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Prediction of the retention of β -diketonato complexes in TLC systems on silica gel by quantitative structure–retention relationships

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Abstract: Quantitative structure–retention relationships for a series of 30 mixed β -diketonato complexes of cobalt(III), chromium(III) and ruthenium(III) were derived by multiple linear regression analyses using molecular descriptors obtained by quantum chemical calculations. The retention parameters were obtained by thin layer chromatography on silica gel using mono and two-component solvent systems. The molecular descriptors included in the multiple linear regression analysis were molecular weight, molecular volume, surface area, hydrophilic–lipophilic balance, percent hydrophilic surface area, dipole moment, polarizability, refractivity, energy of the highest occupied molecular orbital and energy of the lowest unoccupied molecular orbital. High agreement between the experimental and predicted retention parameters was obtained when polarizability and the hydrophilic–lipophilic balance were used as the molecular descriptors. Comparison of the models with those established on polyacrylonitrile showed that the structure of the sorbent is responsible for the chromatographic behaviour of the same compounds. The presented models can be used for the prediction of the retention of new solutes in screening chromatographic systems.

Keywords: quantitative structure–retention relationship; β -diketonato complexes; molecular descriptors; thin layer chromatography.

INTRODUCTION

Quantitative structure–retention relationships (QSRRs) are statistical models which quantify the relationship between the structure of a molecule and its chromatographic retention parameters in different kinds of chromatography.^{1–4} Application of QSRRs allows the prediction of the retention of a new solute, identification of the most informative structural descriptors, elucidation of the mole-

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cular mechanisms of separation in a given chromatographic system, evaluation of complex physicochemical properties of solutes and estimation of biological activities.⁵ In recent QSRR studies, quantum chemical descriptors alone or in combination with conventional descriptors have been extensively applied. In this way, many of the electronic and geometric properties of molecules can be expressed.⁶ The relationship between retention and the structural characteristics of a molecule explains the effect of chemical structure on the retention behaviour in a more accurate way.^{7–9}

Metal–ligand complexes represent an important group of analytes. TLC is utilized as an analytical tool for metal ion analysis, metal speciation studies and characterization of metal complexes of pharmaceutical or industrial importance. Coordination complexes between metals and β -diketones are interesting in this field because of the possibility of making wide varieties of substitutions in the β -diketonato chelate ring.¹⁰ These complexes provide models for different chemical processes and investigations ranging from synthetic, kinetic and structural topics to catalysis and many others, such as electron transfer processes relevant for biological activity.^{11–13}

The objective of this study was to develop models for accurate quantitative relationships between molecular structure and retention parameters of mixed β -diketonato complexes on silica gel stationary phases based on their molecular properties and to identify molecular descriptors most sensitive to the retention parameter R_M . In addition, the obtained models were compared with those established on polyacrylonitrile as the sorbent. The elucidation of these relationships may promote a more profound understanding of chromatographic separation processes and be used to predict the retention behaviour of structurally similar compounds.

EXPERIMENTAL

The retention parameters, R_F , were extracted from a previous work¹⁴ in which 30 mixed β -diketonato complexes of Co(III), Cr(III) and Ru(III) were chromatographed on silica gel with four mono- and five two-component mobile phases. They were converted to R_M values using the Bate-Smith and Westall Equation: $R_M = \log((1/R_F) - 1)$.

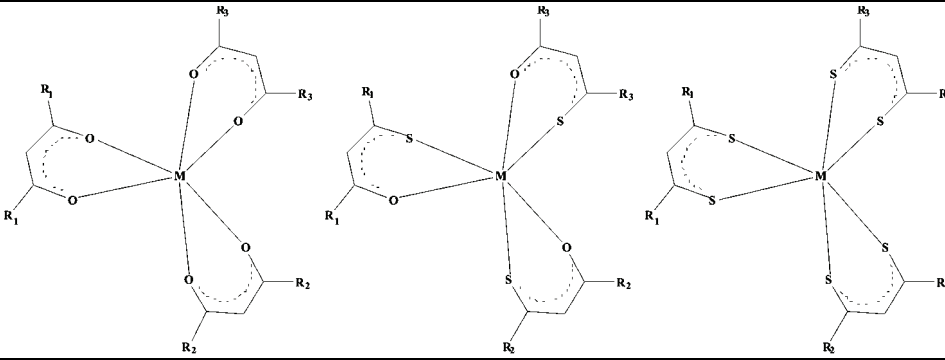
The geometry optimization of the molecules and calculation of molecular descriptors were realised with HyperChem 7.0 software.¹⁵ Additional calculation of the descriptors was developed by the Molecular Modelling Program Plus software. The following descriptors were calculated: molecular weight (MW), molecular volume (MV), surface area (SA), hydrophilic–lipophilic balance (HLB), percent hydrophilic surface area ($PHSA$), dipole moment (μ), polarizability (α), refractivity (R), energy of the highest occupied molecular orbital (E_{HOMO}) and energy of the lowest unoccupied molecular orbital (E_{LUMO}). The QSRR equation was obtained by stepwise multiple linear regressions (MLR).^{15,16} The significance level of the performed calculations was above 95 %.

RESULTS AND DISCUSSION

The structures of the 30 investigated compounds are shown in Table I. The calculated retention parameters, R_M , of these compounds are listed in Table II.

The compositions of the mobile phases are given in Table III. From Table II, it can be seen that substitution of a donor oxygen atom in the phacphac ligand with a less electronegative sulphur atom, to form the corresponding thio ligand, resulted in increased mobility of all the complexes.¹⁴ Also, substitution of the acac ligands leads to decreased R_M values, *i.e.*, the mobility was higher.

TABLE I. The structures of the investigated complexes



		I		II		III	
Compound		Complex		R ₁	R ₂	R ₃	Type
(1) (11) (21)	[M(acac) ₃] ^{a,b}	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	I
(2) (12) (22)	[M(acac) ₂ (phacphac)] ^c	CH ₃	CH ₃	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	I
(3) (13) (23)	[M(acac) ₂ (phacphSac)] ^d	CH ₃	CH ₃	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	II
(4) (14) (24)	[M(acac) ₂ (phSacphSac)] ^e	CH ₃	CH ₃	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	III
(5) (15) (25)	[M(acac)(phacphac) ₂]	CH ₃	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	I
(6) (16) (26)	[M(acac)(phacphSac) ₂]	CH ₃	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	II
(7) (17) (27)	[M(acac)(phSacphSac) ₂]	CH ₃	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	III
(8) (18) (28)	[M(phacphac) ₃]	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	I
(9) (19) (29)	[M(phacphSac) ₃]	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	II
(10) (20) (30)	[M(phSacphSac) ₃]	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	III

^aM = Co(III) (1–10) or Cr(III) (11–20) or Ru(III) (21–30); ^bacac = 2,4-pentanedionato ion; ^cphacphac = 1,3-diphenyl-1,3-propanedionato ion; ^dphacphSac = 3-mercapto-1,3-diphenyl-prop-2-en-1-one ion; ^ephSacphSac = 3-mercapto-1,3-diphenyl-prop-2-en-1-thione ion

The employed approaches were to find quantitative relationships between the intrinsic molecular structure and the physico-chemical properties of the compounds and to establish models that define the effects of molecular structure on the separation mechanisms. The structures of molecules were expressed numerically by quantitative molecular descriptors, which were in agreement with the structure of the compounds, as seen from Table IV.

For all investigated complexes, a correlation check for the descriptors was performed by a correlation matrix for the variables.^{17,18} To find if the structural descriptors of the complexes significantly influence their retention parameters, MLR analysis was used. The best model was selected based on the multiple squared correlation coefficients (r^2), the mean square error (MSE) and the value of the

Fischer significance, F -value (a statistical parameter for assessing the overall significance). For all mobile phases used, the best fitted correlation equations were obtained with selected molecular descriptors, which included polarizability and the hydrophilic–lipophilic balance. The following equations for one mono- and one two-component mobile phase are given as examples.

Compounds **1–10**:

$$R_M = (0.993 \pm 0.533) - (0.024 \pm 0.002)\alpha + (0.134 \pm 0.125)HLB \quad (1)$$

$$r^2 = 0.951, F = 67.989, MSE = 0.013, n = 10$$

$$R_M = (1.372 \pm 0.313) - (0.030 \pm 0.001)\alpha + (0.141 \pm 0.073)HLB \quad (2)$$

$$r^2 = 0.989, F = 311.278, MSE = 0.005, n = 10$$

TABLE II. R_M values of the investigated compounds (the compositions of the mobile phases are given in Table III)

Compd.	Mobile phase								
	1	2	3	4	5	6	7	8	9
1	1.279	0.788	0	1.690	1.005	0.410	1.061	1.061	1.005
2	0.954	0.659	-0.140	0.753	0.525	0.269	0.954	0.954	0.659
3	0.525	0.477	-0.176	0.689	0.389	0	0.659	0.630	0.575
4	0.347	0.231	-0.231	0.524	0.327	-0.194	0.454	0.389	0.432
5	0.659	0.052	-0.288	0.431	0.269	-0.140	0.602	0.659	0.140
6	0.250	-0.122	-0.327	0.07	0.176	-0.308	0.308	0.368	-0.070
7	-0.194	-0.176	-0.347	-0.017	0.122	-0.550	0.231	0.213	-0.194
8	0.052	-0.368	-0.327	0.347	0.105	-0.689	0.231	0.308	-0.368
9	-0.308	-0.410	-0.368	-0.158	-0.213	0.753	-0.052	0	-0.575
10	-0.432	-0.501	-0.389	-0.194	-0.269	-0.908	-0.105	-0.052	-0.689
11	1.380	1.005	-0.017	1.996	0.826	0.250	1.195	0.826	0.788
12	0.575	0.720	-0.087	1.061	0.454	0.070	0.602	0.454	0.659
13	0.231	0.550	-0.140	0.602	0.158	-0.017	0.454	0.347	0.501
14	0	0.389	-0.176	0.140	0.105	-0.176	0.347	0.213	0.432
15	-0.140	0	-0.176	0.308	0.213	-0.250	0.213	0.176	0.140
16	-0.250	-0.231	-0.213	-0.070	-0.158	-0.327	0.176	0.070	-0.194
17	-0.432	-0.368	-0.250	-0.194	-0.327	-0.410	0.105	-0.017	-0.389
18	-0.308	-0.454	-0.250	-0.035	0.052	-0.720	0.070	0.017	-0.368
19	-0.454	-0.501	-0.269	-0.194	-0.432	-0.788	-0.105	-0.017	-0.501
20	-0.602	-0.602	-0.308	-0.432	-0.753	-0.865	-0.231	-0.140	-0.689
21	1.996	1.279	0.070	1.690	1.005	0.368	1.279	0.908	0.954
22	1.279	0.659	-0.158	1.005	0.410	0.035	0.954	0.788	0.525
23	0.550	0.431	-0.176	0.389	0.347	-0.158	0.659	0.659	0.410
24	0.368	0.231	-0.194	0.070	0.105	-0.432	0.454	0.477	0.250
25	0.550	-0.070	-0.194	0.213	0.231	-0.327	0.659	0.525	0.052
26	0.269	-0.194	-0.213	-0.140	0.105	-0.410	0.213	0.432	-0.052
27	-0.176	-0.454	-0.250	-0.327	-0.347	-0.865	0.070	0.250	-0.368
28	-0.194	-0.410	-0.231	-0.194	0.052	-0.659	0.087	0.035	-0.368
29	-0.432	-0.550	-0.250	-0.525	-0.288	-0.865	-0.140	-0.035	-0.550
30	-0.788	-0.575	-0.288	-0.826	1.195	-1.061	-0.308	-0.231	-0.659

TABLE III. Mobile phases used

No.	Composition	Proportions (v/v)
1	Toluene	–
2	Dichloromethane	–
3	Chloroform	–
4	Xylene	–
5	1,2,3,4-tetrahydronaphthalene	–
6	<i>n</i> -Butyl acetate–carbon tetrachloride	40:60
7	Chloroform–carbon tetrachloride	50:50
8	Chloroform–carbon tetrachloride	30:70
9	Dichloromethane–carbon tetrachloride	80:20

Compounds **11–20**:

$$R_M = (1.097 \pm 0.699) - (0.029 \pm 0.003)\alpha + (0.175 \pm 0.148)HLB \quad (3)$$

$$r^2 = 0.953, F = 70.687, MSE = 0.020, n = 10$$

$$R_M = (0.836 \pm 0.717) - (0.027 \pm 0.003)\alpha + (0.196 \pm 0.151)HLB \quad (4)$$

$$r^2 = 0.942, F = 57.160, MSE = 0.021, n = 10$$

Compounds **21–30**:

$$R_M = (0.620 \pm 1.037) - (0.030 \pm 0.004)\alpha + (0.322 \pm 0.246)HLB \quad (5)$$

$$r^2 = 0.924, F = 42.467, MSE = 0.036, n = 10$$

$$R_M = (0.435 \pm 0.474) - (0.027 \pm 0.002)\alpha + (0.300 \pm 0.112)HLB \quad (6)$$

$$r^2 = 0.978, F = 158.351, MSE = 0.007, n = 10$$

Equations (1), (3) and (5) present the QSRR models for dichloromethane and Eqs. (2), (4) and (6) for dichloromethane–carbon tetrachloride as mobile phases.

By interpreting the descriptors in the regression models, it is possible to gain some insight into factors affecting the affinity of the investigated compounds for the stationary phase. It is known that, under the conditions of adsorption chromatography on silica gel, hydrogen bonds formed with the silanol groups of the sorbent, dipole–dipole and other electrostatic interactions determine the retention of the analysed compounds.¹⁹

Polarizability as a quantum-chemical descriptor of a molecule depends on the symmetry of the various covalent bonds in the molecule.²⁰ Highly polarisable compounds are expected to have strong attractions with the sorbent, resulting in shorter migration distance as seen from Tables II and IV. The repulsive steric interactions between the surface of silica gel and the phenyl rings of the complexes are reflected by the *HLB* descriptor on the QSRR models. A molecule with a high *HLB* has a high ratio of hydrophilic groups to lipophilic groups and *vice versa*. The *HLB* values are determined by calculating the values for different regions of a molecule.²¹ The proposed nonlinear QSRR models exhibit a high degree of correlation between the experimental and predicted retention factors. The obtained statistical results are presented in Table V.

TABLE IV. The calculated molecular descriptors

Compd.	MW^a	MV^b Å ³	SA^c Å ²	HLB^d	$PHSA^e$	μ^f D	α^g Å ³	R^h Å ³	E_{HOMO}^i eV	E_{LUMO}^j eV
1	356.26	173.62	23.94	4.066	24.02	0.384	28.60	81.99	-6.870	5.110
2	480.40	239.36	30.43	3.931	23.44	0.724	44.25	122.13	-6.738	4.885
3	480.40	239.81	30.49	3.961	23.57	5.119	46.62	128.57	-6.587	4.401
4	513.54	252.28	31.98	3.613	22.06	2.522	46.62	135.01	-6.506	3.826
5	604.54	304.87	36.83	3.824	22.97	0.317	59.90	162.26	-6.727	4.925
6	636.68	317.50	38.36	4.170	24.48	5.621	64.63	175.14	-6.251	3.616
7	670.83	332.61	40.46	3.470	21.44	4.168	64.63	188.03	-5.791	1.474
8	728.69	370.07	43.26	3.742	22.62	1.195	75.55	202.39	-6.705	4.797
9	776.89	389.80	45.63	4.216	24.68	5.628	82.64	221.72	-5.650	1.223
10	828.11	411.52	48.34	3.204	20.28	9.492	82.64	241.05	-6.170	1.990
11	349.32	175.94	24.45	4.409	25.52	0.356	28.60	81.99	-2.213	5.854
12	473.47	241.39	30.86	4.175	24.50	1.596	44.25	122.13	-2.222	4.866
13	489.54	247.40	31.61	4.389	25.43	5.480	46.62	128.57	-2.347	4.540
14	506.61	254.53	32.49	3.875	23.19	3.932	46.62	135.01	-2.267	3.554
15	597.61	306.72	37.27	4.015	23.81	0.949	59.90	162.26	-2.234	4.937
16	629.74	318.70	38.73	4.364	25.32	5.858	64.63	175.14	-2.387	4.470
17	663.89	333.13	40.56	3.563	21.84	5.706	64.63	188.03	-2.184	3.441
18	721.75	372.10	43.67	3.903	23.32	1.030	75.55	202.39	-2.152	4.976
19	769.95	389.93	45.81	4.330	25.17	6.935	82.64	221.72	-2.046	4.412
20	821.17	412.91	48.85	3.380	21.04	8.302	82.64	241.05	-2.935	2.790
21	398.40	174.38	23.90	4.045	23.94	0.865	28.60	81.99	-0.926	6.487
22	522.54	239.54	30.27	3.851	23.09	1.618	44.25	122.13	-0.912	4.915
23	538.61	245.69	31.00	4.080	24.09	6.081	46.62	158.57	-1.057	4.516
24	555.68	251.55	31.88	3.690	22.39	3.348	46.62	135.01	-1.099	3.710
25	646.68	305.12	36.71	3.759	22.69	2.037	59.90	162.26	-0.863	4.869
26	678.81	317.12	38.13	4.087	24.12	6.916	64.63	175.14	-1.308	4.334
27	712.96	329.56	39.96	3.438	21.29	2.604	64.63	188.03	-1.272	3.697
28	770.82	370.70	43.15	3.693	22.40	2.469	75.55	202.39	-0.809	4.809
29	819.02	388.77	45.29	4.122	24.27	8.280	82.64	221.72	-1.476	4.119
30	870.25	411.94	48.69	3.360	20.96	10.770	82.64	241.05	-1.755	2.580

^aMolecular weight; ^bmolecular volume; ^csurface area; ^dhydrophilic-lipophilic balance; ^epercent hydrophilic surface area; ^fdipole moment (1 D = 3.336×10⁻³⁰ C m); ^gpolarizability; ^hrefractivity; ⁱenergy of the highest occupied molecular orbital; ^jenergy of the lowest unoccupied molecular orbital

TABLE V. Statistical results obtained

Compd.	Mobile phase	Intercept	Slope	r^2	F	MSE
1-10	2	0.003 (±0.034)	0.951 (±0.076)	0.951	155.732	0.011
	9	0.001 (±0.020)	0.989 (±0.037)	0.989	709.096	0.004
11-20	2	0.002 (±0.041)	0.953 (±0.075)	0.953	161.270	0.017
	9	0.002 (±0.042)	0.942 (±0.082)	0.942	130.611	0.017
21-30	2	0.003 (±0.054)	0.924 (±0.094)	0.924	96.926	0.029
	9	0.0005 (±0.025)	0.978 (±0.051)	0.978	362.727	0.006

The relationships between the experimental and predicted R_M values together with their residuals (difference between predicted and experimental value), for the Cr(III) complexes are shown in Fig. 1 as an example.

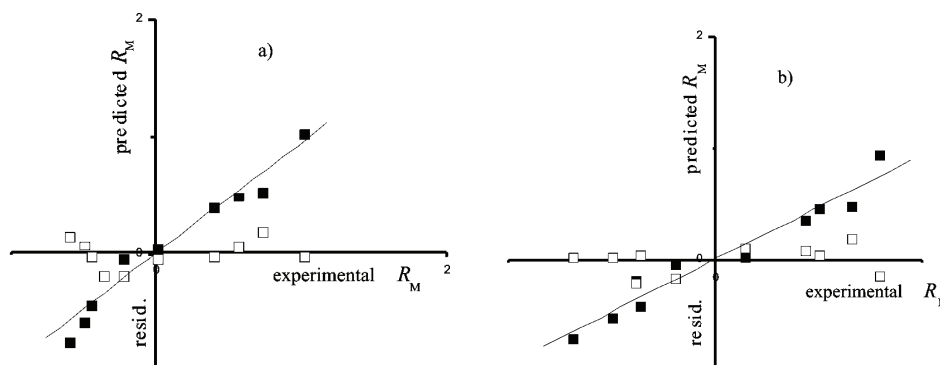


Fig. 1. Relationship between the experimental and predicted R_M values together with their residuals, for Cr(III) complexes; a) dichloromethane, b) dichloromethane-carbon tetrachloride.

The distribution of the residuals on both sides of the zero line indicates that there is no systematic error in the obtained models. Fig.1 reflects the actual predictive power of the established models.

Analysis of these results indicates that the proposed models can correctly represent the relationship between the retention parameters of the investigated compounds on silica gel and the molecular descriptors calculated solely from molecular structure. These models are suitable for prediction of the retention of structurally similar compounds under the same chromatographic conditions.

Finally, the obtained models were compared with those established on polyacrylonitrile sorbent.¹⁵ In the established QSRR models for these sorbents, the retention behaviours are described by different molecular descriptors. This comparison showed that different aspects of the molecular structure are responsible for the separation of the analytes. This is a quantitative confirmation of the previously established separation mechanisms of the investigated compounds on silica gel¹⁴ and polyacrylonitrile.²² Hence, it is clear that differences in the structure of the sorbent determine the chromatographic behaviour of analytes, *e.g.*, the type of the sorbent-molecule interactions. In addition, these QSRR models can be used for selection of the corresponding chromatographic system for separation of structurally similar compounds.

CONCLUSIONS

A QSRR study of a series of mixed β -diketonato complexes of Co(III), Cr(III) and Ru(III) on a thin layer of silica gel has been presented. The established two-parameter models show satisfactory correlation and predictive po-

wer. The main factors influencing retention on silica gel for all employed mobile phases are polarizability and the hydrophilic–lipophilic balance. The QSRR models quantitatively describe the retention of analytes, based on their molecular descriptors, which reflect structural differences between the compounds. A good correlation between the experimental and predicted retention parameters was observed when polarizability and *HLB* were used as the molecular descriptors. The correlations obtained between the retention and the molecular descriptors were highly significant and might be used to predict the retention behaviour of structurally similar compounds with a considerable degree of confidence when the molecules are new or when the experimental determination is rather difficult or subject to large uncertainties. This study gives a quantitative assessment of the relative importance of specific interactions.

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ИЗВОД

ПРЕДВИЂАЊЕ РЕТЕНЦИЈЕ β -ДИКЕТОНАТО КОМПЛЕКСА У TLC СИСТЕМИМА
НА СИЛИКА-ГЕЛУ ПРИМЕНОМ КВАНТИТАТИВНОГ ОДНОСА
СТРУКТУРЕ И РЕТЕНЦИЈЕ

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У овом раду квантификован је однос структуре и ретенције 30 мешовитих β -дикетонато комплекса кобалта(III), хрома(III) и рутенијума(III) применом мултилинеарне регресионе анализе коришћењем молекулских дескриптора, који су добијени помоћу квантно-хемијских израчунавања. Ретенциони параметри су добијени танкослојном хроматографијом на силика-гелу применом моно- и двокомпонентних растварача. Молекулски дескриптори који су укључени у мултилинеарну регресиону анализу су молекулска тежина, молекулска запремина, површина, хидрофилни–липофилни баланс, проценат хидрофилне површине, диполни моменат, поларизабилност, рефрактивност, енергија највише заузете молекулске орбитале и енергија најниже празне молекулске орбитале. Добијена је задовољавајућа корелација између експерименталних ретенционих параметара и ретенционих параметара предвиђених постављеним моделима, који садрже поларизабилност и хидрофилни–липофилни баланс као дескрипторе. Поређења ових модела са моделима добијеним на полиакрилонитрилном сорбенту, за иста једињења, показују да је структура сорбента одговорна за хроматографско понашање. Ови модели се могу користити за предвиђање ретенције нових једињења у датим хроматографским системима.

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