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Gas chromatography silica packings with chemically bonded complexes of Cu(II) and Cr(III)

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Abstract

In the presented work, copper(II) and chromium(III) complexes chemically bonded to silica surface were prepared and used in gas chromatography. Chlorides of these metals were bonded to the silica surface by the use of the ketoimine group originally from 2-(3-triethoxysilylpropylimino)-3-(*n*-butyl)-pentanone-4. Packings obtained in such way were investigated to evaluate their usefulness in the analysis of aliphatic and aromatic halogenated hydrocarbons as well as ethers, thioethers and ketones. Moreover, packings were subjected to elemental analysis and differential scanning calorimetry (DSC), thus some retention parameters were determined to characterize specific interactions between bonded metal and adsorbate molecules. Attempts were also made to separate some mixtures of the nucleophilic compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gas chromatography; Copper(II) and chromium(III) complexes; Chemically bonded phases; Ethers and thioethers; Ketones

1. Introduction

Using packings that are characterized by high selectivity and effectiveness is a base requirement for gas chromatography in the field of separation of complex mixtures. Complexation gas chromatography (CGC) [1,2] is an area of growing importance towards these requirements. A base for a separation in CGC is creating labile complexes with either metal cations or organic complexes. Coordinative compounds of transition elements included in CGC stationary phase are capable of selective interactions with electron-donor adsorbates, thus creating reverse complexes of different stability [3]. Taking into account a fact that creation of such complexes is a very

selective process and depends not only on structures of complexing compounds, but also on a temperature, using such complexes in the chromatography makes it possible to separate compounds of similar chemical structure and boiling temperatures, like different types of isomers, isotopes included. Large number of factors showing an influence to the stability of the created compounds let control retention to obtain required separations. Moreover, the feasibility of wide control of the above parameters makes the packings interesting not only from the analytical, but also from the physical and chemical points of view. These packings allow for investigation of interactions between sorbates and complexes of transition metals. They are characterized by high selectivity (allowing even separation of *cis*- and *trans*-isomers), thermal stability, and high resistance to external factors [4–9].

In the presented work, copper(II) and chromium(III) complexes were chemically bonded to silica surface to

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be used as packings for gas chromatography. Chlorides of these metals were bonded to the silica surface by the use of the ketoimine group originally from 2-(3-triethoxysililpropylimino)-3-(*n*-butyl)-pentanone-4. In the presented work, a comparison of some retention parameters (capacity factor, retention index, specific retention volume, and molecular retention index) was made for the packings under study. It allowed estimating the observed specific interactions as well as to determine dependencies among a structure of an adsorbate molecule, retention time, and a type of a packing. Ethers, thioethers and ketones were used as adsorbates.

A packing containing no bonded metal was also investigated and treated as a reference. The physical and chemical properties of the packings were determined and compared to the corresponding properties of the reference packing.

Several possibilities of analytic use of the packings under study were discussed.

2. Experimental

2.1. Reagents

Silica gel (Porasil C 80–100 mesh) was purchased from Waters Associates, Inc., Milford, USA. Silane (2-(3-triethoxysililpropylimino)-3-(*n*-butyl)-pentanone-4)), which was used for the modification of the silica surface, was obtained from the Metalloorganics Department of the Adam Mickiewicz University, Poznan, Poland. Hexamethyldisilazane, which was used to deactivate free silanol groups in the “end capping” reaction, was purchased from Riedel-Dehaen (Germany).

Other reagents were from POCh (Gliwice, Poland) or Fluka (Buchs, Switzerland). The compounds used

for the determination of chromatographic properties of packings were manufactured by different companies. They were either certified or of analytical grade.

2.2. Apparatus

Chromatographic measurements were carried out on a gas chromatograph CHROM 5 (Czech Republic) equipped with a flame-ionization detector. The temperature in the oven was determined using a DT 2000 thermometer (Digital Thermometer, Slandi, Warsaw, Poland) and the pressure at the column inlet was measured with a mercury manometer. Helium, dried on molecular sieve 4 Å, was used as carrier gas. The flow rate of the carrier gas was measured with a digital flowmeter (J&W Scientific, Falsom, CA, USA). Stainless steel columns were used (2 m in length, 3 mm in i.d.).

The obtained packings were characterized by performing: (1) elemental analysis, (2) measurement of nitrogen adsorption/desorption isotherms, and (3) differential scanning calorimetry (DSC).

Elemental analysis was performed on 2400 CHN Elemental Analyzer (Perkin-Elmer, Norfolk, USA). The obtained results are presented in Table 1.

Measurement of nitrogen adsorption/desorption isotherms at liquid nitrogen temperature was performed on ASAP 2010 sorptometer (Micromeritics, Nacross, GA, USA). It is well known that chromatographic materials should be free of micropores, i.e. those below 20 Å in diameter [10], because their presence slows down mass transfer [11–14]. Fig. 1A shows that this is the case for packings studied by us. Moreover, the packings should have a homogeneous pore shape. The latter is not easy to determine, but the analysis of the shape of hysteresis loop on the adsorption/desorption isotherm can give some infor-

Table 1
Physico-chemical characteristics of the investigated packings

Number	Packing	Elemental analysis (%)				Surface area (m ² g ⁻¹)
		C	H	N	Metal	
1	Without metal	5.51	1.10	1.07	–	87
2	Modified with CuCl ₂	5.62	1.87	1.00	1.71	88
3	Modified with CrCl ₂	8.19	1.59	1.66	0.05	83

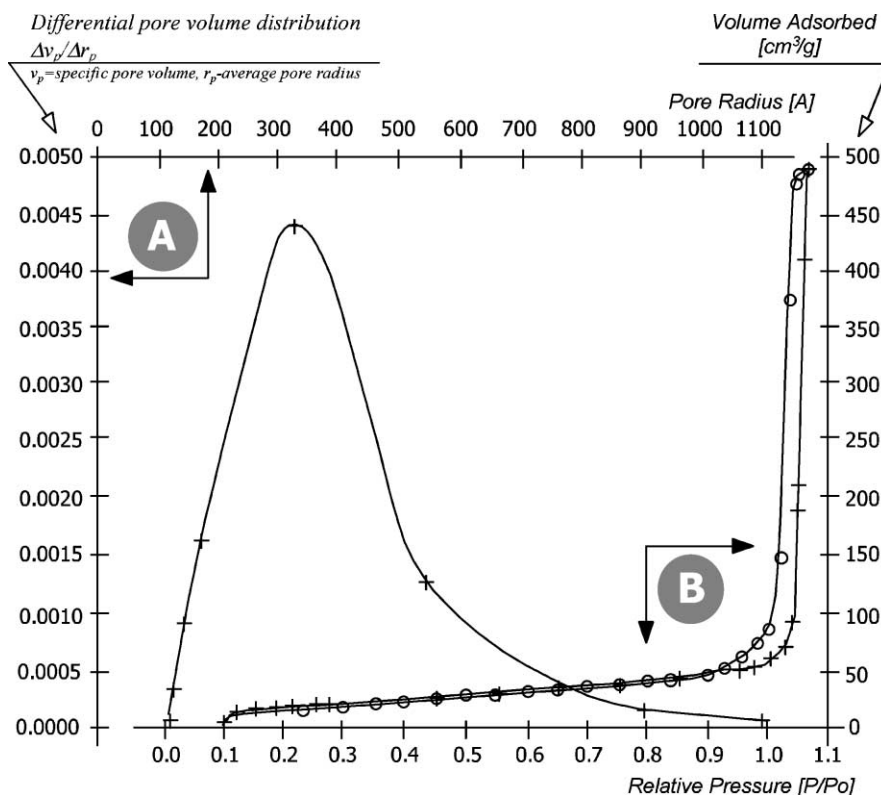


Fig. 1. Pore-size distribution in silica support (A); and isotherms of adsorption–desorption of nitrogen for packings with bonded CuCl_2 (B).

mation on the pore structure. The hysteresis loop shown in Fig. 1B is almost vertical with almost parallel branches and hence it belongs to type H1 according to the IUPAC classification [10]. The above type of hysteresis is usually associated with the porous materials consisting of agglomerates or compacts of approximately uniform spheres in fairly regular array, and therefore they have relatively narrow pore-size distribution.

Pore volumes of the packings studied were: $0.83 \text{ cm}^3 \text{ g}^{-1}$ for the starting material, $0.72 \text{ cm}^3 \text{ g}^{-1}$ for packing with bonded 2-(3-triethoxysililpropylimino)-3-(*n*-butyl)-pentanone-4, $0.68 \text{ cm}^3 \text{ g}^{-1}$ and $0.57 \text{ cm}^3 \text{ g}^{-1}$ for packings with CuCl_2 and CrCl_3 , respectively. Surface areas determined by BET method are listed in Table 1.

The packings were also subject for analyze by DSC. The DSC analysis was performed on DSC-50 calorimeter (Shimadzu, Japan).

2.3. Preparation of columns

The modification of the silica was performed in three stages.

1. *Stage I*: During the first stage, dry silica (Porasil C) was immersed in a mixture of anhydrous xylene and 3-aminopropyltriethoxysilane. The mixture was boiled for 12 h in a vessel provided with a reflux condenser under continuous stirring and careful protection against moisture. Unreacted silane was extracted with xylene and hexane in a Soxhlet apparatus. After this operation, the silica was subjected to drying under vacuum, and then to so-called “end capping” reaction with hexamethyldisilazane (HMDS), in order to deactivate free silanol groups remaining at its surface.
2. *Stage II*: The second step was the reaction aiming at bonding amino groups with *n*-butylpentanone. As

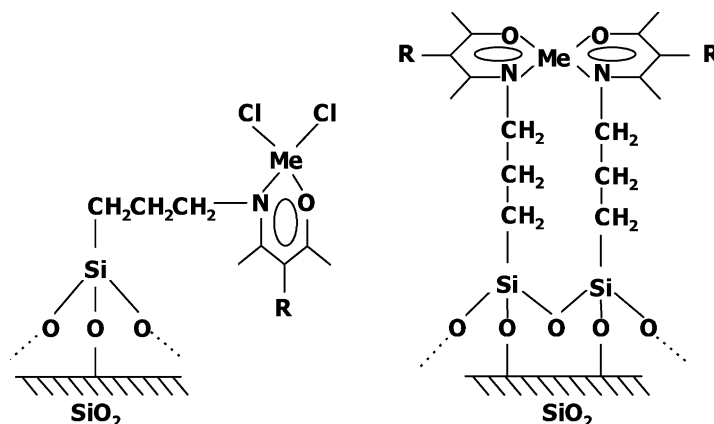


Fig. 2. Scheme of MeX complexes chemically bonded with silica surface.

the previous one, this reaction was also performed in anhydrous xylene for 12 h under continuous stirring. During this time, the system was protected against humidity. The final product of the reaction was extracted by the use of xylene first, and next hexane in a Soxhlet apparatus. Finally, the silica was dried under vacuum.

3. *Stage III*: During the third stage, the last reaction was performed—bonding copper(II) and chromium(III). To this goal, dry silica brained in the previous stage was immersed in an anhydrous tetrahydrofuran solution of either copper(II), or chromium(III) chloride, and allowed to stand for 7 days in a room temperature. The system was protected against the moisture. Finally, the silica was filtered off, the excess of CuCl_2 was extracted with tetrahydrofuran in a Soxhlet apparatus, and the silica was subjected to drying.

The complexes formed at the silica surface are shown in Fig. 2.

3. Results and discussion

One of the most important parameters of packings for gas chromatography is their thermal stability. Thermograms obtained by the use of classical thermogravimetrics analysis usually do not reflect all the changes taking place at the silica surface, because silica gel being more than 90% of the total packing mass does

not let to characterize precisely changes for other packing components (remaining 10%). Due to this fact, the DSC [15] method was used to obtain more detailed information about energetic changes at the silica surface at different temperatures. Beside an advantage of measuring changes taking place only at the silica surface rather than for the whole support, a formation of complexes at the support surface can be proved by the use of the DSC analysis. Note, however, that the DSC analysis was not used to precisely characterize physico-chemical properties of the packings under study, but only to determine their thermal stability.

The results of DSC analysis of the packings bonded with CuCl_2 , CrCl_3 , and with no metal are presented in Fig. 3. As it can be seen, the bonding of Cu(II) and Cr(III) chlorides is practically complete, because the peak characteristics of the free ligand (curve 1) disappeared completely after introducing copper (curve 2) and chromium (curve 3). Complexes formed at the surface are considerably more stable than the free ligand.

All the obtained packings were investigated to evaluate their usefulness in the analysis of ethers, thioethers, and ketones. Specific metal-donor-type electron interactions can be affected by many factors characterizing the packing and the adsorbate, so at first an attempt was made to identify and characterize them. Assessment of the charge-transfer interactions between the metal bound in complexes and substances of electron-donor properties was based on the retention times determined for a specifically chosen group of adsorbates. On the basis of these times such

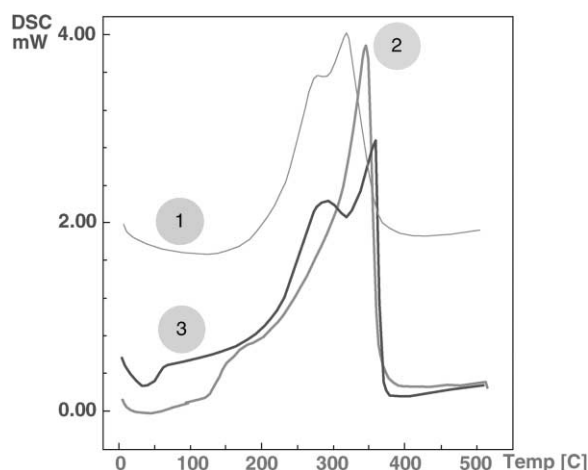


Fig. 3. DSC curves for silica-bonded: without metal (curve 1), with copper chloride (curve 2) and with chromium chloride (curve 3).

retention parameters were calculated, as: capacity factor (k), retention index (I), specific retention volume (V_g), and molecular retention index (ΔM_e). Detailed definition of the latter can be found in [16]. Based on the computed retention parameters, a trial was performed to determine an influence of a metal bonded in the complex to the retention of the adsorbates under study, to find dependence between the structures of adsorbate complexes and values of interactions of charge-transfer type with bonded metal complexes.

The obtained results are reported in Tables 2 and 3. The sample mixture chromatograms show separation capabilities of the tested packings. The presented chromatograms have symmetric peaks which points to homogeneity of surface adsorption centers. Fig. 4A–D show separation of mixtures of ethers and thioethers. The first two chromatograms illustrate separation of a mixture of cyclic ethers and thioethers, while the third one shows a separation of a mixture of furan and thiophene derivatives. The last chromatogram presents a separation of a mixture of aliphatic ethers. Some retention parameters for these groups of adsorbates are presented in Table 2.

Analyzing the obtained results and the chromatograms presented above, it may be noted that in the case of cyclic ethers, in particular, tetrahydrofuran and tetrahydrothiophene, the interactions were stronger than for linear ethers. This results from the fact that in cyclic ethers the access to lone electron

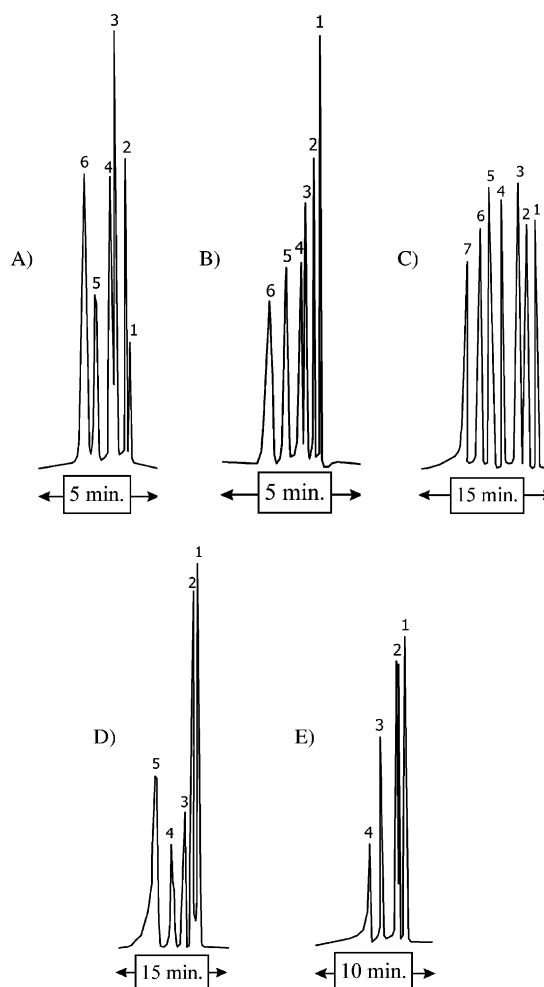


Fig. 4. (A) Separation of mixture of cyclic ethers and thioethers; packing with CuCl_2 ; column temperature 120°C ; $V_{\text{He}} = 18.0 \text{ ml min}^{-1}$; peaks: (1) furan, (2) 2-methylfuran, (3) thiophene, (4) 2,5-didydrofuran, (5) tetrahydrofuran, (6) 2-methylthiophene. (B) Separation of mixture of cyclic ethers and thioethers; packing with CrCl_3 ; column temperature 120°C ; $V_{\text{He}} = 18.0 \text{ ml min}^{-1}$; peaks: (1) furan, (2) 2-methylfuran, (3) thiophene, (4) 2,5-didydrofuran, (5) 2-methylthiophene, (6) 2-chlorothiophene, (7) 2,5-dihydrofuran. (C) Analysis of a mixture of furan and thiophene derivatives; packing with CuCl_2 ; column temperature 120°C ; $V_{\text{Ar}} = 20.4 \text{ ml min}^{-1}$; peaks: (1) furan, (2) 2-methylfuran, (3) thiophene, (4) 2,5-dimethylfuran, (5) 2-methylthiophene, (6) 2-chlorothiophene, (7) 2,5-dihydrofuran. (D) Separation of mixture of aliphatic ethers; packing with CuCl_2 ; column temperature 130°C ; $V_{\text{He}} = 20.0 \text{ ml min}^{-1}$; peaks: (1) diethyl ether, (2) diisopropyl ether, (3) dipropyl ether, (4) dibutyl ether, (5) methylbutyl ether. (E) Separation of mixture of ketones; packing CuCl_2 ; column temperature 130°C ; $V_{\text{He}} = 20.0 \text{ ml min}^{-1}$; peaks: (1) diethylketone, (2) methylpropylketone, (3) ethyl-propylketone, (4) butyl-methylketone.

Table 2
The retention parameters for studied packings at 133 °C

Number	Adsorbate	Without metal				Modified with CuCl ₂				Modified with CrCl ₃			
		<i>k</i>	ΔM_e	<i>V_g</i>	<i>I_R</i>	<i>k</i>	ΔM_e	<i>V_g</i>	<i>I_R</i>	<i>k</i>	ΔM_e	<i>V_g</i>	<i>I_R</i>
1	Diethyl ether	1.56	−0.24	1.98	512	2.33	7.16	2.09	565	3.83	14.71	0.28	619
2	Vinylethyl ether	1.60	2.37	1.39	517	6.91	31.63	5.95	725	n.e.	n.e.	n.e.	n.e.
3	Methylbutyl ether	3.19	2.96	2.79	635	4.45	6.53	3.84	661	9.60	19.84	8.60	756
4	Ethylbutyl ether	5.01	−0.26	4.38	712	7.27	2.64	6.26	733	n.e.	n.e.	n.e.	n.e.
6	<i>tert</i> -Butylmethyl ether	2.54	−2.54	2.22	596	3.90	3.78	3.35	641	5.69	8.79	5.10	677
7	<i>tert</i> -Butylethyl ether	3.59	−8.26	3.13	655	4.64	−6.65	4.00	667	7.98	1.83	7.14	727
9	Dipropyl ether	4.77	−1.43	4.17	704	6.90	1.55	5.94	725	9.56	5.73	8.56	755
10	Diisopropyl ether	3.35	−9.92	2.92	643	4.25	−8.45	3.66	654	5.65	−5.39	5.06	676
14	Furan	1.39	17.97	1.21	492	1.55	19.74	1.34	505	2.44	26.36	2.18	552
15	2,3-Dihydrofuran	2.02	9.98	1.76	556	4.59	25.20	3.95	665	8.20	34.51	7.34	731
16	2,5-Dihydrofuran	2.75	17.48	2.40	610	4.77	26.00	4.11	671	8.34	34.89	7.47	734
17	Tetrahydrofuran	3.00	17.51	2.62	625	5.60	27.26	4.82	694	n.e.	n.e.	n.e.	n.e.
18	Methylfuran	2.44	2.60	2.13	589	3.13	5.35	2.70	609	4.39	9.51	3.93	639
19	2-Methylfuran	2.41	2.29	2.11	587	2.85	3.43	2.46	595	4.84	11.53	4.33	653
20	2,5-Dimethylfuran	1.65	−11.77	1.71	587	1.69	−10.61	1.55	595	3.24	−3.02	2.55	649
21	3,4-Dihydro-2H-pyran	3.77	11.01	3.30	664	5.38	14.45	4.64	688	8.60	21.51	7.70	739
22	Thiophene	3.63	9.11	3.18	650	4.18	9.26	3.60	651	6.34	14.99	5.67	692
23	2-Methylthiophene	6.23	7.99	5.45	749	8.46	9.81	7.28	755	11.23	13.20	10.05	779
24	2-Chlorothiophene	9.01	−2.62	7.87	801	11.58	−4.07	9.97	802	n.e. ^a	n.e.	n.e.	n.e.
25	Tetrahydrothiophene	7.19	22.39	6.28	774	9.94	23.16	8.56	779	n.e.	n.e.	n.e.	n.e.

n.e.: not eluted.

Table 3
The retention parameters for studied packings at 133°C

Number	Adsorbate	Without metal				Modified with CuCl ₂				Modified with CrCl ₃			
		<i>k</i>	ΔM_e	<i>V_g</i>	<i>I_R</i>	<i>k</i>	ΔM_e	<i>V_g</i>	<i>I_R</i>	<i>k</i>	ΔM_e	<i>V_g</i>	<i>I_R</i>
1	Dimethylketone	2.00	24.75	1.76	576	4.81	38.79	4.70	676	2.88	29.08	2.51	607
2	Methyl-ethylketone	2.38	23.06	2.97	663	8.08	35.74	7.91	754	16.59	53.45	14.44	880
3	Methyl-propylketone	3.38	8.90	2.25	663	8.08	21.66	5.99	754	16.59	39.33	10.80	880
4	Diethylketone	2.00	335	1.33	576	4.81	10.81	3.56	677	2.88	9.26	1.87	598
5	3-Methyl-2-butanone	9.24	32.33	6.16	830	11.23	28.52	8.32	803	22.43	46.15	14.61	929
6	Butyl-methylketone	11.42	19.41	7.61	838	31.70	36.51	23.51	960	45.69	51.43	29.76	1066
7	Ethyl-propylketone	5.20	8.74	3.47	762	12.04	15.45	8.93	810	22.43	26.85	14.61	891
8	Methyl-pentylketone	21.10	16.57	14.06	897	62.08	37.00	46.03	1063	n.e.	n.e.	n.e.	n.e.
9	Ethyl-butylketoane	18.12	13.70	12.08	883	48.65	31.76	36.08	1026	n.e.	n.e.	n.e.	n.e.
10	Dipropylketone	9.81	11.64	6.54	813	24.78	17.24	18.37	923	n.e.	n.e.	n.e.	n.e.
11	Cyklopropanone	16.68	48.89	11.12	734	42.90	87.21	31.81	1007	n.e.	n.e.	n.e.	n.e.

pairs at oxygen atom is significantly easier than for linear aliphatic compounds. Other reasons are that the molecule is stiffer because of its cyclic structure and that the oxygen is exposed outside the molecule. The above can be easily noticed if we compare two compounds of the same number of carbon atoms in molecule: diethyl ether and tetrahydrofuran.

Strength of the effect exerted on specific interactions by free electron pairs at oxygen atom can also be seen when one compares the values of retention parameters for furan and tetrahydrofuran. In the case of furan, oxygen (assuming sp^2 hybridization) donates two p electrons to an aromatic sextet. A presence of these electrons in the aromatic sextet implies that they will be partially distributed within the whole ring, which as a result will be negatively charged, while the oxygen atom will assume a partial positive charge.

In the case of aliphatic ethers, a length of a carbon string bonded with the oxygen atom influences the values of specific interactions. It was determined that more this string is longer or branched, lower the specific interactions are. It can be seen while comparing values of ΔM_e , which are highest for small molecules (ethyl ether and methylbutyl ether). Succeeding ethers with growing number of carbon atoms in their molecules are characterized by lowering values of ΔM_e , moreover, in the case of diisopropyl ether, a negative value of this parameter was detected. It proves the great influence of the steric factor to the specific interactions among ethers and complexes of transient metals.

Table 3 contains results obtained for the ketones under study. This group of compounds (like ethers), due to free electron pairs by the oxygen atom, is capable of specific interactions with electron-donor

centers at the silica surface. It was determined that more the carbonyl group is shifted to the middle of the sorbate molecule, less the specific interactions are. This is particularly visible while comparing retention parameters for ketones, such as diethylketone and methyl-propylketone, ethyl-propylketone and butyl-methylketone, respectively. The strongest interactions were observed for cyclic ketones (similarly to the case of ethers). A separation of a sample mixture of ketones is presented in Fig. 4E.

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