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NEW CRITERION FOR POLARITY OF STATIONARY PHASES IN GAS CHROMATOGRAPHY

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SUMMARY

A criterion A is introduced for the classification of stationary phase polarity. It is evaluated from the ratio of retention time differences for adjacent n-alkanes: $A = (t'_{R_{n+1}} - t'_{R_n})/(t'_{R_n} - t'_{R_{n-1}})$. The polarity criterion A represents dispersive interactions of the methylene group with the stationary phase. Its depends on the structure and the number of functional groups in the stationary phase and its temperature: $A = a \exp(bT^{-1})$. The constants a and b have an unequivocal physical meaning, and allow the prediction of the polarity of a stationary phase at any temperature. The influence of pressure and carrier gas flow-rate on the polarity criterion A were found to be insignificant.

The high precision of the evaluation of criterion A leads to a high discrimination of stationary phase polarities. It allows the *in situ* control of the actual polarity of the stationary phase used and is thus a controlling parameter of the reliability of a separation system. Consequences for selection of stationary phases are discussed.

INTRODUCTION

After column efficiency, characterized by the height equivalent to a theoretical plate (HETP) and/or by the number of plates, the polarity of stationary phases is the next most important characteristic of a separation system. This is reflected by the fact that there are more than 350 different stationary phases commercially available.

Various criteria have been used for the classification of stationary phases[1–25]. The measurement of Kováts' retention indices[10] for particular stationary phases[11–13] is the method that is used most often. But these approaches evaluate only the selectivity of a stationary phase, in terms of the selective interactions of the selected solutes on a particular stationary phase. Recent attempts to develop a theoretically based classification system have focused on the utilization of various thermodynamic parameters for the description of solute–solvent interactions[19–23]. The experimental determination of the specific retention volumes, the determination of the average molecular weight of a stationary phase and establishing the purity of a stationary phase are limiting factors for the applicability of the mentioned approaches.

The measurement of the polarity of stationary phases, and its quantitative evaluation is of great importance for the practice and theory of gas chromatography

(GC). Because a stationary phase is not defined by means of a numerical description (*e.g.*, the molecular weight distribution of the stationary phase can vary within batches[17,18], the stationary phase can be oxidized, etc., but still be sold under the same name), large differences between retention indices are observed; *e.g.*, the retention index of 1-butanol in more than 40 % of 217 stationary phases differs by more than 10 retention index units[16].

The aim of this study was to establish a polarity criterion that will allow objective classification of the polarity of stationary phases and their mixtures in a single column technique (see, for example, refs. 26–29) or a multi-column technique (see, for example, refs. 30 and 31). A criterion should be stationary phase oriented only, generally valid and discriminatory, thermodynamically related (temperature, structure) and easy and precise to evaluate.

The method used fulfills the above requirements and permits the prediction of stationary phase polarity at different temperatures. Optimization of preferred stationary phases is indicated and, together with the solution of polarity in the temperature programmed mode, will be the subject of further study.

THEORETICAL

The retention behaviour of a solute on a particular stationary phase is a complex function of solute–solvent interactions. While the effective proportions of a particular interaction (dispersive, orientative, acid–base) and its temperature dependence are unknown, retention changes could not be linked with one variable only and the stationary phase classification is not rigorous.

Hydrocarbons exhibit only one type of interaction, namely dispersive. Their retention is determined by the additivity of the enthalpy, which differs for methyl and methylene groups. Therefore, the retention behaviour of *n*-alkanes is not fully correlated with the number of carbon atoms. This fact is verified by several bulk properties of *n*-alkanes, such as free energy, boiling point, density, refractive index and adjusted retention time.

The difference in retention times between adjacent *n*-alkanes gives the contribution of the methylene group only. It follows that

$$\Delta_{n+1} = t'_{R_{n+1}} - t'_{R_n} = t_{R_{n+1}} - t_{R_n} \tag{1}$$

$$\Delta_{n+1} = \frac{t_M}{\beta} \cdot e^{-\frac{\Delta G_{n+1}}{RT}} - \frac{t_M}{\beta} \cdot e^{-\frac{\Delta G_n}{RT}} \tag{2}$$

The ratio of neighbouring retention time differences is defined as the polarity criterion A:

$$A = \frac{\Delta_{n+1}}{\Delta_n} \tag{3}$$

After substitution of retention time differences by eqn. 2 and division by (t_M/β) exp $(-\Delta G_n/RT)$, the polarity criterion A could be rewritten in the form

$$A = \frac{e^{-(\Delta G_{n+1} - \Delta G_n)} - 1}{1 - e^{-(\Delta G_{n-1} - \Delta G_n)}} \tag{4}$$

Eqn. 4 demonstrates the physical meaning of the constant A. It shows the relative changes between adjacent n-alkanes with respect to a centrally positioned n-alkane with n carbon atoms. The exponential term expresses the contribution of one methylene group. With an increasing proportion of dispersive interactions of a solute–solvent pair, the free energy change of a methylene group becomes larger and consequently A will increase. Thus A is large for non-polar stationary phases, and with increasing polarity of stationary phase A decreases.

An implicit form of the stationary phase polarity criterion A expresses structural and temperature dependences. It follows that

$$A = a \, e^{bT^{-1}} \tag{5}$$

The constant a demonstrates static contributions related to the total number of functional group of a stationary phase and the constant b represents dynamic contributions related to the molecular movements of functional groups of a particular stationary phase. Thus, with increasing temperature the polarity of a stationary phase will increase (criterion A will decrease).

The polarity of a stationary phase is understood as a quantitative measure of dispersive interactions of the methylene group–stationary phase system. This criterion is a function of stationary phase variations only.

Selectivity describes the selective interactions, such as orientation, polarization and charge transfer, of a solute–solvent pair. The selectivity describes a minor part of the overall interactions (the retention index shift on a polar column is seldom greater than the retention index on a non-polar column) and is both solute and solvent specific. Therefore, there will be stationary phases of the same polarity (having the same proportion of dispersive interactions) and simultaneously of different selectivity (different proportions of selective interactions).

EXPERIMENTAL

Experiments were carried out on various columns. Stainless-steel packed columns (3 m × 2 mm I.D.) were packed with the following stationary phases coated on Chromosorb P AW (80–100 mesh); didecyl phthalate (7.42 %), tricresyl phosphate (10.32 %), ethylene glycol phthalate (10.32 %) and neopentyl glycol succinate (10.38 %). Glass packed columns (2 m × 2 mm I.D.) were packed with 5 % OV-101 on Chromosorb W (60–80 mesh) and 9.75 % SE-30 on Chromosorb W AW (80–100 mesh).

Stainless-steel, capillary columns were also used, as follows: 50 and 100 m × 0.20 mm I.D., coated with squalane; 50 m × 0.20 mm I.D., coated with OV-17; 50 m × 0.20 mm I.D., coated with Citroflex A 4; and 50 m × 0.20 mm I.D., coated with ethylene glycol adipate. A glass capillary column (22 m × 0.24 mm I.D.), coated with OV-101, was also used.

RESULTS AND DISCUSSION

Stationary phase polarity and polarity criterion A
Before starting the experiments, we examined published retention data.

Phthalate stationary phases were considered from the point of view of the solubility parameter model[32,33]. It has been found that the total solubility parameter is best correlated with dispersive parameters, whereas the orientation parameter is less correlated (see Fig. 1). It could be said that for phthalate stationary phases the dispersive parameter is redundant with total solubility parameter or, in other words, the dispersive interactions describe quantitatively the behaviour on phthalate stationary phases. A similar situation was observed for silicone stationary phases. The specific retention volumes of certain solutes (see Table I) have been correlated with the percentage of phenyl groups in a number of stationary phases from OV-101 to OV-25[34]. Table I demonstrates that the highest correlation coefficient is obtained for n-heptane, i.e., the dispersive interactions are dominant interactions for this type of stationary phase.
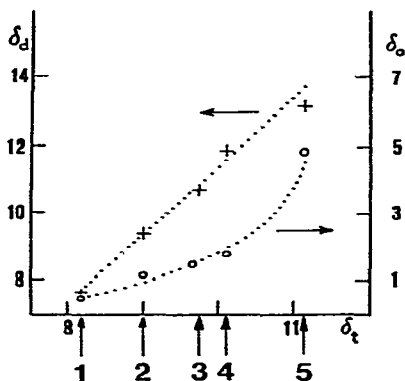

Fig. 1. Correlation of solubility parameters of stationary phases: 1 = dinonyl phthalate; 2 = dibutyl phthalate; 3 = diphenyl phthalate; 4 = dicyclohexyl phthalate; 5 = β,β'-oxydipropionitrile[32]. δ_t = overall solubility parameter; δ_d = dispersive solubility parameter; δ_o = orientation solubility parameter.

TABLE I

CORRELATION COEFFICIENTS FOR SPECIFIC RETENTION VOLUME OF SOLUTES AS A FUNCTION OF PERCENTAGE OF PHENYL GROUPS FOR SILICONE PHASES OV-101 TO OV-25

Original data from ref. 34.

Solute	Correlation coefficient
Benzene	0.5134
Nitromethane	0.9548
Acetone	0.7280
n-Heptane	−0.9746

To test the proposed criterion, packed and capillary columns were used. Criterion A was evaluated from the retention time differences for n-alkanes (see also refs. 35–37). The results are summarized in Table II. It can be seen that criterion A changes significantly between different stationary phases.

Fig. 2 gives a correlation plot of criterion A versus existing polarity criteria,

TABLE II

POLARITY CRITERION A OF VARIOUS STATIONARY PHASES AT DIFFERENT FLOW-RATES AND TEMPERATURES

Stationary phase	Column flow-rate (ml/min)	A				
		80°C	90°C	100°C	120°C	140°C
Didecyl	17			2.0226	1.8913	1.7795
phthalate	13				1.8868	
	17				1.8843	
	21.3				1.8892	
	25.5				1.8839	
Tricresyl	17	2.0766	1.9967	1.9252		
phosphate	13	2.0790				
	17	2.0764				
	21.3	2.0702				
	25.5	2.0677				
Neopentyl glycol succinate	17			1.7759	1.6611	1.5853
SE-30	17	2.1000		1.9400	1.8160	1.7170

such as relative retention $(t'_{C12}/t'_{C10})^{1/2}$ and $\Sigma \Delta I$. It can be seen that there is a high correlation for relative retention, whereas for the sum of the retention index shifts the low correlation can be explained by selective interactions. These interactions are not taken into account in the evaluation of criterion A.

Our results and conclusions are in agreement with those of previous studies[19-22,38], in which the interactions of n-alkanes with the stationary phase are seen as the most sensitive and universal criterion of stationary phase classification. The use of the relative retention of a fixed pair of n-alkanes, t'_{C10}/t'_{C8} (refs. 39 and 40) or $(t'_{C12}/t'_{C10})^{1/2}$ (ref. 15), has certain drawbacks. The retention of particular n-alkanes can, under particular experimental conditions (type stationary phase and experi-
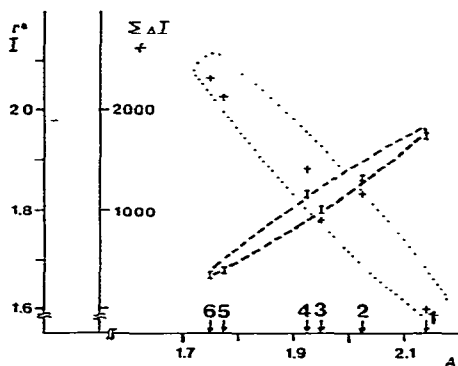

Fig. 2. Correlation plot of stationary phase polarity criteria: $r^* = (t'_{C12}/t'_{C10})^{1/2}$ (ref. 15), $\Sigma \Delta I$ (ref. 14) and proposed criterion A. 1 = Squalane; 2 = didecyl phthalate; 3 = OV-17; 4 = tricresyl phosphate; 5 = neopentyl glycol succinate; 6 = Carbowax 20M.

mental temperature), be either too short or too long. In spite of the fact that the relative retention is, according to definition, related to the free energy of the methylene group only, it has been shown[41] that the relative retention of short chain n-alkanes is a function of its chain length.

The polarity criterion A is related to relative retention according to the equation

$$A = r_n \cdot \frac{r_{n+1} - 1}{r_n - 1} \qquad (6)$$

The ratio on the right-hand side of eqn. 6 approaches unity with increasing chain length ($r_n \approx r_{n+1}$). Under this condition, criterion A is equal to the relative retention. Eqn. 6 indicates that the relative retention of n-alkanes increases with decreasing chain length for constant A.

The advantage of the evaluation of criterion A lies in the statistical significance of measurement with more n-alkanes in a mixture[35-37] and exclusion of the dead time measurement. The determination of criterion A does not need a special analytical run and can be carried out at any temperature.

Temperature dependence of criterion A

The temperature dependence of the polarity criterion A has been evaluated from the implicit form of eqn. 5. Characteristic values for different stationary phases

TABLE III

TEMPERATURE DEPENDENCE OF POLARITY CRITERION A FOR VARIOUS STATIONARY PHASES

$A = ae^{bT^{-1}}$. The numbers in parentheses indicate polarity order at the given temperature.

Stationary phase	a	b	A		
			$323°K$	$373°K$	$473°K$
Squalane	0.501	541.1	2.675 (1)	2.137 (1)	1.573 (1)
Citroflex A 4	0.499	525.5	2.539 (3)	2.042 (2)	1.516 (3)
Didecyl phthalate	0.539	493.1	2.481 (4)	2.022 (3)	1.529 (2)
OV-17	0.510	500.0	2.399 (6)	1.950 (4)	1.469 (5)
SE-30	0.524	489.5	2.385 (7)	1.947 (5)	1.475 (4)
Ethylene glycol phthalate	0.491	513.4	2.406 (5)	1.945 (6)	1.454 (6)
Tricresyl phosphate	0.506	498.3	2.367 (9)	1.925 (7)	1.451 (7)
OV-101	0.439	544.8	2.371 (8)	1.891 (8)	1.389 (8)
Ethylene glycol adipate	0.153	920.4	2.644 (2)	1.800 (9)	1.071 (10)
Neopentyl glycol succinate	0.547	438.2	2.124 (10)	1.771 (10)	1.381 (9)

are listed in Table III. The different values of the intercepts (constant *a*) and slopes (constant *b*) indicate that at certain temperatures different stationary phases will have the same polarity. This is demonstrated in Fig. 3. The practical consequences of this behaviour are known as "retention order" changes when applying a temperature programme mode. Relatively high selectivity changes within a narrow temperature range were found to be a powerful method in the separation of complex mixtures[42,43]. Fig. 4 shows the retention order on two columns in series maintained at different temperatures. The significant shift in the retention of butanol-1, octene-1 and toluene with respect to *n*-octane can be seen. The retention index shift for butanol-1 is positive, whereas it is negative for octene-1. It can be seen that selectivity is not a general criterion of the classification of stationary phases.
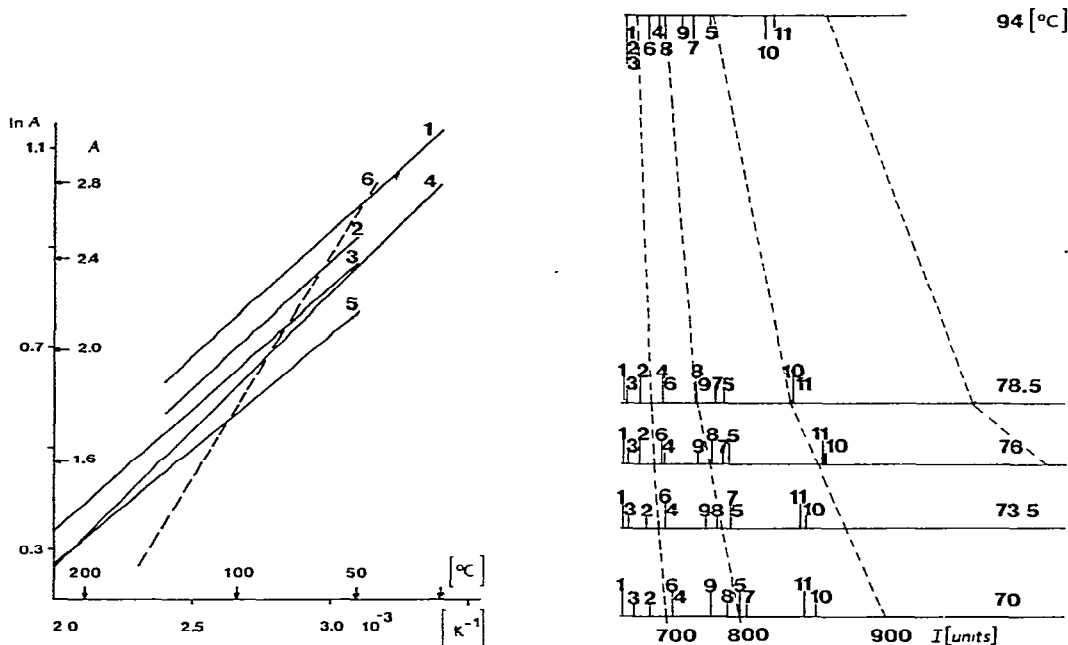
Fig. 3. Temperature dependence of polarity criterion *A* for various stationary phases: 1 = squalane; 2 = didecyl phthalate; 3 = SE-30; 4 = OV-101; 5 = neopentyl glycol succinate; 6 = ethylene glycol adipate.

Fig. 4. Elution order of various compounds with two columns in series held at different temperatures[43]. Carbowax HP at 70°C, OV-101 at indicated temperatures. Solutes: 1 = acetone; 2 = acetonitrile; 3 = diisopropyl ether; 4 = propanol-1; 5 = butanol-1; 6 = benzene; 7 = toluene; 8 = octene-1; 9 = dioxane; 10 = cyclopentanone; 11 = nitropropane.

The number of stationary phases required for general application in gas chromatography may be limited. Many attempts have been devoted to the selection of preferred stationary phases[44-53] and, in brief, each of the methods used found certain low correlated phases and discriminatory factors, which led to a maximum information content of the separation system. The main problem of the optimization methods is the origin of the data used, namely selectivity–retention index shifts. It has been shown that the sum of retention index shifts is not generally a valid criterion of

polarity of stationary phases and thus the superior stationary phases selected were limited to the original set of solutes used for optimization.

Polarity criterion A according to eqn. 5 offers optimization of stationary phases, only constants a and b in eqn. 5 needing evaluation. Columns of high, medium and low polarity with a small temperature dependence, and columns of low polarity with a high temperature gradient, can be selected. It is assumed that about six stationary phases will cover the overall polarity range.

Optimization carried out by means of criterion A shows that it is not desirable to use stationary phases with similar structures, because of their similar $\Delta G/T$ characteristics. These conclusions are in full agreement with the previous results correlating the retention index distribution on various stationary phases. Of ten stationary phases leading to a maximum information content, only two stationary phases with similar structures (phthalates) were used. A high correlation coefficient indicates an almost identical retention index distribution and thus no improvement in the information content when used simultaneously.

Flow-rate and pressure dependence of criterion A

The flow-rate and pressure dependence of A were measured as shown in Fig. 5. In the absence of a restriction after the column, the column outlet was at atmospheric pressure and the results with different flow-rates (see Table II) corresponded to GC conditions under different optimal flow-rates. It can be seen that there are no significant changes in A = f (flow-rate). This conclusion is in agreement with eqn. 5.
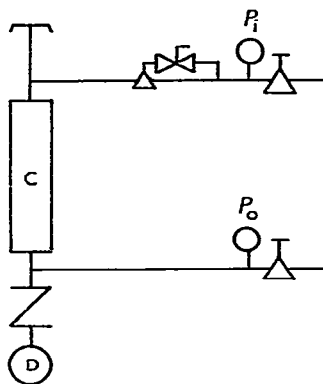

Fig. 5. Experimental arrangement for measurement of pressure dependence of polarity criterion A. P_i and P_0 are inlet and outlet pressures, respectively. Restriction in front of the detector is adjustable.

The influence of pressure on the retention characteristics of solutes has been reported in the literature since the early 1960s[54-59]. For a quantitative description of selectivity changes, the coefficient $\Delta I/\Delta P$ has been proposed[56]. In our experimental arrangement we evaluated criterion A at different mean pressures by adjusting the column outlet pressure to different values. Keeping the flow-rate constant, the ratio P_i/P_0 was changed. The results are summarized in Table IV.

It can be seen that there is no significant change in criterion A with changing mean pressure and pressure drop within given limits. The highest value of the coefficient of variation is 0.34 %, thus the possible changes in criterion A are smaller. This

TABLE IV

PRESSURE DEPENDENCE OF STATIONARY PHASE POLARITY CRITERION A

Didecyl phthalate at 120°C; constant flow-rate of 17 ml/min (measured at atmospheric pressure and 20°C).

Column pressure (bar)		P_i/P_0	A	S.D.
Inlet (P_i)	Outlet (P_0)			
3.23	1.05	3.08	1.8946	0.0055
3.7	2.0	1.85	1.8975	0.0064
4.3	3.0	1.43	1.8954	0.0042
6.6	5.5	1.20	1.8918	0.0011

is in agreement with the pressure dependence of the entropy (molecular volume changes are negligible). It follows that pressure changes do not influence the dispersion forces, but can lead to certain changes in the selectivity of interactions to which the retention index shift can be related.

Significance of changes of criterion A

It is shown here and by our previous results[35,36] that the precision of the evaluation of criterion A is very high. Even for repeated measurements over longer time intervals (for example, an EGA capillary column at 100°C gives $A = 1.7976$ and after 1 year $A = 1.7995$) the coefficient of variation does not exceed 1 %, with a characteristic value of 0.5 %. It is necessary to point out that these values include the possible changes in the polarity of the stationary phase (losses of the stationary phase and influence of the support materials, changes in the ambient temperature and pressure, of the carrier gas purity, etc.). The precision of criterion A evaluated between different n-alkanes in one analysis run is much better.

Criterion A changes with changing polarity of the stationary phase over the range 1.5–2.6, which is about 40 % of the span. Assuming that the difference in the polarities will be significant at a 99 % probability level, it holds that

$$\bar{A}_1 - \bar{A}_2 = 2.576v \tag{7}$$

where v is the coefficient of variation. Under the given conditions (constant temperature), criterion A will allow the classification of more than 30 polarity groups of stationary phases for gas–liquid chromatography. The temperature dependence of criterion A not only permits an adjustment of the polarity of a stationary phase, but is also a powerful classification parameter. The slope changes (constant b) are in the range 3–7 % and up to six significant slopes can be found for one value of A.

Therefore, with the proposed system, 200 stationary phases can be classified as being significantly different. The high precision, and thus the significance of the measured A value, helps to make correct conclusions in daily practice. The data in Table V show an increase in the elution time of methane and a simultaneous decrease in the elution time of n-butane[60]. After evaluation of A and direct calculation of the adjusted retention times, the initial hypothesis concerning the polarity change can be

rejected, and the correct conclusion about the decrease in the stationary phase load (decrease in the elution time of n-butane) and the decrease in the column permeability due to rearrangement of the support (increase in the elution time of methane) can be drawn. If the support material becomes active, the value of criterion A will change.

TABLE V

RETENTION TIMES FOR C_1 AND C_4 ALKANES[60] AND CALCULATED STATIONARY PHASE POLARITIES, A, ON 5% SQUALANE ON ALUMINA AT 50°C

Alkane	t_R (min) after			
	1 week	2 weeks	4 weeks	8 weeks
Methane	7.60	7.64	7.68	7.85
n-Butane	119.55	117.80	116.00	115.90
A	3.523	3.505	3.538	3.668

CONCLUSION

The polarity of stationary phases is characterized by means of the criterion A, which is ratio of the retention time differences for adjacent n-alkanes. The high precision of the evaluation of A yields a sensitive criterion of the stationary phase polarity. The evaluation is easy to carry out, as it requires only the evaluation of the retention time differences for adjacent n-alkanes (it is not necessary to know t'_R or the total t_R).

The temperature dependence of criterion A is described by eqn. 5 and allows the polarity to be calculated at any temperature. The constants a and b provide a quantitative description of stationary phase polarity.

It was shown that criterion A is independent of carrier gas flow-rate and pressure, and also of the chain length of n-alkanes, because it is related to dispersion forces of the methylene group only.

Criterion A differentiates between different structures of stationary phases (the number and origin of functional groups of a particular stationary phase will determine the proportion of dispersive interactions, and it is related to the constant a) and their temperature dependence (molecular movement of functional groups is related to the constant b). Criterion A is large for apolar phases and low temperatures, and decreases for stationary phases with a large number of selective functional groups and with increase in temperature.

Criterion A allows immediate (in situ) control of the polarity of the stationary phase used, and becomes an additional control parameter in experimental work. Constants a and b form a deterministic model of a stationary phase, which is mandatory if there is to be only a small ultimate uncertainty in the retention index identification[61]. High-precision measurements and the significance of retention indices and their changes gain a general understanding after checking the actual and claimed polarities of the stationary phase.

Optimization of superior stationary phases for gas–liquid chromatography and polarity changes in the temperature-programmed mode will be the subject of further study.

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