



Retention indices and quantum-chemical descriptors of aromatic compounds on stationary phases with chemically bonded copper complexes

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ABSTRACT

In this paper, Kováts retention indices determined on stationary phases with chemically bonded copper complexes were correlated with molecular structural parameters for aromatic compounds. Principal component regression (PCR) was applied to extract principal components from the set of 13 descriptors compiled in 5 theoretical models. Extracted components were used to model theoretical retention indices. Significant correlations were found among the retention indices of these compounds and, among others: molecular surface and molecule area, boiling point, HOMO and LUMO energies, dipole moment, dielectric energy, and double bond count. These correlations provide insights into the mechanism of chromatographic retention at the molecular level for the packings and the compounds under study.

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1. Introduction

The chromatographic properties of sorbents modified with the surface layers of pure chelates and with the stationary phases containing metal complexes depend on many factors, the most essential of which are the nature of the metal, distribution of the electron density in the complex, and geometry of the complex after its bonding to the support surface or its inclusion into the liquid phase [1]. Due to possibly high number of these factors, sophisticated analysis methods should be applied. Thanks to chemometric methods it is fast and simple to find similarities and/or differences between the probes and the parameters to be measured. By the use of mathematics, relativity theory, statistics, computer science and decision-support theory one may optimize the experiments and extract a lot of useful information from multivariate experimental data. Dependencies among the parameters of multivariate chemical data is a key to reduce number of variables for efficient analysis and in turn to visualize the data. By means of different techniques of data mining and data visualization, it is possible to find answers to the following questions:

- Which samples are similar, taking into account the domain if values of selected parameters?
- Which parameters provide the information about the samples?

- Which parameters influence the similarities (differences) the most?
- What is a complexity of the system under study?

Principal Component Regression (PCR) is a multivariate method formed from combining *Principal Component Analysis* (PCA) and *Multilinear Regression* (MLR). The main goal of the method is related to data compression, providing in turn simplicity and clarity of the analysis process. The method is based on a creation of new mutually perpendicular axis called principal components. Each axis is created in such a way the variance is maximized. Each new compound is orthogonal against the others, thus a new diversity is introduced that is not covered by previous steps of the analysis. Successively, extracted components are correlated with another set of dependent data resulting in creation of a new set of predictive data.

Characterization using principal component analysis (PCA) were used for different compounds [2]. Quantum-chemical calculations provide acceptable descriptors for a characterization of molecular properties in the QSRR (quantitative structure–retention relationship). Good correlations were obtained between gas chromatographic retention data and theoretically calculated data for some molecules with different functional groups: ketones and aldehydes [3], alkanes [4], alkenes [5], methylalkanes [6], alkylbenzenes [7–10], PAH [11–15], terpenes [16], and other organic compounds [17–19].

The main goal of this work is to extract some components that characterize, in the most effective way, the interactions between selected set of aromatic hydrocarbons and the chromatographic packings with copper complexes chemically bonded with silica via

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Table 1
Compounds under study including abbreviations as well as experimental and calculated retention parameters; temperature of measurement 130 °C. I – experimental Kováts retention indices; I_A, I_B, I_C, I_D, I_E – calculated retention indices obtained for models A–E.

No.	Compound	Abbr.	I	I_A	I_B	I_C	I_D	I_E
1	Benzene	B	720	702	696	697	703	698
2	Ethylbenzene	EB	928	924	933	935	927	940
3	Propylbenzene	PB	1025	1024	1029	1031	1032	1036
4	1,3,5-Trimethylbenzene	135TMB	1070	1103	1068	1059	1091	1051
5	1,2,4-Trimethylbenzene	124TMB	1112	1117	1107	1097	1108	1095
6	1,2,3-Trimethylbenzene	123TMB	1192	1141	1109	1106	1134	1097
7	<i>tert</i> -Butylbenzene	tBB	1071	1077	1085	1081	1076	1085
8	<i>sec</i> -Butylbenzene	sBB	1066	1084	1089	1091	1084	1095
9	<i>iso</i> -Butylbenzene	iBB	1087	1067	1086	1087	1068	1097
10	<i>n</i> -Butylbenzene	nBB	1120	1099	1113	1115	1119	1116
11	Toluene	T	831	845	862	861	855	864
12	2-Ethyltoluene	2ET	1054	1063	1065	1066	1061	1068
13	<i>para</i> -Xylene	pX	962	967	976	965	961	968
14	<i>meta</i> -Xylene	mX	964	969	977	973	976	972
15	<i>ortho</i> -Xylene	oX	979	986	995	993	991	994
16	Styrene	S	974	964	961	966	959	967
17	2-Methylstyrene	2MS	1075	1091	1075	1073	1080	1068
18	3-Methylstyrene	3MS	1092	1088	1090	1099	1098	1094
19	4-Methylstyrene	4MS	1096	1096	1113	1119	1109	1119
20	Cumene	C	997	1003	1006	1008	1003	1011
21	3-Phenyl-1-propene	3P1P	1026	1040	990	1002	999	989
22	<i>trans</i> -1-Phenyl-1-propene	t1P1P	1102	1091	1117	1120	1110	1118

iminoketone groups. In addition, multivariate regression method was applied to model retention indices based on principal components earlier extracted by means of PCA method. The following quantum-chemical descriptors were calculated, among others: HOMO and LUMO energies, dipole moment, dielectric energy, and vapour pressure. These descriptors were then related to retention indices of the adsorbents under study. Kováts retention indices of aromatic hydrocarbons on silica modified by β -iminoketone groups have been a topic of our previous work [20]. Similar research was also performed by some other research groups. For example, a prediction of retention index of organic compounds was successfully applied by Farkas et al. [21–23] as well as by some other researches [11,24–26]. However, these works were applied for different packings.

2. Experimental

2.1. Experimental response data

The column with copper complexes chemically bonded with silica surface *via* ketoimine group were used. Chromatographic measurements were performed on a gas chromatograph CHROM 5 (Czech Rep.) equipped with a flame – ionization detector. Stainless steel columns were used 1.5 m in length, 3 mm in ID. Temperature in the thermostat chamber was determined using DT 2000 Thermometer (Digital Thermometer, Slandi, Warsaw, Poland), and the pressure at the column inlet was measured with a mercury manometer. Helium dried on a molecular sieve 4 Å was used as a carrier gas. The flow-rate of the carrier gas was measured with a digital flowmeter (J&W Scientific, Folsom, CA, USA).

Retention indices (I_i) of each hydrocarbon (i) were calculated from corresponding retention times (t_R) using the following equation:

$$I_i = 100z + 100 \frac{\ln(t'_{R,i}/t'_{R,z})}{\ln(t'_{R,z}/t'_{R,z+1})} \quad (1)$$

where t'_R is adjusted retention time ($t'_R = t_R - t_M$), and z denotes a number of carbon atoms in n -alkane elutes before considered hydrocarbon (i). The retention times of the n -alkanes and other hydrocarbons should increase in the following order: $t_{R,z+1} > t_{R,i} > t_{R,z}$.

The compounds included in this study are presented in Table 1, followed by the values of retention indices of the compounds under study, both practical and calculated. Modelled retention indices were calculated on the basis of Eqs. (2)–(6) obtained from multilinear regressions on five models. Built theoretical models (Table 2) include two sets of descriptors. First, constant set is fixed due to contemporary literature [27], incorporating these variables that highly affecting chromatography retention. The second set of five descriptors includes the variables dependent on the molecule electronic properties. All the above-mentioned models were chosen in order to find correlations between retention mechanism and electronic properties of the adsorbate. Fig. 1 presents a example curve

Table 2
Descriptors used for model building.

No.	Model	Descriptors	
		Primary descriptors	Secondary descriptors (electronic)
1.	A		DBC, LUMO, HOMO, DE
2.	B		DM, LUMO, HOMO, DE
3.	C	MW, A, V, P, MV, TE, BP, VP, LogP	DM, DBC, HOMO, DE
4.	D		DM, DBC, LUMO, DE
5.	E		DM, DBC, LUMO, HOMO

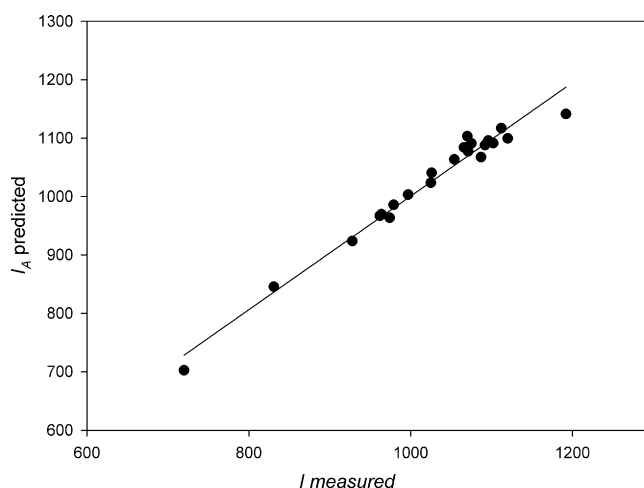


Fig. 1. Plot of the predicted versus measured retention indices (model A).

Table 3
Variables used as descriptors.

No.	Electronic and other molecular descriptors	Abbreviation	Unit	Method of calculation or database	
1	Molecular weight	MW	g mol ⁻¹		
2	Boiling point	BP	°C	PhysProp	–
3	Number of double bonds	DBC	–		
4	Molar volume	MV	cm ³		
5	Parachor	P	cm ³	–	ACD/Labs
6	Partition coefficient between octanol and water	LogP	–		
7	Vapour pressure	VP	mm Hg		
8	Total energy	TE	kcal mol ⁻¹		
9	Molecule surface	A	Å ²	QSAR	
10	Molecule volume	V	Å ³		
11	Dielectric energy	DE	kcal mol ⁻¹		Hyperchem
12	Total dipole moment	DM	debye	AM1	
13	Highest occupied molecular orbital, energy level	HOMO	eV		
14	Lowest unoccupied molecular orbital, energy level	LUMO	eV		

reflecting a dependence among measured and computed retention indices for model A.

2.2. Calculations

Different physico-chemical properties of the aromatic hydrocarbons were obtained from PhysProp database. Properties collected from the database were as follows: molecular weight (MW), boiling point (BP), and number of double bonds (DBC).

HyperChem (Professional 8.06) were used to calculate physico-chemical properties. The calculated properties were: different molecular energies and the QSRR properties (Table 2); total energy (TE), dielectric energy (DE), highest occupied molecular orbital energy level (HOMO), lowest unoccupied molecular orbital energy level (LUMO), molecular surface (A), molecular volume (V), total dipole moment (DM).

ACD/Labs (12.0 ChemSketch) was applied to the calculation of molar volume (MV), parachor (P), partition coefficient between octanol and water (LogP), and vapour pressure (VP).

The following parameters were determined by performing quantum-chemical calculations: dielectric energy (DE), total dipole moment (DM), highest occupied molecular orbital energy level (HOMO) and lowest unoccupied molecular orbital energy level (LUMO). Geometry optimization of the molecules were performed in semi-empirical AM1 Hamiltonian calculations and MM2 force field calculations. All calculations were carried out using the CACHE program, version 7.5.0.85.

The statistical evaluation – principal component regression (PCR) – of the data was processed by STATISTICA software.

Obtained retention parameters were subjected to QSRR modelling, resulting in the quantitative description of the effect of particular elements of the adsorbate structure on its interactions with the adsorbents studied.

3. Results and discussion

All descriptive data given in Table 3 was initially used to calculate the most effective model among all the PCR models. In order to achieve this goal, five principal components were extracted among

five sets of 13 descriptors (models A–E). Next, extracted components were correlated with experimental Kováts retention indices. All the models were tested using variance analysis (Table 3). The whole process included the following operations:

1. Five PCR models were built.
2. Obtained descriptors were subjected to auto-scaling.
3. The auto-scaled values were analysed by STATISTICA software, using PCA method. Significant loadings of extracted principal components are given in Table 6. All the necessary explanations as well as mathematical formulas used are given in [22].
4. Among 13 descriptors, 5 principal components were extracted. STATISTICA software built-in Krzanowski cross-validation function was applied to determine the optimum number of principal components. The criterion of variable selection was the value of principal component loading (see Eq. (2)). If at least one PC loading value is higher than the limit (L_n), the n principal component is regarded as significant (see Eq. (2)), where DF_n is the ratio of the degree of freedom and DF_n^{total} is the total degree of freedom of the PC model:

$$L_n = \frac{DF_n}{DF_n^{total}} \quad (2)$$

5. By the use of MLR, extracted components were correlated with experimental retention indices, resulting in Eqs. (3)–(7) from which modelled retention indices were calculated (Table 1). A plot of the calculated versus measured retention indices for model A is presented in Fig. 1. Statistical analysis of linear regressions is presented in Table 4. Correlation coefficients for studied PCR models are given in Table 5.

$$I_A = 1025(\pm 4.239) + [33.78(\pm 1.565) \cdot C_{1A}] - [14.70(\pm 2.166) \cdot C_{2A}] - [20.66(\pm 5.279) \cdot C_{3A}] - [19.74(\pm 6.792) \cdot C_{4A}] + [57.13(\pm 12.34) \cdot C_{5A}] \quad (3)$$

$$I_B = 1025(\pm 5.878) + [33.58(\pm 2.144) \cdot C_{1B}] - [17.07(\pm 3.339) \cdot C_{2B}] + [7.325(\pm 6.518) \cdot C_{3B}] - [20.81(\pm 7.335) \cdot C_{4B}] + [16.90(\pm 14.42) \cdot C_{5B}] \quad (4)$$

Table 4

Statistical analysis of linear regression models: b_0 – intercept; b_1 – slope; R^2 – correlation coefficient; SE – standard error of estimate; F – Fisher ratio; NT – normality test.

LR model	b_0	b_1	R^2	SE	F	NT
A	28.646 (±37.959)	0.972 (±0.037)	0.972	17.533	695.272	<0.001
B	55.079 (±51.929)	0.946 (±0.050)	0.946	23.986	352.041	<0.001
C	54.878 (±51.835)	0.946 (±0.050)	0.946	23.943	353.473	<0.001
D	32.382 (±40.286)	0.968 (±0.039)	0.968	18.608	612.641	<0.001
E	70.131 (±58.142)	0.932 (±0.057)	0.932	26.856	272.181	<0.001

Table 5

Statistical analysis of PCR models. R^2 – correlation coefficient; SE – standard error of estimate; F – Fisher ratio; NT – normality test; CV – constant variance test.

Model	R^2	SE	F	NT	CV
A	0.972	19.883	111.239	0.129	0.269
B	0.946	27.569	56.324	<0.001	0.498
C	0.946	27.516	56.555	<0.001	0.864
D	0.968	21.141	98.024	0.006	0.844
E	0.932	31.108	43.551	<0.001	0.805

$$I_C = 1025(\pm 5.866) + [33.56(\pm 2.140) \cdot C1_C] + [17.89(\pm 3.396) \cdot C2_C] + [8.518(\pm 6.304) \cdot C3_C] - [20.16(\pm 7.317) \cdot C4_C] - [3.162(\pm 10.96) \cdot C5_C] \quad (5)$$

$$I_D = 1025(\pm 4.507) + [33.17(\pm 1.648) \cdot C1_D] + [16.78(\pm 2.523) \cdot C2_D] + [9.432(\pm 4.868) \cdot C3_D] - [26.85(\pm 6.066) \cdot C4_D] - [46.96(\pm 10.83) \cdot C5_D] \quad (6)$$

$$I_E = 1025(\pm 6.632) + [33.38(\pm 2.420) \cdot C1_E] - [16.36(\pm 3.857) \cdot C2_E] + [10.92(\pm 7.075) \cdot C3_E] - [22.49(\pm 8.433) \cdot C4_E] - [6.758(\pm 12.31) \cdot C5_E] \quad (7)$$

It has been proven already that electronic properties of organic molecules play a significant role in the retention mechanism on stationary phases with bonded metal complexes [28]. The simplest way to link particular electronic descriptors to Kovats retention indices is to build different theoretical PCR models and test their ability to predict experimental retention indices. Each model lacked one of the secondary descriptors given in Tables 2 and 3 – in model A dipole moment (DM) was excluded, in model B – double bond count (DBC), in model C – LUMO energy, in model D – HOMO energy, and model E – dielectric energy (DE). In the case of every model, first extracted principal component ($C1_A$ – $C1_E$) included nine highly correlated primary descriptors, mainly topological (MW, V, A, P, MV), and other (TE, BP, VP, LogP). A correlation between topological descriptors and total energy is easy to notice because size of a molecule is equivalent with an increase of total number of atoms and bonds. Vapour pressure and boiling point generally increase proportionally with the size of a molecule. The correlation is stronger when structure variations are smaller, which turn out to be true more often for small molecules containing single aromatic ring and short substituent, studied in this work. Strong linear dependence can be noticed between topological descriptors and partition coefficient octanol/water. This effect can be explained basing on the fact, that large aromatic molecules dissolve weaker in aqueous solvents. Fig. 2 presents an example of correlation PCA loadings for model A on the first two principal components, where some significant correlations can be found. $C1_A$ principal compo-

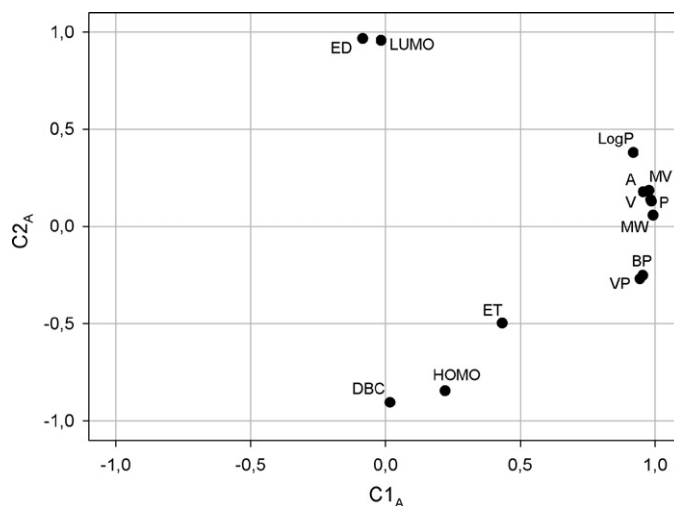


Fig. 2. Correlation loadings for the aromatic compounds on the first two principal components (model A).

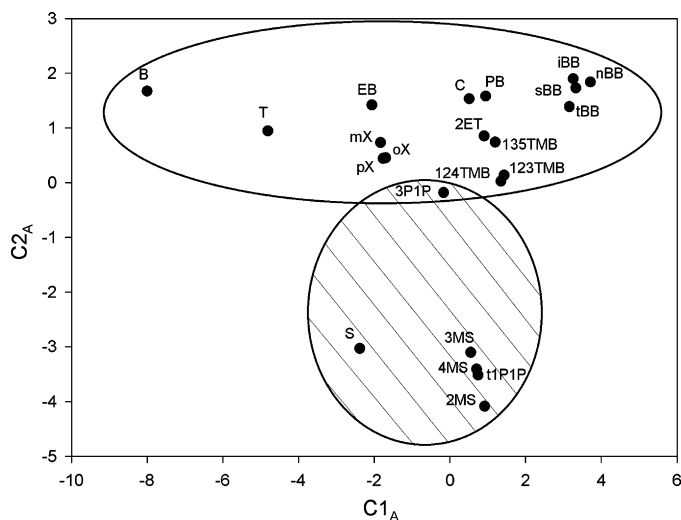


Fig. 3. Scores for the aromatic hydrocarbons on $C1_A$ and $C2_A$ principal components (model A).

nent is highly correlated with all primary descriptors (Table 2), with the exception of TE descriptor. Component $C2_A$ is correlated with LUMO and DE descriptors and reverse-correlated with HOMO and DBC descriptors. The second extracted principal component ($C2_B$ – $C2_E$) is highly correlated with dipole moment (DM). For model A, $C2_A$ is correlated with total energy. All studied correlations are briefly presented in Table 6.

Fig. 3 presents correlation scores of model A for the aromatic hydrocarbons on $C1_A$ and $C2_A$ principal components. Component $C1_A$ separates studied compounds according to molecule topology, while component $C2_A$ separates molecules according to the LUMO energy and dielectric energy (DE). Several groups of similar objects

Table 6

Descriptors showing significant loadings ($C_n \geq 0.7$) for principal components in all theoretical models, less significant (0.4–0.7) values are marked with an asterisk: $C1$ – $C5$ – principal components; R^2X – a sum of squares explained by the model.

Model	C1	C2	C3	C4	C5	R^2X (%)
A	MW, A, V, P, MV, BP, VP, LogP	LUMO, DE	TE	DBC*	–	99.2505
B	MW, A, V, P, MW, BP, VP, LogP	LUMO, DE	DM	TE	–	98.6189
C	MW, A, V, P, MV, BP, VP, LogP	DBC, HOMO	DM	TE	–	99.0878
D	MW, A, V, P, MV, BP, VP, LogP	DBC	DM	TE*	–	98.7351
E	MW, A, V, P, MV, BP, VP, LogP	LUMO	DM	TE*	–	98.7669

Table 7

Retention orders and differences between modelled and experimental Kovats retention indices for chosen isomers: R_{I_0} – retention order; $\Delta I = I - I_N$, where: I – experimental retention index, I_N – modelled retention index, N – symbol of the particular model (A–E).

Isomer	Exp. R_{I_0}	Model A		Model B		Model C		Model D		Model E	
		R_{I_0}	ΔI	R_{I_0}	ΔI	R_{I_0}	ΔI	R_{I_0}	ΔI	R_{I_0}	ΔI
1,3,5-Trimethylbenzene	1	1	33	1	–2	1	–11	1	21	1	–19
1,2,4-Trimethylbenzene	2	2	5	2	–5	2	–15	2	–4	2	–17
1,2,3-Trimethylbenzene	3	3	–51	3	–83	3	–86	3	–58	3	–95
<i>sec</i> -Butylbenzene	1	3	18	3	23	3	25	3	18	2	29
<i>tert</i> -Butylbenzene	2	2	6	1	14	1	10	2	5	1	8
<i>iso</i> -Butylbenzene	3	1	–20	2	–1	2	0	1	–19	3	10
<i>n</i> -Butylbenzene	4	4	–21	4	–7	4	–5	4	–1	4	–4
<i>para</i> -Xylene	1	1	5	1	14	1	3	1	–1	1	6
<i>meta</i> -Xylene	2	2	5	2	13	2	9	2	12	2	8
<i>ortho</i> -Xylene	3	3	7	3	16	3	14	3	12	3	15
2-Methylstyrene	1	2	16	1	0	1	–2	1	5	1	–7
3-Methylstyrene	2	1	–4	2	–2	2	7	2	6	2	2
4-Methylstyrene	3	3	0	3	17	3	23	3	13	3	23

can be found on the plot. Homologues are separated along axis x , and compounds with saturated and unsaturated substituent are separated along axis y . The only exception is 1-phenyl-1-propene, which stays close to aromatics with saturated side chain.

Statistical analysis (Table 5) shows that model A (without DM descriptor) and model D (without HOMO energy) describe the variables in the most effective way. Both models passed the normality test and produced the highest correlation coefficients. Fisher ratio for model A was relatively high, and the sum of squares explained by the model was the highest among all models (see Table 6). The worst model was the E model (without DE descriptor). Generally, predictive power of the studied models can be ordered as follows:

$$E < B < C < D < A$$

According to the sequence mentioned above, a significance of electronic properties affecting retention of aromatic compounds on stationary phases with bonded metal complexes, can be written in such way:

$$DM < HOMO < LUMO < DBC < DE$$

Trueness of shown descriptor sequence is maintained only in case of small one-ring aromatic compounds with short substituent, without any heteroatoms.

Experimental and modelled retention orders of studied aromatic isomers are shown in Table 7. Retention order of xylenes and trimethylbenzenes can be correctly predicted using all five models. That is because of small differences between electronic properties of listed isomers and stable geometry of molecules (no conformation changes). Isomers of aromatics substituted with unsaturated side chain have greater differences in dipole moments. In result, model A (build without DM descriptor) was not able to predict retention order of methylstyrenes. The most difficult isomers for prediction of their retention order were buthylbenzenes. These compounds have relatively long side chain, moreover four carbon atom chain is submitted to constant conformation change. Without taking into consideration conformation of buthylbenzenes and incorporating it into studied theoretical models it is impossible to predict their retention order. Additionally, it can be proven by comparison of ΔI for butylbenzenes (Table 7). Compound with stable geometry of the substituent (*tert*-butylbenzene) often have the lowest ΔI .

4. Conclusions

The applicability of molecular descriptors for multivariate characterisation of aromatic hydrocarbons was investigated. Accepted model in most cases showed good ability for predicting retention order of simple aromatic isomers, but this model was not precise enough to predict their exact retention times. Descriptors were derived from databases and semi-empirical (AM1), empirical (QSAR parameters), and quantum-chemical calculations. The influence of the molecular descriptors was visualized and interpreted using principal component regression PCR method. In the scope of the analysis of aromatic hydrocarbons by the application of packings with copper complexes chemically bonded to silica via iminoketonate groups, the following descriptors were identified as the most selective ones: dielectric energy (DE), double bond count (DBC), and the LUMO energy. To obtain correct prediction of retention indices for aromatic compounds it is necessary to introduce mentioned descriptors into theoretical models. Studied methods as PCA and MLR can be successfully applied for sophisticated study of interactions between simple organic molecules and stationary phases with bonded metal complexes.

References

- [1] Yu.G. Slizhov, A. Gavrilenko, Russ. J. Coord. Chem. 28 (2002) 736.
- [2] S. Jonsson, L.A. Eriksson, B. van Bavel, Anal. Chim. Acta 621 (2008) 155.
- [3] T. Kortvelyesi, M. Gorgenyi, K. Heberger, Anal. Chim. Acta 428 (2001) 73.
- [4] M.H. Fatemi, J. Chromatogr. A 955 (2002) 273.
- [5] B. Ren, Chemometr. Intell. Lab. 66 (2003) 29.
- [6] B.D. Junkes, R.D. Amboni, R.A. Yunes, V.E.F. Heinzen, Anal. Chim. Acta 477 (2003) 73.
- [7] Q.S. Xu, D.L. Massart, Y.Z. Liang, K.T. Fang, J. Chromatogr. A 998 (2003) 155.
- [8] Y.P. Du, Y.Z. Liang, D. Yun, J. Chem. Inform. Comput. Sci. 42 (2002) 1283.
- [9] A.R. Katritzky, K. Chen, U. Maran, D.A. Carlson, Anal. Chem. 72 (2000) 101.
- [10] N. Dimov, A. Osman, Ov. Mekenyan, D. Papazova, Anal. Chim. Acta 298 (1994) 303.
- [11] J.M. Sutter, T.A. Peterson, P.C. Jurs, Anal. Chim. Acta 342 (1997) 113.
- [12] R.S. Zhang, A.X. Yan, M.C. Liu, H. Liu, Z.D. Hu, Chemometr. Intell. Lab. 45 (1999) 113.
- [13] A.X. Yan, G.M. Jiao, Z.D. Hu, B.T. Fan, Comput. Chem. 24 (2000) 171.
- [14] M.M.C. Ferreira, Chemosphere 44 (2001) 125.
- [15] S.S. Liu, C.S. Yin, S.X. Cai, Z.L. Li, Chemometr. Intell. Lab. 61 (2002) 171.
- [16] M. Jalali-Heravi, M.H. Fatemi, J. Chromatogr. A 915 (2001) 177.
- [17] B. Lucic, N. Trinajstic, S. Slid, M. Karelson, A.R. Katritzky, J. Chem. Inform. Comput. Sci. 39 (1999) 610.
- [18] M. Pompe, M. Novic, J. Chem. Inform. Comput. Sci. 39 (1999) 59.
- [19] M. Jalali-Heravi, Z. Garkani-Nejad, J. Chromatogr. A 945 (2002) 173.
- [20] I. Rykowska, W. Wasiaik, Chem. Anal. (Warsaw) 46 (2001) 489.
- [21] O. Farkas, I.G. Zenkevich, F. Stout, J.H. Kalivas, K. Heberger, J. Chromatogr. A 1198–1199 (2002) 188.
- [22] O. Farkas, K. Heberger, I.G. Zenkevich, Chemometr. Intell. Lab. Syst. 72 (2004) 173.

- [23] O. Farkas, K. Heberger, *J. Chem. Inform. Model.* 45 (2005) 339.
- [24] B.D. Škrbič, *Chromatographia* 47 (1998) 721.
- [25] R. Zhang, A. Yan, M. Liu, H. Liu, Z. Hu, *Chemometr. Intell. Lab. Syst.* 45 (1999) 113.
- [26] A. Yan, G. Jiao, Z. Hu, B.T. Fan, *Comp. Chem.* 24 (2000) 171.
- [27] I.G. Zenkevich, *New Methods of Precalculation for Chromatographic retention Indices. Application of Lin-Log Correlation Equations, Principles of Structural Analogy and Methods of Molecular Dynamics*, in *100 Years of Chromatography*, Nauka Publ. House, Moscow, 2003, pp. 311 (in Russian).
- [28] I. Rykowska, W. Wasiak, *J. Chromatogr. A* 1216 (2009) 1713.