Chemometric Study of Retention on Binary Stationary Phases in Gas Chromatography

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Using gas chromatography, data analysis is performed on a dataset consisting of 486 retention indices, 27 standards (ramified alkanes, aliphatic alcohols, and aromatic compounds), 6 pure and binary stationary phases, and three temperatures. The behavior of the pure stationary phases (OV-3, OV-225, OV-61-OH, and OV-1701-OH) and the binary stationary phases (OV-3/OV-225 and OV-61-OH/OV-1701-OH) at different temperatures (60°C–100°C) is investigated with factor and topological analysis. The influence of temperature and the nature of the mixed stationary phases on the retention indices is studied by correspondence factor analysis (CFA). The non-additivity of the retention properties of the pure phases used as mixed phases is clearly established by CFA. The topological analysis of the substituent's effect is investigated with a DARC/PELCO procedure and shows the particular influence of the stationary phase composition on the retention. The substituent effect is measured for the pure and binary stationary phases at various temperatures. The evolution of the substituent effect from the pure stationary phases to the binary phases is discussed.

Introduction

For a few years, two-dimensional gas chromatography (GC×GC) has opened new prospects for the separation of complex samples. In the most recent studies in GC×GC (1), the two columns contain stationary phases of different polarity. The first column preferentially consists of a non-polar stationary phase, while the second column contains a polar stationary phase (2). The benefit of these orthogonal systems is to allow the first separation ordered of the solutes according to the same physicochemical property, which is often their volatility. The second dimension is related to the separation of each group of solutes on a stationary phase, offering a mechanism of interaction. The choice of the various stationary phases of two dimensions is of course crucial. For example, Cordero et al. (3) proposed to use for the first column a non-polar phase (OV-1) and, for the second column, a mixed stationary phase resulting from a binary mixture of phase CW20M (polyethylene glycol) and OV-1 in a ratio between 25% and 75%. The authors underlined the great interest of the use of a mixed phase in the second dimension, particularly for the analysis of polar compounds. Indeed, according to the authors, the mixed phases make it not only possible to modify the selectivity, but also the efficiency by improving the kinetics of the mass transfer of the compound between the gas phase and the liquid phase. The use of the mixed phases is not reserved for the two-dimensional GC; they can also be implemented for one-dimensional separation. For example, the mixed phases can be of a remarkable contribution for multiple chiral separations (4–7). In the same way, the ionic liquid mixtures constituting the stationary phases described by Baltazar et al. (8) have proved very promising because of the simple control of the selectivity by the mixture of the liquid phases. In the one-dimensional applications, the mixed phases propose the unique advantage of being able to vary the selectivity while playing on the mixture of the pure phases. According to Zenkevich and Makarov (9), the combination of the two pure phases allows for inaccessible selectivity to be reached with pure phases. The authors have showed how stationary phases consisting of binary mixtures can be characterized by predicting their McReynolds constants. However, it was established in the past that the properties of the mixed phases did not always result in a simple linear combination from the properties of the pure phases (10). This non-additivity of the properties of the phases can be due to their physico-chemical interactions or their low mutual solubilities.

The purpose of this study was to characterize the lack of additivity of the properties of pure stationary phases on the retention of the standards during the use of binary mixtures of phases at various temperatures. For the successful treatment of the retention data, a chemometric technique was used (11, 12). This chemometric procedure has already been employed in chromatography for the identification of the basic factors influencing retention and separation; the comparison of various pure and binary phases and the assessment of the relationship between the molecular structure and the retention behavior (13–17). In this study, retention indices of congeneric series of ramified alkanes, aliphatic alcohols, and aromatic compounds have been calculated on several polymethylphenylsiloxane pure and binary fill materials impregnated on a glass capillary column (18) at a low temperature range of 60°C to 100°C. The retention indices were obtained starting from the mathematical method, the multiparametric least-squares non−linear adjustment (MP) (19–23), developed for the isothermal calculation of retention indices. In the first part, the behavior of the compounds was investigated by using the correspondence factor analysis method (CFA) (24, 25) as a potential tool for evaluating the experiments on pure and binary system phases. In the second part, the effect of the temperature on the retention was examined by topological analysis (26).

Experimental

The chromatographic experiments were carried out on Hewlett-Packard Model 6890 gas chromatograph (GC) with a dual flame ionisation detector (FID), a split/splitless injector, and an HP 3395 recorder (Palo Alto, CA). The carrier gas was helium with an average flow rate of 1 mL/min. The measurements were performed isothermally at oven temperatures

ranging from 60°C to 100°C, in 20°C steps. The injector and detector port temperatures were 250°C.

The glass capillary columns were made of borosilicate glass (30 m × 0.25 mm, i.d.). After etching, according to the method of Franken (27), and deactivation with carbowax (20 M), the capillary was coated dynamically with a 10% solution of stationary phase in chloroform.

Six glass capillary columns were prepared and investigated. Four capillary columns were coated with pure polysiloxane phase OV-3 (10% phenyl, methyl; viscosity 500 mPa.s), OV-225 (25% cyanopropyl, 25% phenyl, methyl; viscosity 9000 mPa.s), OV-61-OH (OH-terminated polysiloxane, 33% phenyl, methyl; 19900 mPa.s), and OV-1701-OH [OH-terminated polysiloxane (7% cyanopropyl, 5% phenyl, methyl; viscosity 5300 mPa.s]. Two columns were coated with the binary phases OV-3 and OV-225 for the first, and OV-61-OH and OV-1701-OH for the second. The binary stationary phases were prepared in an equimolar percentage starting from the pure phases. The OV stationary phases (OV-3, OV-225, OV-61-OH, and OV-1701-OH) were purchased from Ohio Valley Specialty Chemical Company (Marietta, Marietta, OH).

The n-alkanes (C_6–C_{14} chromatographic reagent grade), the ramified alkanes, aliphatic alcohols, and the aromatic compounds were selected as congeneric series. All these solutes were obtained from VWR (Paris, France).

Calculation of retention indices: method

To obtain a more accurate estimation of retention indices, a multiparametric (MP) iterative non-linear least-squares method was applied. Under the assumption of linearity as described by Equation 1:

$$\ln(t_{ri} - t_M) = b.Z_i + c$$

Where Z_i and t_{Ri} are the carbon number and the uncorrected retention time of the i-th n-alkane examined. In addition to the dead time (t_M) calculation, equation 1 permits the determination of the slope (b) and the intercept (c) of the n-alkane retention time curve.

The multiparametric iterative non-linear least-squares adjustment method (MP) is based on equation 2:

$$T_r = t_m + A.e^{BZi}$$

$$B = b\ln 10$$

$$A = e^c$$

From these equations one can obtain reliable estimations of the standard deviations for the parameters (t_M, b, and c), and the derived quantities (corrected retention times and the retention indices) are obtained by a usual error propagation formula.

Finally, the retention indices are calculated using equation 3:

$$I_i = (100/B)\ln[(t_{Ri} - t_M)/A]$$

CFA of the retention indices

The factorial analysis of the correspondences is an alternative of the simple factorial analysis in which the data are weighted in line or column by the respective marginal values (24). The original matrix of data is transformed into a normalized matrix. This standardization makes it possible to represent the data in line or column in the same factorial space, and to analyze the graphs defined by the first two factorial axes by considering the relative positions of the solutes and the stationary phases. The essential advantage of the CFA is to focus the study on the selectivity, or the variation of the selectivity between the various studied chromatographic systems (25). The indices calculated with MP method are gathered in order to obtain a complete table of 27 lines and 18 columns representing the 27 compounds and 6 phases OV-3, OV-225, OV-61-OH, and OV-1701-OH, and the binary phases studied at the three temperatures 60°C, 80°C, and 100°C.

Topological analysis

The environment of each compound is described starting from an origin taken as the focus in accordance with the DARC system (Description, Acquisition, Retrieval, and Computer-aided design) combined with a PELCO (Perturbation of an Environment Limited, Concentric and Ordered) procedure (26).

The influence of each substituent on the retention indices is calculated in the form of a perturbation term corresponding to the formal replacement of a hydrogen atom by the substituent. The evaluation of the perturbation term is done on a statistical basis and is an average one, taking into account all the compounds in which the substituent is found.

Results and Discussion

Data analysis of retention indices of pure and binary phases

Three independent data matrices are studied. The first gathers the whole retention data relating to the 27 compounds and the 6 phases studied at three temperatures: 60°C, 80°C, and 100°C. The second study is focused on the retention of the compounds on two non-polar phases, OV-3 and OV-225, as well as the binary phase at the three described temperatures. Finally, the third matrix relates to the retention data of the compounds on polar phases OV-61-OH and OV-1701-OH like on the binary phase, measured at three temperatures. The labels of the compounds and the phases at the various temperatures are given in Tables I and II.

Table I

Labels of Compounds

Compounds	Labels	Compounds	Labels	Compounds	Labels
2,4-Dimethyl pentane	C5-1	Benzene	AR-1	1-Propanol	C3OH-1
3-Ethyl pentane	C5-2	Methyl benzene	AR-2	1-Butanol	C4OH-1
2,2-Dimethyl hexane	C6-1	Ethyl benzene	AR-3	2-Butanol	C4OH-2
2,4-Dimethyl hexane	C6-2	Propyl benzene	AR-4	Iso-butanol	C4OH-3
3,4-Dimethyl hexane	C6-3	o-Xylene	AR-5	2-Pentanol	C5OH-1
3-Ethyl hexane	C6-4	m-Xylene	AR-6	3-Pentanol	C5OH-2
2,2,3-Trimethyl pentane	C5-3	p-Xylene	AR-7	3-Methyl butanol	C4OH-4
2,3,4- Trimethyl pentane	C5-4			1-Hexanol	C6OH-1
2-Methyl heptane	C7-1			1-Heptanol	C7OH-1
3-Methyl heptane	C7-2				
4-Methyl heptane	C7-3				

The result of the first matrix analysis is represented in Figure 1. The first factorial plane shows that the first axis is defined by the two phases, OV-3 and OV-225. The phase OV-3 is projected on the right part, and the phase OV-225 is projected on the opposite one, at three temperatures: 60°C, 80°C, and 100°C. These two phases define the first factorial axis, which represents 74.15% of the information content, and the second one represents 13.63% of the total informational content. The second axis is mainly defined by phases OV-61-OH and OV-1701-OH, which are projected on both sides of Axis 2. The effect of the temperature contributes to the inertia described by this second axis. The whole of the pure and mixed phases associated with the temperature 100°C are projected systematically, contrary to the phases of comparable nature, which are associated with 60°C. The combinations of phases OV-3 and OV-225 are projected in the center of Axis 1. The effect of the temperature is more noticeable on the mixed phase than on the pure phases. Indeed, it can be noted that the projections of the pure phases at various temperatures are not different according to the second factorial axis. A first property relating to the mixed phase OV-3/OV-225 shows its selectivity, modified by the temperature, which is more

important than the pure phases. The same observation can be made with the phases OV-61-OH and OV-1701-OH. Projections of the binary phase are extended along the second axis, compared with those of the pure phases; this shows a noticeable effect of the temperature on the binary phase compared with that on the pure phases. The compounds are projected along the first axis according to their polarity. The side phase, OV-3, is alkanes are located, whereas in the side phase, OV-225, is where alcohols and the most polar compounds are situated. The aromatic compounds do not take part significantly in the inertia of the first axis. They are projected along the second axis. For example, benzene (AR-1) has a contribution to the inertia of 2.3% in the first axis and of 43% on the second one. This reflects a greater sensitivity relating to the aromatic compounds under the effect of the temperature compared to alcohols and alkanes. The difference in behavior between the various phases will be studied more in-depth during the data analysis of the sub-matrices relating to phases systems OV-3/OV-225 and OV-61-OH/OV-1701-OH.

Factorial analysis limited to the pure and mixed phases, OV-3 and OV-225, led to the results represented in Figure 2. The first factorial plane, representing 94.33% of the informational contents, is identical to that of the analysis of the whole phases (Figure 2). The pure phases defines the first factorial axis. Alcohols are projected near the OV-225 phase, and the alkanes are projected near the OV-3 phase. The systems relating to the mixed phase are projected near the origin value of Axis 1. They do not take part in the inertia on the first axis. This phase presents a behavior resulting from an additive combination of the two pure phases. The second axis represents the effect of the temperature, as stated previously. It should be noted that the aromatic compounds define mainly the second axis within, particularly the propyl benzene (AR-4), which has a contribution of 51.7% to the inertia explained by the second axis. This confirms the characteristic of the retention mechanism observed on the mixed phase. The effect of the temperature is noted more with the mixed phase than the pure phases.

The results obtained on the pure phases OV-61-OH, OV-1701-OH, and on the binary phase are illustrated in Figure 3. The first factorial plane accounts for only 79.40% of the informational contents, 64.0% and 15.40% on the first and second axes, respectively. The first axis is defined by the two

Table II
Labels of the phases at various temperatures

| Labels	Phases	Temperatures (°C)
3-60	OV-3	60
3-80	OV-3	80
3-100	OV-3	100
225-60	OV-225	60
225-80	OV-225	80
225-100	OV-225	100
3 / 225-60	OV-3 / OV-225	60
3 / 225-80	OV-3 / OV-225	80
3 / 225-100	OV-3 / OV-225	100
61-60	OV-61-OH	60
61-80	OV-61-OH	80
61-100	OV-61-OH	100
1701-60	OV-1701-OH	60
1701-80	OV-1701-OH	80
1701-100	OV-1701-OH	100
61-1701-60	OV-61-OH / OV-1701-OH	60
61-1701-80	OV-61-OH / OV-1701-OH	80
61-1701-100	OV-61-OH / OV-1701-OH	100
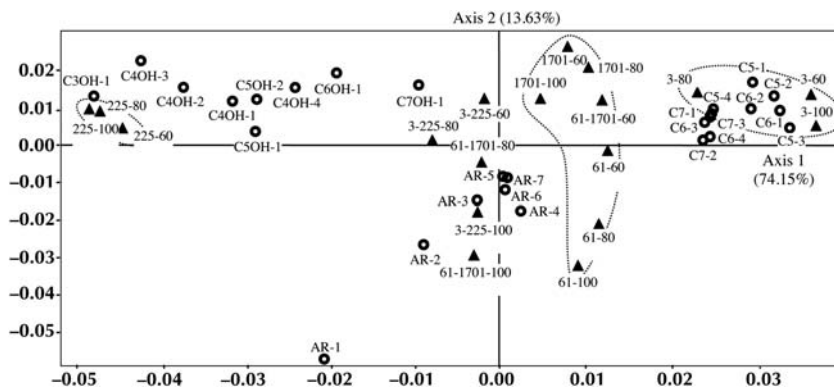
Figure 1. Correspondence factor analysis of the retention indices, measured on the pure phases OV-3, OV-225, OV-61-OH, and OV-1701-OH, and on the binary phases OV-3/OV-225 and OV-61-OH/OV-1701-OH at 60°C, 80°C, and 100°C. Projection of the compounds (●) and the phases (▲) on the first factorial plane, which accounts for 87.78% of the total information content. For labels, see Tables I and II.

pure phases projected on both axis sides. System OV-61-OH is projected according to its temperature in the axis center (60°C) and at its extremity (100°C). System OV-1701-OH is projected towards the opposite extremity. The system at 100°C is closest to the center, and it is the most distant at 60°C.

On the second axis, systems OV-61-OH and OV-1701-OH are projected according to the same order of temperature 60°C, 80°C, and 100°C. The systems with mixed phase are projected in an unexpected way. The system at 100°C, which contributes for 24.7% to the inertia, is projected at the end of Axis 1, close to phase OV-61-OH at 100°C, which has a closest contribution of 20.5%. The system at 60°C is projected at the opposite and at the extremity of the pure phase OV-1701-OH, with a contribution close to the system at 100°C. The system at 80°C has very weak contribution (0.9%) to the inertia explained by Axis 1. On the other hand, it contributes for 24.7% to the inertia explained by Axis 2. Moreover, it is projected on Axis 2, contrary to the system OV-61-OH at 80°C, which has a contribution of 27.6%. From these observations, it comes out that the mixed phase has a different behavior from what was expected. The combination of the chromatographic properties observed on the pure phases is not additive. Indeed, when the mixed phase is used at a low temperature, the compound's retention is correlated to that of the pure phase, OV-1701-OH, independently of the pure phase

OV-61-OH temperature. On the other hand, when the binary phase is used at 100°C, the compounds retention is correlated with that observed on the pure phase OV-61-OH at the same temperature. The mixed phase seems to behave in a similar way as the pure phase OV-1701-OH when this latter is used at a low temperature. However, the mixed phase behaves in an identical way when the pure phase OV-61-OH is used at a high temperature. This observation is illustrated by the variation of the correlation coefficients between the indices obtained on the pure phases and the ones obtained on the mixed phase at various temperatures (Table III).

The best correlation between the retention indices measured with the mixed phase OV-61OH/OV-1701-OH and those measured with the pure phase OV-61-OH, is obtained at 100°C ($r^2 = 0.973$; $t = 30.28$). This indicates that, at high temperature, the behavior of the compounds on the mixed phase is similar to that observed in the pure phase. At 60°C, the behavior of these compounds on these two phases are different, and the correlation coefficients are below 0.95. Considering the determined correlation coefficients between the retention indices measured with the binary phase at 100°C and those measured with the pure phase OV-1701-OH at three temperatures, the retention of the compounds on the mixed phase is not correlated to that observed with the pure phase, OV-1701-OH.
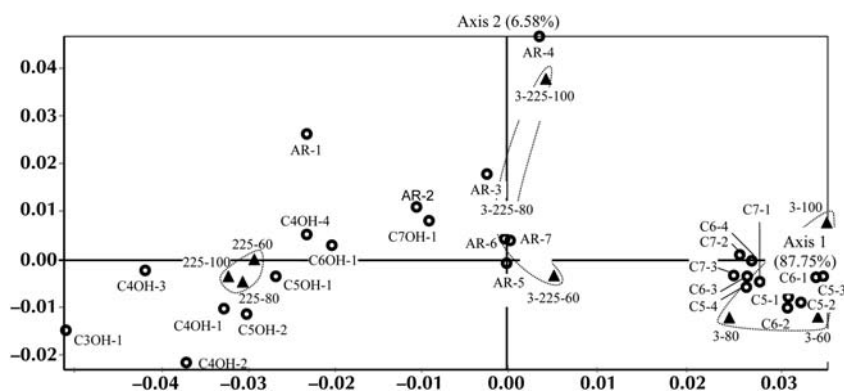
Figure 2. Correspondence factor analysis of the retention indices, measured on the pure phases OV-3 and OV-225, and on the binary phases OV-3/OV-225 at 60°C, 80°C, and 100°C. Projection of the compounds (●) and the phases (▲) on the first factorial plane, which accounts for 94.33% of the total information content. For labels, see Tables I and II.
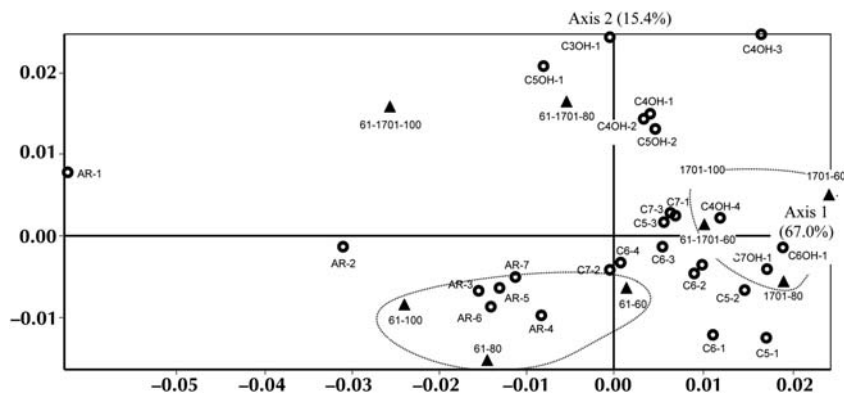
Figure 3. Correspondence factor analysis of the retention indices, measured on the pure phases OV-61-OH and OV-1701-OH, and on the binary phases OV-61-OH/OV-1701-OH at 60°C, 80°C, and 100°C. Projection of the compounds (●) and the phases (▲) on the first factorial plane, which accounts for 82.40% of the total information content. For labels, see Tables I and II.

The binary phase has a good correlation with the pure phase OV-61-OH used at the same low temperature with the correlation coefficient of the retention indices of 0.984 (t = 40.315). When the temperature of the pure phases increases, the correlation between the retention indices measured on the binary phase and the pure phase becomes more important with the pure phase, OV-1701-OH.

Thus, at a high temperature, the mixed phase has a contribution to the retention identical to that of the phase OV-61-OH at 100°C. However, at low temperature, the binary phase has a contribution to the retention identical to that of pure phases OV-61-OH (60°C) and OV-1701-OH (100°C).

Topological analysis

The perturbation terms were calculated (Tables IV–VI) with the retention indices measured for each congeneric series of compounds, alkanes, aromatics, and alcohols (Figure 4), on each pure and binary stationary phase at three temperatures: 60°C, 80°C, and 100°C. The influence of the binary phase on the variation of the perturbation terms is investigated with the stationary phases systems OV-3/OV-225 and OV-61-OH/OV-1701-OH.

With the system of phase OV-3/OV-225, the variation of the perturbation terms according to the temperature are examined. For the alkanes on phase OV-3, the perturbation terms increase by 8% to 12% when the temperature is increased by 60°C to 100°C. The same observation can be made with phase OV-225, but the increased perturbation terms increased on phase OV-3, but decreased on OV-225 and the binary phases. By considering the whole of the compounds, the binary phase is interesting at a low temperature because of the alkanes; it behaves like phase OV-3. For the alcohols, perturbation terms are slightly higher than those measured on the non-polar phase, OV-3. The terms are weak in the surrounding of 2%. The evolution of the perturbation terms on the binary phase made up of the two pure phases follows a similar progression with an increase of 3% to 6%. At a high temperature, the perturbation terms on the binary phase are lower than those measured on the pure phases. On the binary phase, the sensitivity related to different substituents decreases with the temperature. For aromatic derivatives, the fluctuations are weaker on the three phases. The perturbation terms values of the binary phase are between OV-3 and OV-225. It is noteworthy that a high value of the perturbation term CB (C3H7) at 100°C is obtained on the binary phase, this value is greater than those measured on the two pure phases. With regard to the polar compounds, the

Table III

Values of Correlation Coefficients (r^2) and Student's t test (t) Between the Retention Indices Measured on the Pure and Binary Phases OV-61-OH/OV-1701-OH at Various Temperatures

		Binary phase OV-61-OH/OV-1701-OH					
		60°C		80°C		100°C	
Pure phases		r^2	t	r^2	t	r^2	t
OV-61-OH	60°C	**0.9849**	40,31	0.9628	25,43	0.9126	16,15
OV-61-OH	80°C	0.954	22,77	0.9494	21,64	0.9472	21,18
OV-61-OH	100°C	0.9116	16,06	0.9388	19,58	**0.973**	30,02
OV-1701-OH	60°C	0.9693	28,1	0.9127	16,17	0.7895	9,68
OV-1701-OH	80°C	0.969	27,93	0.9232	17,33	0.8105	10,33
OV-1701-OH	100°C	**0.9897**	48,94	0.9677	27,37	0.8827	13,71

Table IV

Perturbation Terms Expressed in Unit of Retention Index and Bracketed as a Percentage of Alkanes Measured on Pure Phases OV-3, OV-225, OV-61-OH, OV-1701-OH, and on Binary Phases OV-3/OV-225, OV-61-OH / OV-1701-OH at Three Temperatures 60°C, 80°C, and 100°C. Pentane Indicates the Retention Index of the Focus.

60°C	OV-3		OV-225		OV-61-OH		OV-1701-OH		OV-3 / OV-225		OV-61-OH / OV-1701-OH	
Pentane	480		473		417		410		541		420	
A_P (CH$_3$)	85	(18)	80	(17)	102	(25)	103	(25)	66	(12)	100	(24)
B_P (C$_2$H$_5$)	204	(43)	210	(44)	263	(63)	266	(65)	184	(34)	259	(62)
C_P (CH$_3$)	89	(19)	80	(17)	110	(26)	115	(28)	77	(14)	111	(27)
D_P (CH$_3$)	71	(15)	61	(13)	66	(16)	97	(24)	63	(12)	93	(22)
E_P (CH$_3$)	106	(22)	118	(25)	135	(32)	131	(32)	91	(17)	127	(30)
F_P (CH$_3$)	98	(20)	96	(20)	110	(27)	102	(25)	77	(14)	107	(26)
G_P (CH$_3$)	108	(22)	114	(24)	142	(34)	140	(34)	101	(19)	136	(32)
80°C	**OV-3**		**OV-225**		**OV-61OH**		**OV-1701-OH**		**OV-3 / OV-225**		**OV-61-OH / OV-1701-OH**	
Pentane	456		464		409		452		337		441	
A_P (CH$_3$)	87	(18)	78	(17)	106	(25)	80	(20)	120	(22)	92	(22)
B_P (C$_2$H$_5$)	229	(48)	203	(43)	267	(64)	220	(54)	315	(58)	247	(59)
C_P (CH$_3$)	91	(19)	79	(17)	114	(27)	85	(21)	135	(25)	104	(25)
D_P (CH$_3$)	68	(14)	53	(11)	67	(16)	72	(17)	108	(20)	74	(18)
E_P (CH$_3$)	111	(23)	119	(25)	139	(33)	119	(29)	159	(29)	125	(30)
F_P (CH$_3$)	91	(19)	92	(19)	116	(28)	104	(25)	126	(23)	92	(22)
G_P (CH$_3$)	122	(25)	111	(23)	148	(36)	113	(27)	175	(32)	131	(31)
100°C	**OV-3**		**OV-225**		**OV-61OH**		**OV-1701-OH**		**OV-3 / OV-225**		**OV-61-OH / OV-1701-OH**	
Pentane	358		429		408		408		399		451	
A_P (CH$_3$)	116	(24)	87	(18)	102	(25)	102	(25)	111	(21)	93	(22)
B_P (C$_2$H$_5$)	299	(62)	235	(50)	270	(65)	263	(64)	303	(56)	235	(56)
C_P (CH$_3$)	117	(24)	94	(20)	112	(27)	105	(25)	124	(23)	101	(24)
D_P (CH$_3$)	85	(18)	73	(16)	60	(14)	78	(19)	103	(19)	70	(17)
E_P (CH$_3$)	149	(31)	124	(26)	145	(35)	140	(34)	152	(28)	119	(28)
F_P (CH$_3$)	113	(24)	107	(23)	122	(29)	116	(28)	115	(21)	87	(21)
G_P (CH$_3$)	170	(35)	129	(27)	153	(37)	136	(33)	164	(30)	127	(30)

60°C	OV-3		OV-225		OV-61-OH		OV-1701-OH		OV-3 / OV-225		OV-61-OH / OV-1701-OH	
Benzene	659		732		863		733		748		648	
A_B (CH_3)	112	(17)	105	(14)	86	(10)	99	(13)	98	(13)	151	(23)
B_B (C_2H_5)	207	(31)	200	(27)	172	(20)	202	(28)	179	(24)	257	(40)
C_B (C_3H_7)	301	(46)	285	(39)	248	(29)	293	(40)	267	(36)	349	(54)
D_B (CH_3)	142	(22)	132	(18)	125	(15)	136	(19)	117	(16)	148	(23)
E_B (CH_3)	115	(17)	106	(14)	95	(11)	108	(15)	92	(12)	111	(17)
F_B (CH_3)	110	(17)	103	(14)	93	(11)	95	(13)	91	(12)	116	(18)
80°C	OV-3		OV-225		OV-61OH		OV-1701-OH		OV-3 / OV-225		OV-61-OH / OV-1701-OH	
Benzene	667		763		868		787		783		676	
A_B (CH_3)	104	(16)	103	(14)	69	(8)	79	(11)	67	(9)	134	(21)
B_B (C_2H_5)	216	(33)	180	(25)	153	(18)	172	(23)	146	(20)	232	(36)
C_B (C_3H_7)	295	(45)	257	(35)	242	(28)	253	(34)	228	(30)	328	(51)
D_B (CH_3)	145	(22)	104	(14)	139	(16)	125	(17)	116	(16)	142	(22)
E_B (CH_3)	121	(18)	86	(12)	95	(11)	96	(13)	85	(11)	116	(18)
F_B (CH_3)	117	(18)	81	(11)	89	(10)	91	(12)	82	(11)	111	(17)
100°C	OV-3		OV-225		OV-61OH		OV-1701-OH		OV-3 / OV-225		OV-61-OH / OV-1701-OH	
Benzene	635		799		851		832		891		720	
A_B (CH_3)	127	(19)	59	(8)	111	(13)	76	(10)	57	(8)	100	(15)
B_B (C_2H_5)	238	(36)	182	(25)	209	(24)	135	(18)	116	(15)	202	(31)
C_B (C_3H_7)	320	(48)	383	(52)	273	(32)	217	(30)	183	(24)	295	(45)
D_B (CH_3)	142	(22)	100	(14)	98	(11)	101	(14)	93	(12)	146	(23)
E_B (CH_3)	115	(18)	87	(12)	72	(8)	71	(10)	59	(8)	107	(16)
F_B (CH_3)	102	(15)	83	(11)	57	(7)	54	(7)	57	(8)	107	(17)

60°C	OV-3		OV-225		OV-61-OH		OV-1701-OH		OV-3 / OV-225		OH	
Propanol	621		684		853		658		692		678	
A_O (CH_3)	78	(13)	122	(18)	87	(10)	90	(14)	93	(13)	113	(17)
B_O (CH_3)	59	(10)	64	(9)	69	(8)	63	(10)	68	(10)	63	(9)
C_O (C_3H_7)	264	(43)	320	(47)	289	(34)	293	(44)	295	(43)	311	(46)
D_O (C_4H_9)	381	(61)	415	(61)	381	(45)	394	(60)	392	(57)	413	(61)
E_O (CH_3)	32	(5)	108	(16)	61	(7)	63	(10)	57	(8)	64	(9)
F_O (CH_3)	27	(4)	24	(4)	22	(3)	29	(4)	26	(4)	12	(2)
G_O (CH_3)	97	(16)	134	(20)	98	(11)	113	(17)	119	(17)	120	(18)
80°C	OV-3		OV-225		OV-61OH		OV-1701-OH		OV-3 /OV-225		OH	
Propanol	626		689		868		652		693		679	
A_O (CH_3)	66	(11)	115	(17)	82	(10)	87	(13)	80	(12)	64	(10)
B_O (CH_3)	90	(15)	71	(10)	60	(7)	91	(14)	58	(8)	102	(15)
C_O (C_3H_7)	282	(45)	307	(45)	270	(32)	298	(45)	278	(40)	304	(45)
D_O (C_4H_9)	376	(61)	414	(60)	372	(44)	403	(61)	376	(54)	409	(60)
E_O (CH_3)	37	(6)	86	(13)	70	(8)	32	(5)	71	(10)	59	(9)
F_O (CH_3)	83	(13)	26	(4)	28	(3)	23	(3)	29	(4)	7	(1)
G_O (CH_3)	106	(17)	130	(19)	99	(12)	103	(16)	102	(15)	115	(17)
100°C	OV-3		OV-225		OV-61OH		OV-1701-OH		OV-3 / OV-225		OH	
Propanol	528		676		888		656		739		684	
A_O (CH_3)	145	(23)	91	(13)	71	(8)	116	(18)	101	(15)	98	(14)
B_O (CH_3)	123	(20)	98	(14)	83	(10)	43	(7)	26	(4)	65	(10)
C_O (C_3H_7)	337	(54)	317	(46)	263	(31)	281	(43)	223	(32)	297	(44)
D_O (C_4H_9)	473	(76)	429	(63)	330	(39)	390	(59)	326	(47)	401	(59)
E_O (CH_3)	99	(16)	78	(11)	53	(6)	31	(5)	30	(4)	65	(10)
F_O (CH_3)	52	(8)	42	(6)	25	(3)	34	(5)	17	(2)	24	(3)
G_O (CH_3)	167	(27)	101	(15)	83	(10)	133	(20)	110	(16)	112	(16)

perturbation terms are high on the mixed phase at a low temperature (60°C). When temperature increases, these pertubation terms increase on phase OV-3, but they decrease on OV-225 and binary phases. By considering the whole of the compounds, the binary phase is interesting at a low temperature because of the alkanes; it behaves like phase OV-3. For alcohols, perturbation terms are slightly higher to those measured on non-polar phase, OV-33.

The variation of the perturbation terms on the two polar pure phases, OV-61-OH and 0V-1701-OH, are examined. At a
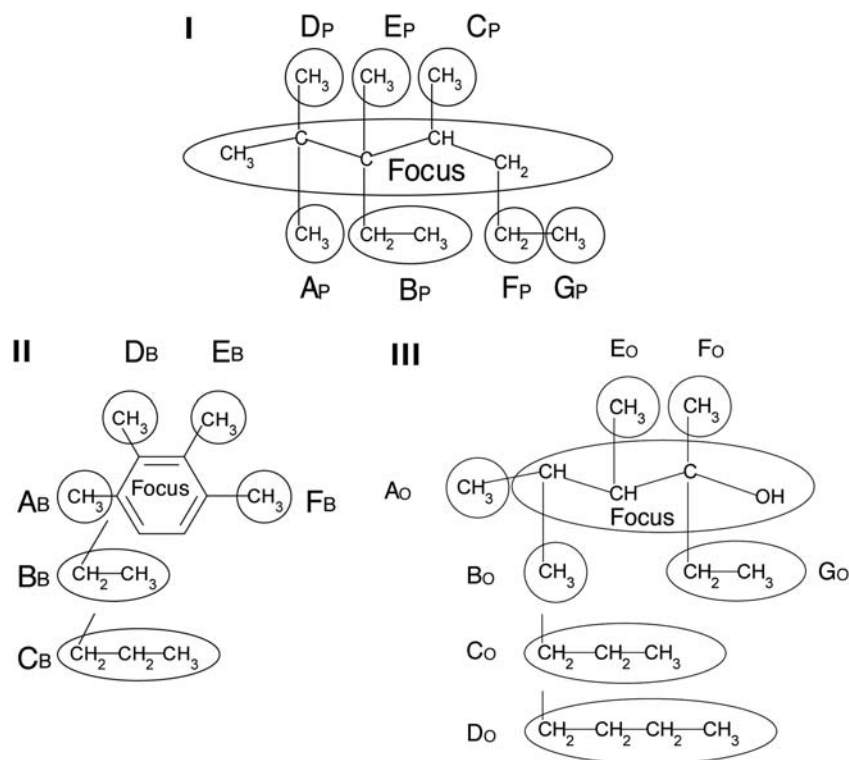
Figure 4. Description of the perturbation terms of each substituent on the focus of the three series alkanes (I) labeled from A_P to G_P, aromatoic (II) labeled from A_B to F_B, and alcohols (III), labeled from A_O to G_O.

low temperature, the binary phase presents perturbation terms lower than those measured on the pure phases. When the temperature is at 80°C, the perturbation terms values measured on the binary phase strongly increased to reach values comparable with those measured on phase OV-1701-OH. The perturbation terms of these two systems remain correlated at the temperature of 100°C. For the aromatic derivatives series, the perturbation terms measured on the binary phase are lower than those measured on the pure phases for all the temperatures. For the alcohols, the values of the perturbation terms are in general lower on the binary phase than on the pure phases. This difference between the perturbation terms is more noticed when the temperature increases from 60°C to 100°C.

The comparison of the perturbation terms measured on these phases shows that the values of the perturbation terms on the binary phases are not a linear combination of the perturbation terms values measured on the pure phases. The temperature plays an important role in the modification of the perturbation terms with the binary phases. The origin of this influence could be explained by a difference in viscosity of the pure phases, and the modification of the viscosity of each phase with the temperature or their low mutual solubility. This modification of viscosity or solubility could induce a significant modification of the stationary phase, involving a variation of the chromatographic behavior of the compounds.

Conclusion

The retention of the compounds on the mixed stationary phases did not result from a simple linear combination of the retentions obtained on the pure phases. The temperature has a very important role on the modification of the compound retention with the mixed phases. The retention measured on a binary phase can be correlated with the retention measured on one or another pure phases, but the importance of the phase in the mixture depends on the temperature. In addition, for a congeneric compounds series, the influence of the substituents depends at the same time on the nature of the binary phase and the temperature. The perturbation terms measured on the binary phases did not result from a linear combination of those measured on the pure phases. This highlights the difficulty of predicting the retention indices on the mixed phases from the retention indices on the pure phases, but this does not affect their use in single or bi-dimensional GC.

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