHRSCHNEIDER<sup>1</sup> who developed the general solution of the problem, giving a simple interpretation to the interactions between a substance and the stationary phase.

In the work of ROHRSCHNEIDER, a distinction must be made between the theoretical part and its practical applications. First, ROHRSCHNEIDER's concept should be discussed. In distinguishing between the interactions between an investigated material and the stationary phase from the point of view of polarity, the different pairs polar material/non-polar stationary phase and non-polar material/polar stationary phase must be distinguished, in addition to pairs with the same polarity, *viz.* polar material/polar stationary phase and non-polar material/non-polar stationary phase. The interaction forces in such coupling (dispersion or London forces, inductivity, orientation and filling-transfer forces, and hydrogen-bonds) can be differentiated as

*non-polar* (dispersion) and *polar* (the others) forces. When investigating a non-polar molecule or using a non-polar stationary phase, the interactions are determined by the dispersion forces.

ROHRSCHEIDER stated that when measuring the retention index of the same substance on a non-polar stationary phase (squalane) and on a polar stationary phase and calculating the difference in the data obtained, the following relation can be written:

$$\Delta I = I^P - I^S = ax + by + cz + du + es \quad (1)$$

where

$I^P$  = the retention index on a polar stationary phase;  $I^S$  = the retention index on the squalane stationary phase;  $x = \Delta I$  (Benzene):100;  $y = \Delta I$  (Ethanol):100;  $z = \Delta I$  (Methyl ethyl ketone):100;  $u = \Delta I$  (Nitromethane):100;  $s = \Delta I$  (Pyridine):100 and  $a, b, c, d$  and  $e$  are the ROHRSCHEIDER constants.

One of the components of the products to be added is characteristic for the substance to be examined; the other one is a polarity factor characterizing the stationary phase. It is well known, as ROHRSCHEIDER also showed, that all retention index values contain some measurement errors and these have an effect on the values for the substance obtained, *i.e.*, stationary phase-polarity characteristics. To study the effect of these errors, calculations were made with a computer, using the measured data.

Retention data were measured for eight different stationary phases. Feeding the corresponding data into the computer, a program was developed making possible the determination of the ROHRSCHEIDER constants for a wide range of stationary phases (252 cases).

The constants show a significant deviation, the cause of which is the variation in the size of the error made in the determination of the single index values. The deviation of the numerical values of the constants from the average was 3%.

The historical development of ROHRSCHEIDER's method (he first made calculations using three factors) poses the question as to whether the presently used five additive members are sufficient or not.

McREYNOLDS<sup>8</sup>, in one of his latest papers, recommends for the characterization of the liquid phases the use of the retention index differences of ten standard substances: benzene, butanol, 2-pentanone, nitropropane, pyridine, 2-methyl-2-pentanol, 1-iodo-butane, 2-octyne, 1,4-dioxan and *cis*-hydrindane.

Without discussing his proposal in detail, the following remarks must be made. There is a basic difference between ROHRSCHEIDER's method and McREYNOLDS's, which was developed after the ROHRSCHEIDER concept. While ROHRSCHEIDER's method is suitable not only for the characterization of the stationary phase polarity but also for the pre-calculation of the corresponding retention, the method of McREYNOLDS, although it may possibly be used for this pre-calculation, can be used in its present form only for the characterization of the liquid phase. Also the system consisting of five additive members recommended by ROHRSCHEIDER is enough to characterize the interaction relations formed and to pre-calculate the retention.

Because of the possibilities of the ROHRSCHEIDER concept, we considered his

method in detail. During this work it was found that it is better to study the interaction relations formed from the point of view of the substance to be investigated, rather than from the interaction forces.

This study was based on the supposition that the retention index consists of the following additive members<sup>9</sup>:

$$I = I_a + I_b + I_t \quad (2)$$

where

$I$  = the retention index under isothermal conditions;  $I_a$  = the atomic index contribution;  $I_b$  = the bond index contribution;  $I_t$  = the interaction index contribution.

The interaction index contribution consists of two additive members:

$$I_t = I_{ta} + I_{ti} \quad (3)$$

where

$I_{ta}$  = the average interaction index contribution;  $I_{ti}$  = the individual interaction index contribution.

The  $I_{ta}$  average interaction index contribution is the sequence of the dispersion forces; the  $I_{ti}$  individual interaction index contribution is the sequence of other interaction forces. From the last statement, it follows that  $I_{ti}$  is zero on a non-polar stationary phase.

Naturally, this does not mean that in the average interaction index contribution there are no material (individual) characteristics, since the interaction is formed in all cases between the investigated substance and the stationary phase.

The average interaction index contribution can be calculated from the following relation:

$$I_{ta} = 0.7455 I \quad (4)$$

Knowing that  $I_{ti} = 0$  for any substance on squalane as stationary phase,  $I_{ti}^P$  can be calculated as follows:

$$\Delta I = I^P - I^S = I_t^P - I_t^S = I_{ta}^P + I_{ti}^P - I_{ta}^S \quad (5)$$

Expressing  $I_{ti}^P$  from eqn. 5 and using eqn. 4:

$$I_{ti}^P = \Delta I + I_{ta}^S - I_{ta}^P = \Delta I - 0.7455 \Delta I = 0.2545 \Delta I \quad (6)$$

Thus, eqn. 6 means that if the value of  $\Delta I$  is known, the individual interaction contributions can be determined.

$\Delta I$  can be calculated even with ROHRSCHNEIDER's method. Therefore it can be written as:

$$\Delta I = \frac{I_{ti}^P(S)}{0.2545} = ax + by + cz + du + es \quad (7)$$

$$I_{ti}^P(S) = a \cdot 0.2545x + b \cdot 0.2545y + c \cdot 0.2545z + d \cdot 0.2545u + e \cdot 0.2545s \quad (8)$$

where (S) = substance.

And since:

$$0.2545x = \frac{0.2545\Delta I(\text{Benzene})}{100} = I_{tt}^P(\text{Benzene}) \quad (9)$$

$$0.2545y = \frac{0.2545\Delta I(\text{Ethanol})}{100} = I_{tt}^P(\text{Ethanol}) \quad (10)$$

$$0.2545z = \frac{0.2545\Delta I(\text{Methyl ethyl ketone})}{100} = I_{tt}^P(\text{Methyl ethyl ketone}) \quad (11)$$

$$0.2545u = \frac{0.2545\Delta I(\text{Nitromethane})}{100} = I_{tt}^P(\text{Nitromethane}) \quad (12)$$

$$0.2545s = \frac{0.2545\Delta I(\text{Pyridine})}{100} = I_{tt}^P(\text{Pyridine}) \quad (13)$$

eqn. 8 can be written as:

$$I_{tt}^P(s) = \frac{a \cdot I_{tt}^P(\text{Benzene})}{100} + \frac{b \cdot I_{tt}^P(\text{Ethanol})}{100} + \frac{c \cdot I_{tt}^P(\text{Methyl ethyl ketone})}{100} + \frac{d \cdot I_{tt}^P(\text{Nitromethane})}{100} + \frac{e \cdot I_{tt}^P(\text{Pyridine})}{100} \quad (14)$$

This means finally that the ROHRSCHEIDER concept makes the pre-calculation of retention data possible through the calculation of the individual interaction contributions using the individual interaction values of the five standard substances.

As an example, the calculation of the individual interaction value and retention index of *tert*.-butanol is shown on DC-710 stationary phase using the data in Table I.

TABLE I

THE DATA USED IN CALCULATING THE RETENTION INDEX OF *tert*.-BUTANOL ON DC-710 STATIONARY PHASE

Rohrschneider constants	$I_{tt}^{DC-710}(s)$	
	S	Value
$a = -11.42$	Benzene	26.72
$b = 76.51$	Ethanol	38.17
$c = 33.75$	Methyl ethyl ketone	40.97
$d = -12.77$	Nitromethane	63.88
$e = 0.21$	Pyridine	48.36

$$100I_{tt}^{DC-710}(\text{tert.-Butanol}) = (-11.42 \times 26.72) + (76.51 \times 38.17) \\ + (33.75 \times 40.97) + (-12.77 \times 63.88) \\ + (0.21 \times 48.36) = 3193.16.$$

From this:

$$I_{II}^{DC-710} (\text{tert.-Butanol}) = 31.93 = 0.25454 I$$

$$= 0.2545 I_{\text{tert.-Butanol}}^{DC-710} - (25.45 \times 471).$$

$$I_{\text{tert.-Butanol}}^{DC-710} = \frac{151.80}{0.2545} = 596.4 \text{ index units.}$$

TABLE II

THE AVERAGE AND INDIVIDUAL INTERACTION VALUES FOR BENZENE ON DIFFERENT STATIONARY PHASES AT 100.0°

Stationary phase	Average interaction value (index units)	Individual interaction value (index units)
Squalane	483.83	0.0
DC-200	495.01	3.82
Apiezon L	507.69	8.14
DC-710	562.11	26.72
Neopentyl glycol succinate	683.62	68.21
Carbowax 20M	720.90	80.93
Diethylene glycol succinate	851.36	125.47
1,2,3-tris(cyanoethoxypropane)	931.13	152.70

The measured value of  $I_{\text{tert.-butanol}}^{DC-710}$  is 594 index units. The deviation between the measured and calculated retention index values is 2.4 index units, which is a fairly good result. Using ROHRSCHNEIDER's concept we can follow the change in the interactions from stationary phase to stationary phase. As an example, the results for benzene are shown in Table II.

After our measurements and practical experience the error in calculating the index values (used in the ROHRSCHNEIDER equations) cannot be greater than one index unit.

Finally, we should like to deal with the question as to whether the five standard substances are suitable from the point of view of material quality. In this question, the opinion of McREYNOLDS coincides with practical experience, *i.e.*, the quality of the five standards used until now is not the best. At the same time, we should like to emphasize that the number and chemical quality of the standards is, in our opinion, optimal. The selection of the material quality of the five standard substances can be the result only of widespread theoretical and practical cooperation, and in this field we should like very much to cooperate with our Czech and Slovak colleagues.

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