

## Mosaic increments for predicting the gas chromatographic retention data of the chlorobenzenes

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### Abstract

The chlorinated organic compounds are very important from the point of view of the chemical industry and environmental protection, and therefore the gas chromatographic analysis of these compounds is very interesting for analytical chemists. In this paper we studied the relationship between the molecular structure and gas chromatographic retention on several stationary phases having different polarity and at several temperatures of benzene and 12 chlorobenzene compounds as model compounds. A coding system involving primary (mosaic increments) and secondary (bond increments) calculation methods was developed. The retention indices of benzene and the chlorobenzenes calculated on HP-5 at 120 °C shows a better performance of the mosaic increments (average absolute deviation  $\delta$  of 1.7 retention index units) compared with the bond increments ( $\delta=11.7$  retention index units). Retention factors,  $k$ , calculated with mosaic increments for chlorobenzenes on SPB-1 and WAX-10, at 140 °C, yield average relative errors of  $\epsilon=0.9$  and 3.5%, respectively. Therefore, the presented paper provides a new possibility for precalculation of the retention data.

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### 1. Introduction

The gas chromatographic analysis of chlorinated organic compounds has high interest as they play an important role in the chemical industry and in environmental protection, more than 1000 articles having been published on this subject. Four tables listing 96 organic compounds, including chlorobenzenes physical data were given by Dreisbach and

Martin [1]. Langer and Purnell [2], as well as Langer, Johnson, and Conder [3], studied the negative deviation from Raoul's equation, using chlorobenzenes as model compounds. Karasek and Fong [4] studied the correlation between the molecular structure of the chlorobenzenes and their interactions with the stationary phase at several temperatures. Karasek and Stepanik [5] found correlation between the boiling points of the chlorobenzenes and their retention indices, showing the possibility of predicting the indices. Cook and Raushel [6] studied retention indices of aromatic derivatives, including

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chlorobenzenes, adding the retention index contributions due to the ring and to the substituent. The results of West and Hall [7] should be mentioned, since they developed a method to predict retention indices of benzene derivatives (including chlorobenzenes) on any stationary phase. Oliver and Bothen [8] determined chlorobenzenes in aqueous matrix by capillary chromatography. Schulz et al. [9] made electron diffraction measurements of 1,4-dichlorobenzene, useful for calculating retention indices of 1,2- and 1,3-dichlorobenzenes, which are not correlated with the vapor pressure.

Similarly Mash and Williams [10] gave molecular parameters for 1,2,3,5-tetrachlorobenzene. Crow et al. [11] performed experiments on an SE-52 capillary column for all the 12 chlorobenzenes. Czerwicz et al. [12] studied retention–structure correlation for chlorobenzenes. Haken and Korhonen [13] studied the interactions between the chlorobenzenes and SE-30 and Carbowax 20M stationary phases at several temperatures using retention index increments. Sabljic [14,15] made calculations on the topological indices and the measured retention indices of chlorobenzenes. Peng et al. [16] predicted the retentions of the chlorobenzenes. Yasuhara and Morital [17] investigated chlorinated hydrocarbons using an SE-54 capillary column. Evans and Haken [18] determined dispersion and selectivity indices using chlorobenzenes. Zlatkis et al. [19,20] measured chlorobenzenes in aqueous solutions. Tessari and Winn [21] published relative retention data of chlorinated pesticides and polychlorinated biphenyls using five stationary phases. One of the most important studies on chlorinated compounds was published by White et al. [22] consisting of retention indices of 480 compounds including those studied here. The correlation between the structures of chlorobenzene molecules and their retention behavior on several stationary phases of different polarity and at several column temperatures was studied by Castello and co-workers [23–26,29,30,33]. Messadi and Ali-Mokh-Nache [27] determined the retention indices of some chlorobenzenes by programmed-temperature gas–liquid chromatography (PTGLC). Spieksma et al. [28] calculated the vapor pressure of low volatility compounds, including chlorobenzenes, using their retention indices. Sun et al. [31] studied the correlation

of the retention in PTGLC and the structure of all 12 chlorinated benzenes. Donovan [32] reported a new chromatographic method for determining the vapor pressure of hexachlorobenzene as well. Huibers and Katritzky [34] correlated solubility and molecular structures of 109 hydrocarbons and 132 halogenated hydrocarbons using gas chromatography.

The aims of this work were: (1) bond and mosaic increments are tabulated for benzene and the chlorobenzenes, and the new respective equations are proven; (2) retention factors,  $k$ , were experimentally determined for the above compounds and  $n$ -alkanes from  $z=8$  to 18 (standard solutes) on HP-5 at four temperatures; (3) retention indices calculated with the two methods were compared with measured values on HP-5 at 120 °C; (4) Measured  $k$ -values are compared with the  $k$ -values calculated with mosaic increments for chlorobenzenes on SPB-1 and WAX-10, two stationary phases from literature; (5) mosaic increments were also tested in 1,4-dichlorobenzene at programmed temperature; (6) examples of calculation of the bond increment equations of benzene and of the amount of stationary phase in a capillary column coated with HP-5 are carried out; and (7) a new magnitude called stationary phase activity ( $\gamma M_s$ ) is defined and calculated for benzene and the chlorobenzenes on SE-30 at various temperatures.

## 2. Theory

Our work is based on Meisel's equation (see Ref. [35]) neglecting the individual interactions:

$$\ln [V_g(x)] = \ln K_s + \sum_{j=1}^n k(j) \cdot \ln [V_g(j)] \quad (1)$$

where:  $\ln$  = natural logarithm;  $V_g$  = the specific retention volume,  $\text{cm}^3/\text{g}$ ;  $x$  = symbol of the substance examined;  $n$  = the number of different bond types in the molecule examined;  $j$  = serial number of different bond types in the molecule studied;  $k(j)$  = the number of  $j$ th identical bonds in the molecule examined, and  $K_s$  = the interaction coefficient,  $\text{cm}^3/\text{g}$  [35]. In this paper:  $K_s = 1$ , and therefore  $\ln K_s = 0$ .

Multiplying both sides of Eq. (1) by  $(100/\ln Q)$  we obtain:

$$(100/\ln Q) \cdot \ln [V_g(x)] = (100/\ln Q) \sum_{j=1}^n k(j) \cdot \ln [V_g(j)] \quad (2)$$

Adding the Kováts coefficient (see Ref. [35]) to both sides of Eq. (2):

$$(100/\ln Q) \ln [V_g(x)] + K_c = K_c + (100/\ln Q) \cdot \sum_{j=1}^n k(j) \ln [V_g(j)] \quad (3)$$

Taking into account the relationship between retention index, molecular structure coefficient and Kováts coefficient (see Ref. [35]):

$$I(x) = (100/\ln Q) \cdot \ln [V_g(x)] + K_c \quad (4)$$

and

$$S_c = (100/\ln Q) \cdot \ln [V_g(x)] \quad (5)$$

where:  $I$  = the isothermal retention index according to Kováts [36];  $K_c$  = the Kováts coefficient [ $-\ln(\text{cm}^3/\text{g})$ ];  $S_c$  = the molecular structural coefficient [ $\ln(\text{cm}^3/\text{g})$ ];  $Q$  is the relative volatility of two consecutive  $n$ -alkanes used [dimensionless]:

$$Q = t'_R(z+1)/t'_R(z) \quad (6)$$

$t'_R$  = the adjusted retention time, (min) is given by:

$$t'_R = t_R - t_M \quad (7)$$

where  $t_R$  = the retention time (min), and  $t_M$  = the hold-up time (min).  $z$  and  $(z+1)$  = the carbon (atom) number of two consecutive  $n$ -alkanes used, respectively.

Replacing the appropriate terms of Eq. (3) with Eq. (4) and Eq. (5):

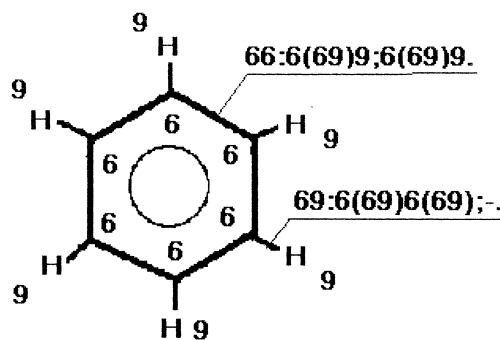


Fig. 1. Atomic code numbers and bond codes of benzene.

$$I(x) = K_c + S_c(x) = K_c + \sum_{j=1}^n k(j) S_c(j) \quad (8)$$

As in the case of hydrocarbons [35], we introduced simulation equations for studying the correlations of the molecular structures of chlorobenzenes and their gas chromatographic interactions. The atomic codes used are summarized in Table 1.

The chemical bonds in benzene and the 12 chlorobenzenes are coded with the following rules in order to obtain a unique code for all bonds, and Figs. 1,2 are shown to illustrate the coding procedure.

Coding rules for bond distance increments:

- (1) The code for a chemical bond starts with the

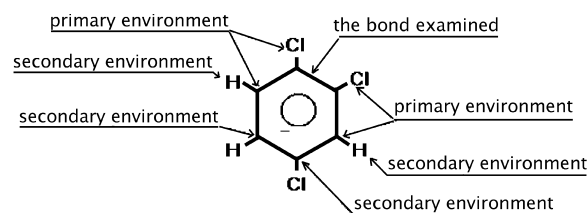


Fig. 2. Primary and secondary environments of the C1–C2 bond in 1,2,4-trichlorobenzene.

Table 1  
Atomic codes for the benzene and the chlorobenzenes

Atomic code	Description
6	Carbon atom in the benzene ring carrying hydrogen (called third order carbon)
7	Carbon atom in the benzene ring carrying a chlorine substituent
8	Chlorine atom bonded to the benzene ring
9	Hydrogen atom bonded to the benzene ring

atomic code numbers of the two atoms between which the bond is formed. The atomic code numbers of benzene and 12 chlorobenzenes are one-digit numbers (see Table 1). The atomic code number with the lowest value appears first 69. A colon is placed after the second atomic code number, 69: (see Table 2).

(2) After the colon, the primary, and then (in brackets) the secondary atoms of the environments of the atom in the first position are coded, in order of increasing magnitude in each case, e.g., 69:6(79)7(68);-.

(3) The code for the complete environment of the first atom ends with a semicolon, thus: 69:6(79)7(68);. The atomic code number for the atoms belonging to the environment of the other atom taking part in the bond should be written after the semicolon: 67:6(79)9;7(78)9.

(4) The complete bond code ends with a full stop (see Table 2).

(5) Frequently, the atomic code numbers of two atoms taking part in a bond are identical. In such a case, the order is decided by the primary and/or secondary environment. In all instances, the atom having an environment with a lower number is given first, e.g., 77:6(69)8;6(79)8.

(6) Chloro- and/or hydrogen atoms have no environments, this being indicated by “-”.

Table 2

The complete bond codes of benzene, chlorobenzene and 1,2-dichlorobenzene

Serial number	Compound	Bond code
1	Benzene	66:6(69)9;6(69)9.
2	Benzene	69:6(69)6(69);-.
3	Chlorobenzene	66:6(69)9;6(79)9.
4	Chlorobenzene	66:6(69)9;7(68)9.
5	Chlorobenzene	69:6(69)7(68);-.
6	Chlorobenzene	69:6(69)6(79);-.
7	Chlorobenzene	67:6(69)9;6(69)8.
8	Chlorobenzene	78: 6(69)6(69);-.
9	Chlorobenzene	69:6(69)6(69);-.
10	1,2-Dichlorobenzene	78:6(69)7(68);-.
11	1,2-Dichlorobenzene	69:6(69)7(78);-.
12	1,2-Dichlorobenzene	69:6(69)6(79);-.
13	1,2-Dichlorobenzene	77:6(69)8;6(69)8.
14	1,2-Dichlorobenzene	67:6(69)9;7(68)8.
15	1,2-Dichlorobenzene	66:6(79)9;6(79)9.
16	1,2-Dichlorobenzene	66:6(69)9;7(78)9.

(7) There are atoms in primary environments of the atom examined which are bound directly to the atom studied.

(8) There are atoms in secondary environments of the atom studied which are in the primary environments of the primary environments of the atom examined.

### 2.1. The bond increments method

It is based on the three-terms Tekler's equation [37], based on the fact that the retention index of a substance is approached as the sum of the contributions of the atoms, the bonds and of the interactions of the molecule. Tekler et al. related bond energies (kJ) of alicyclic hydrocarbons with the distance bonds  $d$  (nm) between the atoms, using just three environmental factors to determine the different increment equations.

Lombosi et al. [38,39] explained a refinement of the equation and extended its application to the aromatic hydrocarbons and chlorinated derivatives, giving a five-terms (five environmental factors) equation for the bond distance:

$$d = 0.819 \sum_{i=1}^2 a_0(i) + 0.157 \sum_{j=1}^p a_1(j) + 0.024 \sum_{k=1}^q a_2(k) + 0.160 \sum_{p=1}^x a_3(p) + 0.021 \sum_{s=1}^y a_4(s) \quad (9)$$

where 0.819 is the bond chemical factor; 0.157 and 0.160 are the factors for the primary environment of the first and second coded atoms in the bond considered, and 0.024 and 0.021 the secondary environment of the first and second coded atoms in the studied bond, respectively.

$a_0$  is the atomic code number of the two-atoms bond,  $a_1$  and  $a_3$  the atomic code number of atoms in the first environment of the first and second coded atoms, respectively, and  $a_2$  and  $a_4$  the atomic code number of atoms in the secondary environment of the first and second coded atoms, respectively.

$i, j, k, p$  and  $s$  are serial numbers of the different atoms conforming the environment of the bond atoms.

$x$ , total number of atoms in the primary environment of second coded atom in the examined bond, and  $y$ , total number of atoms in the secondary

environment of second coded atom in the examined bond.

An example explaining the determination for benzene is given in the section of calculations.

The complete bond codes of benzene, chlorobenzene and the 1,2-dichlorobenzene are listed in Table 2.

The complete bond codes give the possibility of studying the effects of the environment of a certain chemical bond. Bastiansen and Tratteberg [40] already showed how the nature of chemical bonds varies with the environment. The increment equations necessary for the calculation between the molecular structure and the additive parameters, for example retention times, volumes, etc., are given in the left part of Table 3.

The individual interactions of the chlorobenzene molecules cannot be neglected as assumed before ( $K_s = 1$ ) because the individual atoms are influenced by the neighboring atoms [40] (see Fig. 2 and Table 13), and this may lead to a rather high error in the calculations.

### 2.2. The mosaic increments method

In our calculation another method is followed, involving the steps of the formation of the retention index increments. The method applied in the case of methylbenzenes [41] was adopted (see Figs. 3,4).

A molecular mosaic-increment,  $m[abc]$ , is formed by a deltoid in the benzene's ring drawing the two

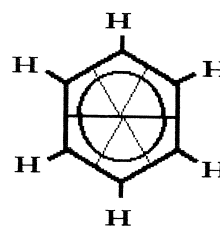


Fig. 3. Mosaics of the benzene molecule.

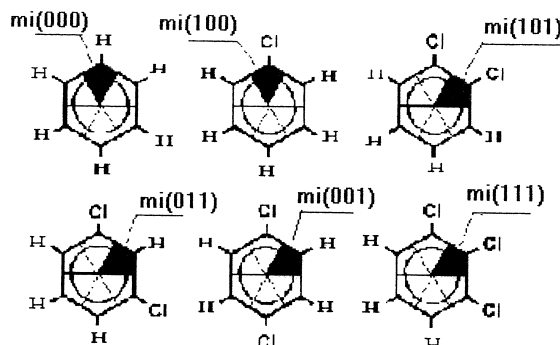


Fig. 4. Mosaic increments of benzene and chlorobenzenes.

neighboring perpendiculars to the middle point of two adjacent bonds (see Fig. 3).

As it can be seen in Fig. 3, six identical mosaic increments are formed in the ring for benzene. One of them is selected and coded as  $m[000]$ . The first “0” atomic code refers to the hydrogen in this increment, while the second and third numerical symbols refer to the hydrogen atoms at the neigh-

Table 3

The distribution of the bond increment and mosaic increments equations for benzene and the chlorobenzenes

Serial number	Compound	Bond increment equation	Mosaic increment equation
1	Benzene	$19.086 \cdot "6" + 7.374 \cdot "9"$	$6 \cdot m[000]$
2	Chlorobenzene	$15.905 \cdot "6" + 3.181 \cdot "7" + 1.229 \cdot "8" + 6.145 \cdot "9"$	$3 \cdot m[000] + 2 \cdot m[001] + 1 \cdot m[100]$
3	1,2-Dichlorobenzene	$12.721 \cdot "6" + 6.365 \cdot "7" + 2.455 \cdot "8" + 4.918 \cdot "9"$	$2 \cdot m[000] + 2 \cdot m[001] + 2 \cdot m[101]$
4	1,3-Dichlorobenzene	$12.724 \cdot "6" + 6.362 \cdot "7" + 2.464 \cdot "8" + 4.910 \cdot "9"$	$1 \cdot m[000] + 2 \cdot m[001] + 1 \cdot m[011] + 2 \cdot m[100]$
5	1,4-Dichlorobenzene	$12.718 \cdot "6" + 6.367 \cdot "7" + 2.464 \cdot "8" + 4.910 \cdot "9"$	$2 \cdot m[100] + 4 \cdot m[001]$
6	1,2,3-Trichlorobenzene	$9.537 \cdot "6" + 9.549 \cdot "7" + 3.681 \cdot "8" + 3.693 \cdot "9"$	$1 \cdot m[000] + 2 \cdot m[001] + 2 \cdot m[101] + 1 \cdot m[111]$
7	1,2,4-Trichlorobenzene	$9.543 \cdot "6" + 9.543 \cdot "7" + 3.693 \cdot "8" + 3.681 \cdot "9"$	$2 \cdot m[001] + 1 \cdot m[011] + 2 \cdot m[101] + 1 \cdot m[100]$
8	1,3,5-Trichlorobenzene	$9.561 \cdot "6" + 9.525 \cdot "7" + 3.705 \cdot "8" + 3.669 \cdot "9"$	$3 \cdot m[011] + 3 \cdot m[100]$
9	1,2,3,4-Tetrachlorobenzene	$6.350 \cdot "6" + 12.727 \cdot "7" + 4.913 \cdot "8" + 2.461 \cdot "9"$	$2 \cdot m[001] + 2 \cdot m[011] + 2 \cdot m[111]$
10	1,2,4,5-Tetrachlorobenzene	$6.356 \cdot "6" + 12.730 \cdot "7" + 4.922 \cdot "8" + 2.452 \cdot "9"$	$2 \cdot m[011] + 4 \cdot m[101]$
11	1,2,3,5-Tetrachlorobenzene	$6.362 \cdot "6" + 12.724 \cdot "7" + 4.922 \cdot "8" + 2.452 \cdot "9"$	$2 \cdot m[011] + 1 \cdot m[100] + 2 \cdot m[101] + 1 \cdot m[111]$
12	Pentachlorobenzene	$3.181 \cdot "6" + 15.905 \cdot "7" + 6.145 \cdot "8" + 1.229 \cdot "9"$	$1 \cdot m[011] + 2 \cdot m[101] + 3 \cdot m[111]$
13	Hexachlorobenzene	$19.086 \cdot "7" + 7.374 \cdot "8"$	$6 \cdot m[111]$

boring increments. If the two neighboring codes are not the same, their order is decided by the increasing code numbers.

The atomic code of chlorine is “1” and the symbol of all mosaic increments is “m”.

The complete code has three digits. There is in the first place the sign of the mosaic examined, the second and third places are the consecutive mosaic codes in order of increasing magnitude:  $m[000]$ ,  $m[001]$ ,  $m[011]$ ,  $m[100]$ ,  $m[101]$ , and  $m[111]$ .

The distribution of the mosaics of benzene and chlorobenzenes is given in the right part of Table 3. The calculations can be simplified introducing some symbols:

$$K1 = 2 \cdot m[001] + 1 \cdot m[100] \quad (10)$$

$$K2 = 2 \cdot m[001] + 2 \cdot m[101] \quad (11)$$

$$K3 = 1 \cdot m[011] + 1 \cdot m[100] \quad (12)$$

$$K4 = 2 \cdot m[101] + 1 \cdot m[011] \quad (13)$$

As the compounds examined have a very wide range of boiling points, and their gas chromatographic analysis can be performed only with programmed temperature, we studied the application of the increment also for the programmed temperature analysis.

For that application the transferring equation [42] can be used:

$$mi(j) = A + \frac{B \cdot \ln [(T_R - C)/(T_0 - C)]}{T_R - T_0} \quad (14)$$

where:  $mi(j)$  is the  $j$ th mosaic increment using PT-GLC;  $A$ ,  $B$  and  $C$  are the constants of Antoine's equation describing the function of the mosaic increment on the column temperature;  $\ln$  is natural logarithm;  $T_R$ , the retention temperature of the compound belonging to the  $i$ th mosaic increment ( $K$ ), and  $T_0$  the initial oven temperature of the compound belonging to the  $i$ th mosaic increment ( $K$ ).

The introduction of the mosaic increments enlarged the application area of the retention index in the gas liquid chromatography. The retention indices are the only data which are universal, unlike the relative retention or specific retention volume, etc.

Using the mosaic increments some other important data, namely, activity coefficients, retention volumes, retention factors, etc., can be calculated.

### 3. Experimental

The gas chromatographic analyses were carried out with the equipment and experimental conditions detailed in Table 4. DB-5, HP-5, OV-1, SE-30 and SE-52 are the stationary phases used in this work.

### 4. Results and discussion

#### 4.1. Calculations

To obtain the results mentioned in this paper many calculations had to be made. Here we would like to show only some of them.

(i) Determination of the bond increment for benzene in Table 2 by means of Eq. (9). The molecule has six identical C–C bonds and six identical C–H bonds (see Fig. 1). According to their codes, the overall bond increment is given as six times the sum of the C–C bond increments plus the C–H bond increments. So, according to Eq. (9):

$$\text{Bond increment (C–C)} = 0.819(\text{“6”} + \text{“6”}) + 0.157(\text{“6”} + \text{“9”}) + 0.024(\text{“6”} + \text{“9”}) + 0.160(\text{“6”} + \text{“9”}) + 0.021(\text{“6”} + \text{“9”}) = (2.000) \cdot \text{“6”} + (0.362) \cdot \text{“9”}$$

$$\text{Bond increment (C–H)} = 0.819(\text{“6”} + \text{“9”}) + 0.157(\text{“6”} + \text{“6”}) + 0.024(\text{“6”} + \text{“9”}) + 0.024(\text{“6”} + \text{“9”}) = (1.181) \cdot \text{“6”} + (0.867) \cdot \text{“9”} \text{ and, therefore,}$$

$$\text{Bond increment (benzene)} = 6[(2.000 + 1.181) \cdot \text{“6”} + (0.362 + 0.867) \cdot \text{“9”}] = (19.086) \cdot \text{“6”} + (7.374) \cdot \text{“9”}$$

(see Table 3).

(ii) Calculation of the absolute amount of the stationary phase (HP-5) using the following equation:

$$\ln [V_g]_{1,2,3\text{-CL3Benzene}}^{\text{HP-5}}(120^\circ\text{C}) = (0.56029/100) \cdot (1228.8 - 205.0) = 5.73625 \quad (15)$$

obtained from the direct application of Eq. (4). So,

Table 4  
Chromatographic columns and operating variables used in this work

	Gas chromatograph				
	Agilent 6850	HP-5890	HP-5880/2	HP-5840 modified	HP-5840 modified
Detector	FID	FID	FID	FID	FID
Attenuation	$1 \cdot 10^{-9}$	$1 \cdot 10^{-9}$	$1 \cdot 10^{-9}$	$1 \cdot 10^{-9}$	$1 \cdot 10^{-9}$
Detector temperature, °C	300	250±0.5	250±0.5	250±0.5	250±0.5
Vaporizer temperature, °C	220	225±0.5	250±0.5	270±0.5	270±0.5
Introduction	ALS	0.4 µl	1.0 µl	1.0 µl	1.0 µl
Column material	Fused silica	Fused silica	Fused silica	Glass	Glass
Column type	WCOT	WCOT	WCOT	WCOT	WCOT
Column parameters	60 m×0.32 mm I.D.	60 m×0.25 mm I.D.	25 m×0.20 mm I.D.	25 mm×0.25 mm I.D.,	25 m×0.25 mm I.D.,
Film thickness (µm)	1	0.25	0.50	0.55	0.55
Stationary phase	DB-5	HP-5	OV-1	SE-52	SE-30
Column temperature, °C	90–120	120–180	90–130	70–130	70–130
Carrier gas	Helium	Nitrogen	Helium	Helium	Helium
Inlet pressure (kPa·cm <sup>-2</sup> )	1.77	1.2<P<1.25	1.85<P<2.82	1.75<P<2.62	1.75<P<2.62
Flow-rate (cm <sup>3</sup> ·min <sup>-1</sup> )	2.7	0.1	0.1–5.2	0.3–15.2	0.3–15.2
Linear flow-rate (cm·min <sup>-1</sup> )	37		Hydrogen, 23.7	Hydrogen, 25.1	Hydrogen, 25.1
Auxiliary gases	Hydrogen: 450		372.0	347.0	347.0
Flow-rate (cm <sup>3</sup> ·min <sup>-1</sup> )	Column+ make-up=45				
Air (cm <sup>3</sup> ·min <sup>-1</sup> )	450				

ALS, automatic liquid sample; FID, flame ionization detection; WCOT, wall-coated open tubular.

from Eq. (15):  $V_g = 309.90$  [cm<sup>3</sup>·g<sup>-1</sup>]. On the other hand, the net retention volume is given by:

$$V_N = jF_C \cdot (t_R - t_M) = jF_C \cdot t'_R \quad (16)$$

where:  $j$  = compressibility factor according to James-Martin [43];  $F_C$  = flow-rate [cm<sup>3</sup>·min<sup>-1</sup>] of the carrier gas; 0.56029 is the  $\ln Q$  value on HP-5 at 120 °C; 100 is the coefficient in the defining equation of retention index; 1228.8 is the retention index of 1,2,3-trichlorobenzene at 120 °C on HP-5, 205.0 is the Kováts coefficient [35] at 120 °C on HP-5;  $t_M = 6.55$  min; 0.45 is the corrected flow-rate [cm<sup>3</sup>·min<sup>-1</sup>] of the carrier gas calculated with the compressibility factor according to James-Martin [43], and 16.133 is the adjusted retention time (min) of 1,2,3-trichlorobenzene at 120 °C on HP-5 stationary phase. Finally, 309.90 is the specific retention volume (cm<sup>3</sup>·g<sup>-1</sup>) of 1,2,3-trichlorobenzene at 120 °C on HP-5.

$$m_S^{\text{HP-5}} = [V_N/V_g]_{1,2,3\text{-CL3Benzene}} = 7.260/309.90 = 0.0234 \quad (17)$$

therefore, there is  $m_S = 23.4$  mg of stationary phase in the capillary column.

(iii) Demonstration of the use of the virtual carbon number for the calculation of retention index that Harangi [43], using the results of Vezzani et al. [33], obtained on DB-5 stationary phase capillary column at 100 °C. Using the operating parameters mentioned, the value of  $\ln Q$  is 0.6330, the adjusted retention time of 1,2-dichlorobenzene (reference compound) is 1.254 (min), and the virtual carbon number of the reference compound: 10.462. A comparison of the adjusted retention time results of Castello et al. [30] and the results found by Harangi [44] are summarized in Table 5.

(iv) The application of the increments in programmed temperature gas chromatography is shown using 1,4-dichlorobenzene as a model compound that can be built with two “K1” mosaics, according to Eq. (10). The analysis was performed on an open tubular column having DB-5 as stationary phase. The heating (3.0 °C·min<sup>-1</sup>) was started after 3.06 min of isothermal period, the initial temperature being 60 °C, and the retention time was 20.17 min. We will have  $T_R - T_0 = rT_R = 3(20.17 + 3.06) = 69.68$ . Using the constants of “K1” the following equation can be obtained:

Table 5

The adjusted retention time data used for virtual retention index calculation on DB-5 at 100 °C [33]

Compound	Adjusted retention time (min)	Retention index (measured)	Retention index (virtual)	Retention index deviation
Benzene	0.142	678.0	676.8	1.2
Chlorobenzene	0.367	850.5	852.1	−1.6
1,2-Dichlorobenzene	1.254	1046.2	Standard	Standard
1,3-Dichlorobenzene	1.059	1020.1	1019.5	0.5
1,4-Dichlorobenzene	1.093	1023.2	1024.5	−1.3
1,2,3-Trichlorobenzene	3.485	1209.0	1207.7	1.3
1,2,4-Trichlorobenzene	2.836	1178.4	1175.1	3.3
1,3,5-Trichlorobenzene	2.189	1137.7	1134.2	3.5
1,2,3,4-Tetrachlorobenzene	8.877	–	1355.4	–
1,2,4,5-Tetrachlorobenzene	6.711	–	1311.2	–
1,2,3,5-Tetrachlorobenzene	6.768	–	1312.5	–
Pentachlorobenzene	19.500	–	1479.7	–
Hexachlorobenzene	53.671	–	1639.6	–

Calculating from the logarithm of the adjusted retention times.

$$K1_{p-CL2Benzene}^{DB-5} = 456.9 - (9958.91/69.678) \cdot \ln [(402.84 - 552.96)/(333.16 - 552.96)] = 511.40 \quad (18)$$

$$I_{p-CL2Benzene}^{DB-5} = 828.1 - (78146.30/69.678) \cdot \ln [(402.84 - 776.20)/(333.16 - 776.20)] = 1020.7 \quad (20)$$

after applying Eq. (14).

The constants of Antoine's equation for the function of the mosaic increments used for retention index calculation of benzene and the 12 chlorobenzene derivatives on SE-52 are in Table 6. Then:

$$I_{p-CL2Benzene}^{DB-5} = 2 \cdot 511.40 = 1022.80 \quad (19)$$

On the other hand, substituting the constants of Antoine's equation *A*, *B* and *C* on SE-52 from Table 7, we obtain:

Table 6

Some mosaic increments and symbols values of increment on SE-52

Mosaic increment	A	B	C
<i>m</i> [000]	104.18	−2277.45	−630.87
K1	456.90	−9958.91	−552.96
K2	966.55	−47501.89	−48.03
K3	713.01	−2889.64	−327.02
K4	388.17	366.09	−460.28
<i>m</i> [111]	270.28	−1600.76	−496.51

The deviation between the two retention indices is 2.1 index units.

#### 4.2. Other experimental results reported in this work

Some more experimental results can be found in Tables 8–12 and 14. Table 8 lists retention indices, specific retention volumes and molecular activities (and natural logarithms in the last column) of benzene and chlorobenzenes on SE-30 at 160 °C. The molecular activity of the stationary phase (see Appendix A) has the dimensions of the molar volume ( $\text{g} \cdot \text{mol}^{-1}$ ) and increases with the chlorine number increase.

Table 9 summarizes the natural logarithm of the molecular activity of the same compounds on SE-30 at four 10 °C equispaced temperatures at the range 145–175 °C. We observe an increment as the chlorine atom number increases with the exception of chlorobenzene at a given temperature. Apparently, however, the parameter decreases as the temperature increases for the terms of higher chlorination (four to



Table 7

The constants of Antoine's equation for the function of the retention indices of benzene and the 12 chlorobenzenes on SE-52

Compound	A	B	C
Benzene	625.46	−13504.02	−629.65
Chlorobenzene	783.05	−15295.92	−566.09
1,2-Dichlorobenzene	966.99	−15732.52	−574.73
1,3-Dichlorobenzene	955.76	−25256.03	−733.17
1,4-Dichlorobenzene	828.81	−78146.30	−776.20
1,2,3-Trichlorobenzene	840.09	−170041.90	−874.59
1,2,4-Trichlorobenzene	1131.81	−18273.63	−582.02
1,3,5-Trichlorobenzene	1138.147	−1101.894	−461.375
1,2,3,4-Tetrachlorobenzene	1335.5	−4302.104	−486.0758
1,2,4,5-Tetrachlorobenzene	1317.414	−2664.838	−478.3378
1,2,3,5-Tetrachlorobenzene	1278.154	−6780.063	−507.793
Pentachlorobenzene	1443.458	−8165.615	−507.2973
Hexachlorobenzene	1544.149	−20629.66	−543.6855

six chlorines), while an opposite trend is seen for the other less substituted chlorobenzenes.

Table 10 lists the capacity factors of *n*-alkanes from  $z=5$  to 18, benzene and chlorobenzenes on HP-5 at four temperatures. At each temperature,  $k$  of the *n*-alkanes clearly increases with the increasing carbon number  $z$ . However,  $k$  decreases from 120 to 180 °C, showing less retention the higher the column temperature. As for benzene and the chlorobenzenes, the test solutes in this column, the trend is approximately the same:  $k$  increases with increasing chlorine atoms at each temperature, observing a remarkable increase in  $k$  from benzene to chlorobenzene, and, in

general, for every chlorine number increase in the ring. Compare for instance, hexachlorobenzene ( $k=31.23$ ) with pentachlorobenzene ( $k=12.24$ ), and 1,2,3-trichlorobenzene ( $k=2.46$ ) with *p*-dichlorobenzene ( $k=0.797$ ).

Table 11 lists the adjusted retention time values of benzene and chlorobenzenes on HP-5 at 120–180 °C, 20 °C equispaced temperatures. The same trend than the previous one holds. Table 12 compares the measured  $I$ -values and the calculated  $I$ -values of benzene and the chlorobenzenes on HP-5 at 120 °C. Retention indices were calculated by applying the mosaic increment's method with the following

Table 8

Retention data obtained on SE-30 at 160 °C

Compound	Retention index, $I$	Specific retention volume, $V_g$	Molecular activity ( $\gamma M_s$ )	$\ln(\gamma M_s)$
Benzene	684.6	7.3	735.15	6.60000
Chlorobenzene	859.3	16.0	1125.09	7.02562
1,2-Dichlorobenzene	1050.0	37.7	1717.47	7.44860
1,3-Dichlorobenzene	1013.8	32.1	1663.69	7.41680
1,4-Dichlorobenzene	1016.0	32.4	1721.87	7.45117
1,2,3-Trichlorobenzene	1224.6	82.4	2023.30	7.61249
1,2,4-Trichlorobenzene	1193.0	71.5	1986.75	7.59425
1,3,5-Trichlorobenzene	1150.0	59.0	2175.69	7.68510
1,2,3,4-Tetrachlorobenzene	1388.0	171.4	2383.62	7.77638
1,2,3,5-Tetrachlorobenzene	1378.6	164.3	2292.37	7.73734
1,2,4,5-Tetrachlorobenzene	1347.0	142.6	2261.46	7.22377
Pentachlorobenzene	1727.4	783.8	2122.53	7.66036
Hexachlorobenzene	1771.8	956.0	1965.28	7.58339

Table 9

Logarithm (molecular activity values),  $\ln(\gamma M_s)$ , of benzene and chlorobenzenes on SE-30 stationary phase at different column temperatures

Compound	Temperature, °C			
	145.0	155.0	165.0	175.0
Benzene	6.507	6.536	6.556	6.562
Chlorobenzene	7.155	7.224	7.273	7.296
1,2-Dichlorobenzene	7.425	7.448	7.441	7.392
1,3-Dichlorobenzene	7.364	7.401	7.402	7.352
1,4-Dichlorobenzene	7.412	7.447	7.445	7.388
1,2,3-Trichlorobenzene	7.499	7.563	7.631	7.693
1,2,4-Trichlorobenzene	7.492	7.560	7.627	7.685
1,3,5-Trichlorobenzene	7.510	7.632	7.732	7.806
1,2,3,4-Tetrachlorobenzene	7.980	7.805	7.768	7.789
1,2,4,5-Tetrachlorobenzene	7.978	7.899	7.898	7.930
1,2,3,5-Tetrachlorobenzene	7.694	7.703	7.751	7.816
Pentachlorobenzene	9.621	8.727	8.467	8.356
Hexachlorobenzene	8.992	8.051	7.872	7.868

mosaic index increments:  $m[000]=113.75$ ;  $m[111]=279.67$ ;  $K1=517.70$ ;  $K2=833.10$ ;  $K3=387.50$  and  $K4=671.90$ . The average absolute deviation was  $\delta=1.7$  retention index units.

The latter  $I$ -values calculated with bond increments with the same chromatographic parameters are given in Table 13 (at the center). The average absolute deviation was  $\delta=11.6\%$ , remarkably larger than those obtained with the mosaic increment equations. Therefore, indisputedly, the mosaic increments algorithm is much better than the bond increments method for the prediction of retention indices of these compounds (average absolute deviations were computed as the arithmetic mean of the retention index absolute values of the 13 solutes).

By applying least mean square regression to the  $I_{\text{calc}}$  vs.  $I_{\text{meas}}$  also better correlation is obtained for the mosaic increments:

Table 10

Experimental retention factors ( $k$ ) of  $n$ -alkanes, and chlorobenzene derivatives on HP-5 stationary phase at four temperatures

Compound	120 °C	140 °C	160 °C	180 °C
<i>n</i> -Pentane	0.021 (0.002)	0.022 (0.003)	0.014 (0.002)	0.100 (0.001)
<i>n</i> -Hexane	0.059 (0.003)	0.042(0.001)	0.030 (0.001)	0.014 (0.000)
<i>n</i> -Heptane	0.100 (0.001)	0.069 (0.003)	0.500 (0.005)	0.022 (0.000)
<i>n</i> -Octane	0.198 (0.008)	0.120 (0.008)	0.083 (0.002)	0.058 (0.001)
<i>n</i> -Nonane	0.363 (0.005)	0.209 (0.009)	0.135 (0.002)	0.091 (0.002)
<i>n</i> -Decane	0.648 (0.007)	0.359 (0.007)	0.218 (0.003)	0.139 (0.002)
<i>n</i> -Undecane	1.161(0.003)	0.605 (0.013)	0.343 (0.011)	0.211 (0.001)
<i>n</i> -Dodecane	2.064 (0.021)	1.020 (0.011)	0.555 (0.001)	0.324 (0.003)
<i>n</i> -Tridecane	3.649 (0.022)	1.705 (0.016)	0.882 (0.005)	0.493 (0.004)
<i>n</i> -Tetradecane	6.457 (0.087)	2.839 (0.020)	1.397 (0.006)	0.743 (0.003)
<i>n</i> -Pentadecane	11.334 (0.056)	4.728 (0.027)	2.208 (0.010)	1.124 (0.004)
<i>n</i> -Hexadecane	19.936 (0.051)	7.838 (0.044)	3.480 (0.014)	1.693 (0.008)
<i>n</i> -Heptadecane	34.903 (0.105)	12.979 (0.057)	5.475 (0.021)	2.544 (0.006)
<i>n</i> -Octadecane	61.137 (0.145)	21.555 (0.356)	8.595 (0.023)	3.818 (0.012)
Benzene	0.100 (0.001)	0.069 (0.001)	0.049 (0.001)	0.037 (0.001)
Chlorobenzene	0.307 (0.001)	0.192 (0.001)	0.127 (0.001)	0.088 (0.000)
1,2-Dichlorobenzene	0.919 (0.001)	0.523 (0.003)	0.320 (0.001)	0.208 (0.001)
1,3-Dichlorobenzene	0.767 (0.010)	0.442 (0.010)	0.275 (0.001)	0.178 (0.002)
1,4-Dichlorobenzene	0.797 (0.002)	0.459 (0.001)	0.280 (0.005)	0.184 (0.000)
1,2,3-Trichlorobenzene	2.463 (0.021)	1.288 (0.018)	0.732 (0.001)	0.443 (0.002)
1,2,4-Trichlorobenzene	2.023 (0.003)	1.075 (0.001)	0.614 (0.007)	0.374 (0.002)
1,3,5-Trichlorobenzene	1.570 (0.013)	0.844 (0.002)	0.498 (0.005)	0.312 (0.002)
1,2,3,4-Tetrachlorobenzene	5.917 (0.034)	2.869 (0.004)	1.515 (0.001)	0.862 (0.002)
1,2,4,5-Tetrachlorobenzene	4.529 (0.006)	2.202 (0.002)	1.215 (0.006)	0.698 (0.002)
1,2,3,5-Tetrachlorobenzene	4.586 (0.007)	2.275 (0.010)	1.219 (0.009)	0.703 (0.001)
Pentachlorobenzene	12.239 (0.045)	5.432 (0.128)	2.780 (0.006)	1.508 (0.007)
Hexachlorobenzene	31.230 (0.086)	13.158 (0.006)	6.124 (0.046)	3.116 (0.007)

The standard deviation of the measurement are given in parentheses.

Table 11

Adjusted retention time (min) of benzene and chlorobenzene derivatives on HP-5 stationary phase at four temperatures

Compound	120 °C	140 °C	160 °C	180 °C
Benzene	0.65	0.47	0.35	0.27
Chlorobenzene	2.01	1.31	0.89	0.64
1,2-Dichlorobenzene	6.02	3.57	2.24	1.51
1,3-Dichlorobenzene	5.02	3.02	1.92	1.30
1,4-Dichlorobenzene	5.22	3.13	1.96	1.33
1,2,3-Trichlorobenzene	16.13	8.79	5.12	3.22
1,2,4-Trichlorobenzene	13.25	7.34	4.29	2.72
1,3,5-Trichlorobenzene	10.28	5.76	3.48	2.27
1,2,3,4-Tetrachlorobenzene	38.76	19.59	10.59	6.26
1,2,4,5-Tetrachlorobenzene	29.66	15.03	8.49	5.07
1,2,3,5-Tetrachlorobenzene	30.04	15.53	8.52	5.11
Pentachlorobenzene	80.16	37.08	19.43	10.96
Hexachlorobenzene	204.56	89.83	42.80	22.64

Table 12

Retention indices measured and calculated using mosaic increments and bond increments on HP-5 at 120 °C

	Bond increments			Mosaic increments		
	$I_{\text{meas.}}$	$I_{\text{calc.}}$	Deviation, $\delta$	$I_{\text{meas.}}$	$I_{\text{calc.}}$	Deviation, $\delta$
Benzene	682.5	682.5	Base datum	682.5	682.5	Base datum
Chlorobenzene	859.0	848.4	10.6	859.0	859.0	Base datum
1,2-Dichlorobenzene	1063.8	1014.0	49.8	1063.8	1060.6	3.2
1,3-Dichlorobenzene	1022.5	1015.1	Base datum	1022.5	1019.0	3.5
1,4-Dichlorobenzene	1037.4	1035.4	2.0	1037.4	1035.4	2.0
1,2,3-Trichlorobenzene	1228.5	1179.5	49.0	1228.5	1226.5	2.0
1,2,4-Trichlorobenzene	1189.6	1181.0	8.6	1189.6	1189.6	Base datum
1,3,5-Trichlorobenzene	1162.5	1182.5	-20.0	1162.5	1162.5	Base datum
1,2,3,4-Tetrachlorobenzene	1385.4	1345.8	Base datum	1385.4	1392.4	-7.0
1,2,4,5-Tetrachlorobenzene	1346.9	1346.9	0.0	1346.9	1343.8	Base datum
1,2,3,5-Tetrachlorobenzene	1338.2	1346.9	-8.7	1338.2	1339.1	-0.9
Pentachlorobenzene	1514.4	1512.1	2.3	1514.4	1510.9	3.5
Hexachlorobenzene	1678.0	1678.0	Base datum	1678.0	1678.0	Base datum
Mean values			11.6			1.7

Table 13

The retention index increments of the carbon–chlorine bonds in 1,4-dichlorobenzene [9]

Compound	Bond length (Å)	Bond code	Retention index increment value
1,4-Dichlorobenzene	1.734	78:6(69)6(69);-	121.4
1,2,3,5-Tetrachlorobenzene	1.724	78:6(79)7(78);-	128.3
1,2,3,5-Tetrachlorobenzene	1.721	78:7(68)7(68);-	133.9
1,2,3,5-Tetrachlorobenzene	1.738	78:6(79)7(78);-	128.3
1,2,3,5-Tetrachlorobenzene	1.744	78:6(79)6(79);-	122.7

$$I_{\text{calc}}(\text{mosaic}) = (1.001 \pm 0.033)I_{\text{meas}} - 2.276 \pm 3.83 \quad (21)$$

(with  $r^2=0.9999$ ) than that obtained for the bond increments:

$$I_{\text{calc}}(\text{bond}) = (1.002 \pm 0.024)I_{\text{meas}} - 13.64 \pm 29.66 \quad (22)$$

in which  $r^2=0.993$ .

Based on published data [9,10], we studied the effects of the carbon–chlorine bonds on the retention indices in 1,4-dichlorobenzene and 1,2,3,5-tetrachlorobenzene. The results are summarized in Table 13.

The new mosaic calculation method is suitable for the precalculation of other retention data of the chlorobenzenes different from the retention indices too. The logarithm of the adjusted retention time (or the retention factor  $\ln k$ ) is additive, and thus we can write the following equation:

$$\ln [k(\text{chlorobenzenes})] = \sum_{j=1}^n mi[\text{abc}] \quad (23)$$

where  $\ln$  = natural logarithm;  $k$  = the retention factor;  $n$  = number of mosaic increments in the molecule examined;  $i$  = serial number of the identical mosaic increments in the molecule examined;  $mi[\dots]_j$  =  $j$ th symbol of a mosaic increment in the molecule examined, and a, b and c = code numbers of the mosaic increment used.

Some results on SPB-1 and WAX stationary phases at 140 °C, obtained by applying Eq. (20) are summarized in Table 14. Average relative errors were  $\varepsilon=0.9\%$  and  $3.5\%$ , respectively.

Good straight lines for the application of least mean square regression to calculated  $k$ -values vs. measured  $k$ -values were obtained for the two stationary phases:

$$k_{\text{calc}} = (1.003 \pm 0.04)k_{\text{meas}} + (0.074 \pm 0.011) \quad (24)$$

with  $r^2=0.9998$  and a standard deviation  $\sigma=0.0285$  for SPB-1, and:

$$k_{\text{calc}} = (0.989 \pm 0.016)k_{\text{meas}} - (0.044 \pm 0.058) \quad (25)$$

with  $r^2=0.997$  and  $\sigma=0.151$  for WAX-10.

## 5. Conclusions

It is well known that the interactions between the solute and stationary phase in GLC cannot be measured directly, only their consequences being amenable to study. In this paper the mosaic retention increment method was used, together with the bond increment method, in order to obtain more information. The mosaic retention increment method offers a possibility of predicting the retention data, as the retention index can be converted easily to specific retention volume. Using the retention volume, the absolute amount of the stationary phase in

Table 14  
Comparison of retention factors,  $k$ , at 140 °C on SPB-1 [30] and WAX-10 [30]

Compound	SPB-1				WAX-10			
	$k_{\text{meas}}$	$K_{\text{calc}}$	Deviation, $\delta$	Error (%)	$k_{\text{meas}}$	$K_{\text{calc}}$	Deviation, $\delta$	Error (%)
Chlorobenzene	0.239	0.239	0.000	0.0	0.291	0.291	0.000	0.0
1,2-Dichlorobenzene	0.472	0.490	-0.018	-3.8	0.703	0.703	0.000	0.0
1,3-Dichlorobenzene	0.422	0.416	0.006	1.4	0.536	0.536	0.000	0.0
1,4-Dichlorobenzene	0.422	0.422	0.000	0.0	0.585	0.585	0.585	0.0
1,2,4-Trichlorobenzene	0.978	0.985	-0.007	-0.7	1.650	1.432	0.218	13.2
1,2,4 Trichlorobenzene	0.834	0.852	-0.018	-2.2	1.190	1.295	-0.105	-8.8
1,3,5-Trichlorobenzene	0.710	0.710	0.000	0.0	0.753	0.753	0.000	0.0
1,2,3,4-Tetrachlorobenzene	1.980	1.980	0.000	0.0	3.314	2.918	0.396	11.9
1,2,4,5 Tetrachlorobenzene	1.630	1.630	0.000	0.0	1.990	1.990	0.000	0.0
1,2,3,5,-Tetrachlorobenzene	1.630	1.640	-0.010	-0.6	2.070	2.010	0.060	2.9
Pentachlorobenzene	3.714	3.714	-0.097	-2.6	4.823	4.540	0.283	5.9
Hexachlorobenzene	8.311	8.311	0.000	0.0	10.356	10.356	0.000	0.0
Mean values			0.013	0.9			0.088	3.5

the column can be calculated. It can be concluded that the introduction of the mosaic increments yields additional possibilities of the use of the retention index system in gas liquid chromatography.

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## Appendix A

Molecular activity. According to the fundamental law of GLC:

$$V_g = RT/p^\circ \gamma M_s \quad (26)$$

where  $\gamma$ ,  $p^\circ$  and  $V_g$  are the solute activity coefficient, partial vapor pressure, and specific retention volume, respectively, and  $M_s$  the stationary phase molecular mass. The molecular activity of the solute is defined as the activity coefficient multiplied by the stationary phase molecular mass [42]:

$$A = \gamma M_s = \frac{RT}{V_g p^\circ} \quad (27)$$

the usefulness of this concept is to circumvent the lack of  $M_s$  data in polymer stationary phases, so often used in gas chromatography.

Introducing the following symbol:

$$P_C = RT/p^\circ \quad (28)$$

where  $P_C$  is the so-called gas liquid chromatographic potential,  $\text{cm}^3 \cdot \text{mol}^{-1}$ , we can rewrite Eq. (22) as follows:

$$A = P_C / V_g \quad (29)$$

It should be noted that  $P_C$  is independent of the stationary phase used.

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