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Journal of Chromatography A, 844 (1999) 239–248

JOURNAL OF
CHROMATOGRAPHY A

Chemically bonded chelates as selective complexing sorbents for gas chromatography

VII. *N*-[3-(Trimethoxysilyl)propyl]diethylenetriamine complexes with CuCl_2 and CrCl_3 [☆]

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Received 9 November 1998; received in revised form 9 March 1999; accepted 10 March 1999

Abstract

The study reported in this work concerns the use of copper and chromium complexes, chemically bonded to silica, in gas chromatography. Chlorides of these metals were bonded to the support through amino groups from [3-(trimethoxysilyl)propyl]diethylenetriamine. The packings were tested in order to verify their usefulness in the analysis of aliphatic and aromatic nucleophilic compounds. The retention parameters characterising specific interactions of the bonded metal with adsorbate molecules, such as: retention factor (*k*), retention index (*I*), specific retention volume (V_R), and molecular retention index (ΔM_c), were determined. For comparison, similar measurements were conditioned on a packing with no bonded metal. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, GC; Metal complexes; Hydrocarbons

1. Introduction

Chemically bonded phases containing amino groups are of particular interest in gas chromatography (GC) as well as in high-performance liquid chromatography (HPLC). Among them are amino-organic alkoxy-silanes having one or more terminal amino groups in the alkyl chain. These groups are responsible for the high reactivity of aminosilanes towards transition metals. The first researchers who obtained and used chemically bonded phases with amino groups in GC were Haken and co-workers

[1–4], who modified the surface with polysiloxanes substituted with aminoalkyl groups. The packing thus prepared was used for separation of aldehydes, lactones and first of all – ketones. This packing was also effective in separation of geometric isomers of alcohols due to the formation of hydrogen bond ($\text{OH} \cdots \text{NH}$) between the amino groups and the alcohols.

Chemically bonded phases comprising amino groups bound to the support surface through an alkyl chain show electron-donor–acceptor properties and due to this fact they can be permanently bonded with the metal cations characterised by electron deficit. Chemically bonded chelates which are selective sorbents [5,6], have been frequently used to separate

[☆]For Part VI, see *J. Chromatogr. A*, 773 (1997) 209–217.

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different organic compounds, e.g., hydrocarbons, alcohols and amines. Khuhawar et al. [7] studied chelate complexes Ni(II) with Schiff's bases. Phases of this kind were used to separate aromatic hydrocarbons, heteroaromatic aldehydes, ketones, amines and alcohols. Transition metals easily enter into specific interactions with electron-donor compounds forming π -complexes. Separation of higher olefins (C_5 and higher) and their isomers have been carried on transition metal complexes of bonded silicas with the carrier groups $-CN$, $-SH$, $-NH_2$ and PPh_2 [8–13]. The packing [14] obtained by introducing dithioamide and then Cu(II) or Co(II) into amino-propylated silica, was used in GC to separate light hydrocarbons (up to C_4). Similarly, bonded dithiocarbamides complexes with cadmium, copper and zinc were successfully used for the separation of dialkyl sulphides [15]. Separation of linear and branched aliphatic, aromatic and cyclic hydrocarbons was achieved on a packing obtained by binding Cu(II) complexes to silica through *N*-[3-(trimethoxysilyl)propyl]diethylenetriamine.

Silica modification with silanes, containing alkoxyl groups on the one side and groups capable of coordinative interactions with metal cations on the other side, provide a good way to obtain selective stationary phases for complexation gas chromatography. This is because metals from “d” and “f” blocks can easily enter into selective interactions with the analysed nucleophilic compounds, thus forming reversible complexes of different stability. Factors affecting stability of the complexes include degree of oxidation, electronic structure, radii of the central cation and ligand, ligand basicity, internal and external effects caused by changes in the coordination sphere of the surface complex. These factors allow, on one hand, a control of retention in order to obtain the selections required and, on the other hand, it permits physical and chemical investigation of the packings.

The presented paper describes the synthesis of chemically bonded Cu(II) and Cr(III) complexes of *N*-[3-(trimethoxysilyl)propyl]diethylenetriamine and $[(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2]$, and their use in GC. The preparation of three new packings with chlorides of the above mentioned metals bonded with silica through silane comprising amino groups is given. The retention properties of

these packings are compared in terms of their retention factor k , retention index I , specific retention volume V_g and molecular retention index ΔM_e . The retention parameters allow an assessment of specific interactions and a relationship between the structure of an adsorbate molecule and the retention time. The test solutes are nucleophilic compounds including linear and branched aliphatic hydrocarbons and cyclic and aromatic hydrocarbons.

2. Experimental

2.1. Apparatus

Chromatographic measurements were performed on a gas chromatograph Chrom 5 (Czech Republic) equipped with a flame ionization detector. The bonded phases were packed to stainless steel columns 1.5 m \times 3 mm I.D. The temperature in the thermostat chamber 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 4A 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).

The new packings were characterised by: (a) elemental analysis on a 2400 CHN elemental analyser (Perkin-Elmer, Norfolk, CT, USA); (b) measurement of nitrogen adsorption/desorption isotherms at liquid nitrogen temperature on an ASAP 2010 sorptometer (Micromeritics, Narcross, GA, USA); and (c) differential scanning calorimetry (DSC) [16] (DSC-50 Shimadzu, Japan).

2.2. Packings preparation

Syntheses of the packings were performed in two stages. First *N*-[3-(trimethoxysilyl)propyl]diethylenetriamine was bonded to Porasil C (80–100 mesh, 177–149 μ m) from Waters Associates (Milford, MA, USA). This reaction was performed in anhydrous xylene. The reagents were heated under reflux condenser for 12 h. During this time, the whole system was protected from the water. The reaction product was filtered off, extracted with

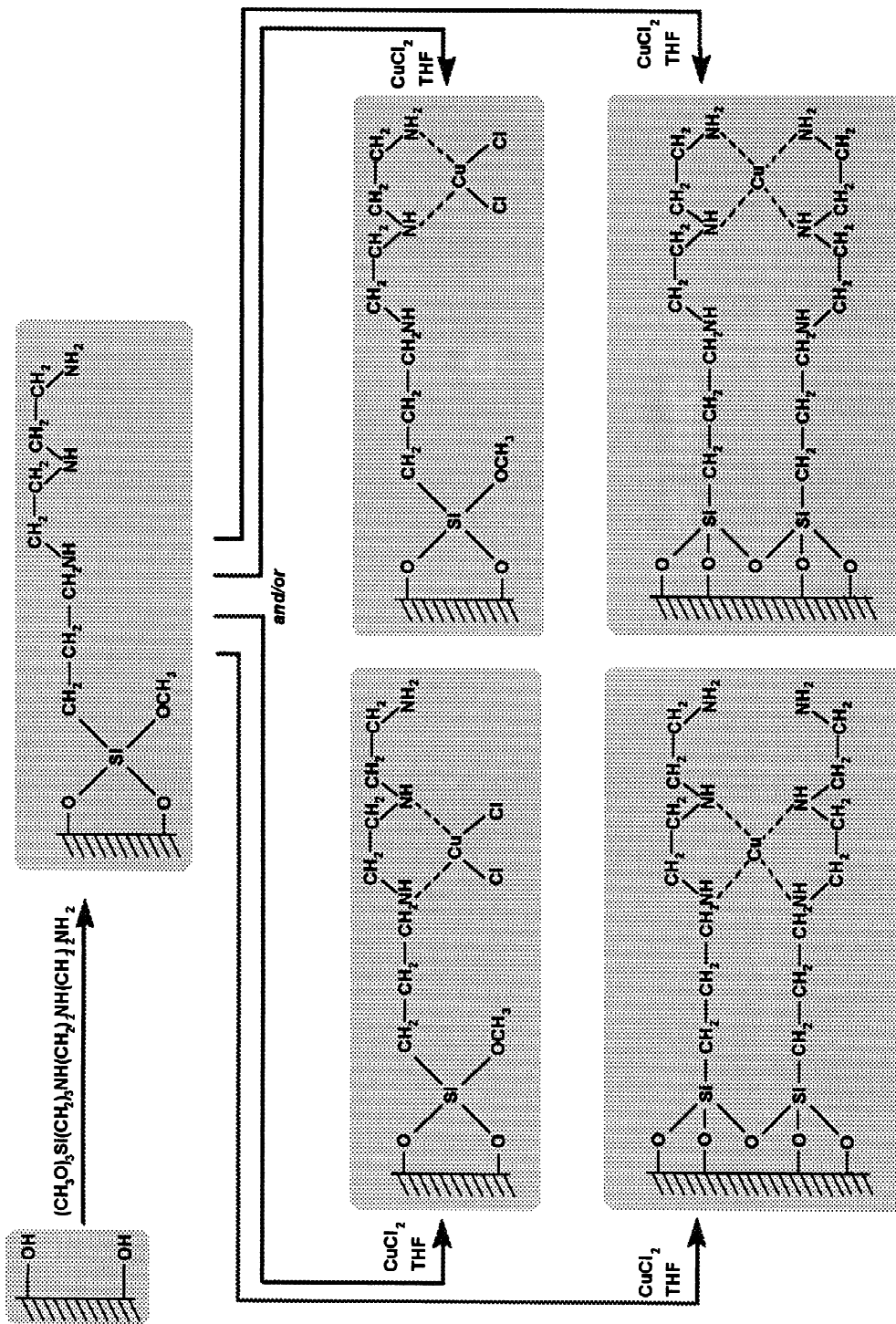


Fig. 1. Structure of the packing studied.

Table 1
Physicochemical characterisation of the investigated packings

No.	Packing	Elemental analysis (%)			Metal (%)	Surface area (m ² g ⁻¹)
		C	H	N		
1	SiO ₂ -Si-(CH ₂)[NH(C ₂ H ₄) ₂ NH ₂	3.30	0.79	1.69	–	73
2	SiO ₂ -Si-(CH ₂) ₃ [NH(C ₂ H ₄) ₂ NH ₂ ·CuCl	3.45	0.80	1.42	1.0	74
3	SiO ₂ -Si-(CH ₂) ₃ [NH(C ₂ H ₄) ₂ NH ₂ ·CrCl ₂	3.77	0.82	1.39	0.001	76

xylene and then hexane in the Soxhlet apparatus and, dried under vacuum at 120°C. Secondly, the packing with *N*-[3-(trimethoxysilyl)propyl]diethylenetriamine was flooded with a saturated solution of copper chloride in tetrahydrofuran, and the mixture was left for 7 days at room temperature. The excess salt was removed by extraction with a xylene and then with hexane in the Soxhlet apparatus. The reaction scheme is shown in Fig. 1.

3. Results and discussion

3.1. Physical characteristics

The elemental composition of surface area of the phases are listed in Table 1.

The main advantage of characterising the phases by DSC [16] is the possibility of measuring energy changes for complexes on the support surface, rather

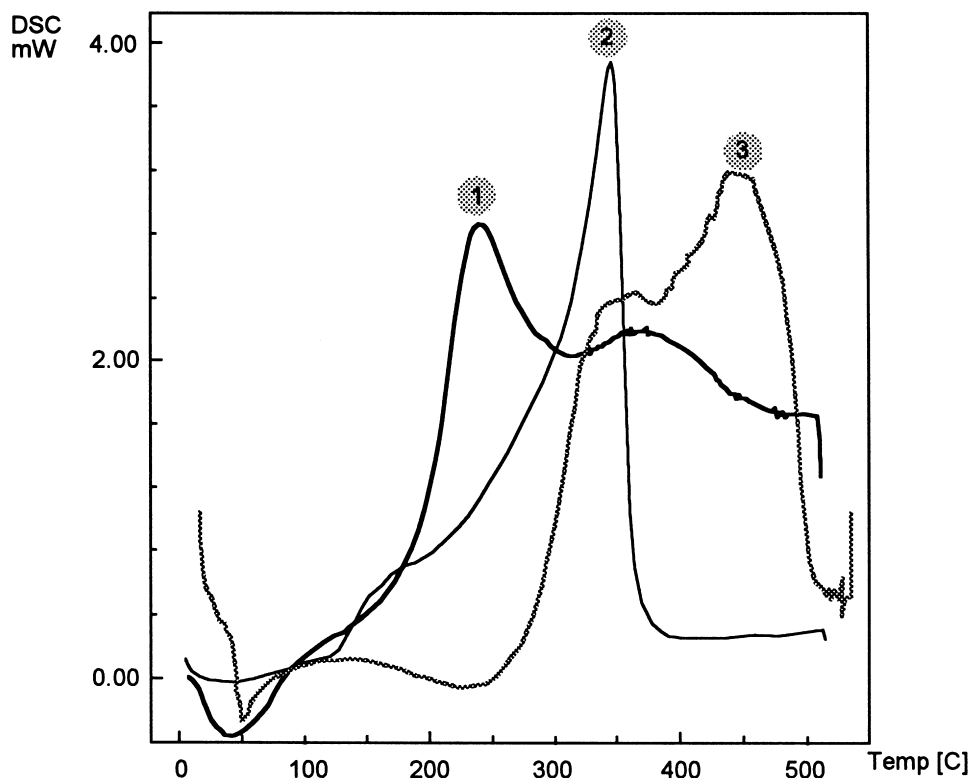


Fig. 2. DSC curves for silica-bonded: *N*-[3-(trimethoxysilyl)propyl] diethylenetriamine (curve 1), with copper chloride (curve 2) and with chromium chloride (curve 3).

than for the whole support. An additional advantage of this method is that a formation of complexes on the support surface can be proved. The results of DSC analysis of the packings bonded with CuCl_2 , CrCl_3 and with no metal are presented in Fig. 2. As 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 introduction of the copper (curve 2 – CuCl) and of the chromium (curve 3 – CrCl_2). The complex formed on the surface is considerably more stable than the free ligand. The characteristic sharp peak on the thermal curve points to high homogeneity of the system.

3.2. Retention parameters

Taking into account the ability of Cu(II) and

Cr(III) to interact with compounds of electron donor properties, studies were performed for such adsorbates like linear and branched aliphatic hydrocarbons, cyclic and aromatic hydrocarbons, in order to determine the effect of structure and configuration of adsorbate molecules on their retention and verify the usefulness of the packings in analysis of hydrocarbons.

For each group of compounds, the following parameters were determined: the retention factor (k), the retention index (I), the specific retention volume (V_g), and the molecular retention index (ΔM_e).

3.2.1. Linear and branched aliphatic hydrocarbons

The values of the retention parameters for the linear and branched aliphatic hydrocarbons are given in Tables 2 and 3. In analysing the effect of structure and configuration of the adsorbate molecules on the

Table 2

The retention parameters: retention factor (k), molecular retention index (ΔM_e), specific retention volume (V_g) for the studied packings at 130°C

No.	Adsorbate	Without metal				Modified with CuCl_2				Modified with CrCl_3			
		k	ΔM_e	V_g	I_R	k	ΔM_e	V_g	I_R	k	ΔM_e	V_g	I_R
1	1-Pentene	0.87	4.30	1.25	530	3.06	14.46	4.87	589	2.20	8.65	1.89	532
2	2-Pentene, <i>cis</i>	0.94	3.98	1.36	514	2.86	13.46	4.54	582	2.30	5.59	1.98	525
3	2-Pentene, <i>trans</i>	0.92	3.52	1.33	511	2.30	10.35	3.65	559	2.23	4.91	1.92	521
4	1-Pentyne	1.19	11.22	1.72	551	n.a. ^a	n.a.	n.a.	n.a.	3.92	18.74	3.37	605
5	Hexane	1.63	0.00	2.34	600	3.42	0.00	5.43	600	3.79	0.00	3.26	600
6	1-Hexene	1.68	2.77	2.42	605	7.85	14.95	12.47	692	4.46	5.28	3.83	623
7	2-Hexene, <i>cis</i>	1.80	4.17	2.58	615	7.26	13.73	11.54	684	4.57	5.79	3.93	627
8	2-Hexene, <i>trans</i>	1.72	3.28	2.48	609	5.57	9.62	8.86	654	4.37	4.86	3.75	620
9	1,3-Hexadiene	2.18	8.36	3.14	645	8.47	16.52	13.37	710	6.92	14.23	5.95	687
10	1,4-Hexadiene	1.84	4.69	2.65	619	9.67	18.64	15.38	719	5.19	8.39	4.46	645
11	1,5-Hexadiene	1.71	3.09	2.46	608	11.80	22.37	18.77	745	4.95	7.40	4.25	638
12	2,3-Hexadiene	2.13	7.80	3.06	641	n.a.	n.a.	n.a.	n.a.	5.75	10.44	4.94	660
13	1,3,5-Hexatriene	2.75	17.40	3.96	681	13.54	28.97	21.53	763	10.03	25.77	8.62	741
14	1-Hexyne	2.33	11.79	3.35	655	n.a.	n.a.	n.a.	n.a.	8.26	19.81	7.10	713
15	2-Hexyne	2.60	14.18	3.74	672	n.a.	n.a.	n.a.	n.a.	8.53	20.46	7.32	717
16	3-Hexyne	2.41	12.53	3.47	661	n.a.	n.a.	n.a.	n.a.	7.67	18.31	6.59	702
17	1-Heptene	3.20	2.64	4.61	704	22.36	19.99	35.55	828	8.97	5.44	7.70	724
18	2-Heptene, <i>cis</i>	3.42	4.06	4.91	715	16.12	14.17	25.63	787	9.44	6.48	8.11	732
19	2-Heptene, <i>trans</i>	3.31	3.36	4.76	710	11.69	8.15	18.58	744	8.85	5.18	7.61	723
20	3-Heptene, <i>cis</i>	3.23	2.84	4.65	706	14.76	12.52	23.47	775	8.85	5.16	7.60	722
21	3-Heptene, <i>trans</i>	3.15	2.26	4.53	702	10.91	6.86	17.34	735	8.37	4.05	7.19	715
22	1-Heptyne	4.49	12.05	6.46	757	n.a.	n.a.	n.a.	n.a.	17.20	20.70	14.77	819
23	1-Octene	5.11	-1.15	7.35	777	n.a.	n.a.	n.a.	n.a.	17.62	5.17	15.14	822
24	1-Octyne	8.57	12.76	12.33	862	n.a.	n.a.	n.a.	n.a.	33.03	20.23	28.37	915
25	1-Nonene	11.08	2.69	15.93	905	n.a.	n.a.	n.a.	n.a.	34.91	5.34	29.99	924

^a n.a.=Non available.

Table 3

The retention parameters: retention factor (k), molecular retention index (ΔM_e), specific retention volume (V_g) for the studied packings at 120.2°C

No.	Adsorbate	Without metal				Modified with CuCl ₂				Modified with CrCl ₃			
		k	ΔM_e	V_g	I_R	k	ΔM_e	V_g	I_R	k	ΔM_e	V_g	I_R
1	2-Methyl-1,3-butadiene	1.46	7.36	1.75	524	3.98	13.69	4.05	569	4.03	13.54	3.77	568
2	3-Methyl-1,2-butadiene	1.47	7.42	1.75	524	3.18	9.34	3.24	538	3.27	9.55	3.06	539
3	2,3-Dimethylbutane	2.04	-2.52	2.44	582	4.21	-3.30	4.28	576	4.33	-3.10	4.06	578
4	2,2-Dimethylbutane	1.86	-4.83	2.22	566	3.77	-5.45	3.83	561	3.85	-5.38	3.60	562
5	2,3-Dimethyl-2-butene	2.51	4.45	3.00	617	5.65	4.42	5.75	617	6.10	5.42	5.71	624
6	3,3-Dimethyl-1-butene	1.76	-4.13	2.10	556	4.66	0.71	4.74	591	4.15	-1.92	3.89	572
7	2-Methylpentane	2.07	-2.25	2.47	584	4.34	-2.70	4.41	581	4.47	-2.53	4.18	582
8	3-Methylpentane	2.13	-1.50	2.54	589	4.44	-2.25	4.52	584	4.60	-1.96	4.31	586
9	2-Methyl-1-pentene	2.24	1.74	2.67	598	5.77	4.82	5.87	620	5.95	4.95	5.57	621
10	3-Methyl-1-pentene	2.04	-0.49	2.44	582	4.44	-0.22	4.52	584	5.09	2.01	4.77	600
11	4-Methyl-1-pentene	2.08	-0.09	2.48	585	5.67	4.47	5.77	618	5.32	2.85	4.98	606
12	2-Methyl-2-pentene	2.35	2.93	2.81	607	5.51	3.94	5.61	614	5.97	5.04	5.59	622
13	4-Methyl-2-pentene, <i>cis</i>	2.07	-0.07	2.47	585	4.95	1.89	5.04	599	5.09	2.01	4.77	600
14	4-Methyl-2-pentene, <i>trans</i>	2.08	0.04	2.48	586	4.73	1.01	4.81	593	4.94	1.45	4.63	596
15	2,2,4-Trimethylpentane	4.96	-11.98	5.93	715	12.66	-10.36	12.88	726	13.17	-9.94	12.33	729
16	2,4,4-Trimethyl-1-pentene	5.47	-8.84	6.53	723	16.87	-2.97	17.17	764	17.52	-2.34	16.40	769
17	2,4,4-Trimethyl-2-pentene	5.52	-8.73	6.60	723	13.93	-6.55	14.18	739	16.47	-3.54	15.43	760

specific interactions, the following facts were considered: the number, kind and positions of unsaturated bonds in the molecule, the number and type of substituents in the main hydrocarbon chain. A characteristic feature of the packings with bonded complexes of group “d” elements is the sequence of elution of alkanes and alkenes. Due to metal capability of coordination interactions with π -electrons of the unsaturated bond, the retention time of alkenes is longer than that of the corresponding alkanes. A comparison of the results obtained for the packings with and without metal shows that the metal complexes show considerable high values of the retention parameters for linear olefins C₅–C₇ (Fig. 3). For unsaturated mono olefins, the increasing factor was approximately two-fold, while for alkynes and dienes it was three-fold and greater. This observation indicates that π -type specific interactions depend on the degree of unsaturation of the adsorbate molecules. For hexadienes, the values of the retention parameters decrease with increasing distance between the unsaturated bonds, thus the observed sequence of elution is as follows: hexadiene-1,5, hexadiene-1,4, hexadiene-1,3. The charge-transfer interactions were established to substantially depend on the accessibility of the unsaturated bond, which was evidenced by the sequence of elution of heptene-1 (extreme posi-

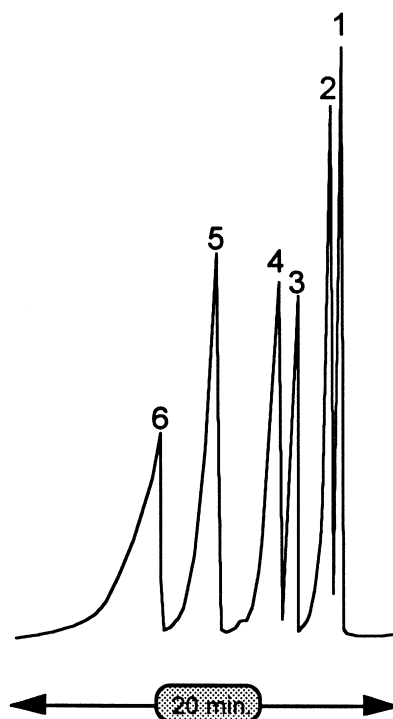


Fig. 3. Separation of a mixture of *cis/trans* isomers of olefins C₅–C₇. Packing: with bonded copper chloride; column temperature, 110°C; $V_{\text{helium}}=21.5 \text{ ml min}^{-1}$. Peaks: 1=pentene-2,*trans*; 2=pentene-2,*cis*; 3=hexene-2,*trans*; 4=hexene-2,*cis*; 5=heptene-2,*trans*; 6=heptene-2,*cis*.

tion of the unsaturated bond) and heptene-3,*trans* in which π -bond is located inside the molecule. Despite the fact that the boiling point of the latter is 2°C lower than that of heptene-3,*trans*, the order of elution is heptene-3,*trans* < heptene-1. The reason for this is the steric effect of substituents at the unsaturated bond which blocks the access to the π -bond in heptene-3,*trans*.

The influence of the adsorbate molecule structure on the strength of the π -type specific interactions can also be observed for geometric isomers. The hexene-2,*trans* isomer is eluted before the *cis* one (similarly as heptene-3,*trans* isomer before the *cis* one), which is a consequence of the differences in accessibility of the unsaturated bond in these compounds. The interactions of the aliphatic hydrocarbons with the packings studied were weaker (frequent negative values of the molecular retention index) than with linear olefins. The influence of substituents is the greater the closer the substitution site is to the double bond. This can be observed for dimethylbutenes. The sequence of elution in this group of compounds is as

follows: 3,3-dimethyl-1-butene; 2,3-dimethyl-2-butene; 2,3-dimethyl-1-butene (Fig. 4).

The presence of unsaturated bonds (π -electrons) in the hydrocarbon chain of olefins capable of specific interactions with the transient metal complexes bonded to the silica surface is responsible for an increase in retention of these compounds relative to that of the corresponding alkanes. As mentioned earlier, specific adsorbate–adsorbent interactions depend on both the structure of adsorbate molecules and on a type of packing. The above can be seen from the values of retention indices based on the structure of a given adsorbate group. The absence of a metal capable of undergoing coordinative interactions, results in low values of retention indices (see Table 3) It is worth noting that in the case of branched aliphatic hydrocarbons, the difference in these values is smaller in comparison with linear hydrocarbons. For linear hydrocarbons increase in

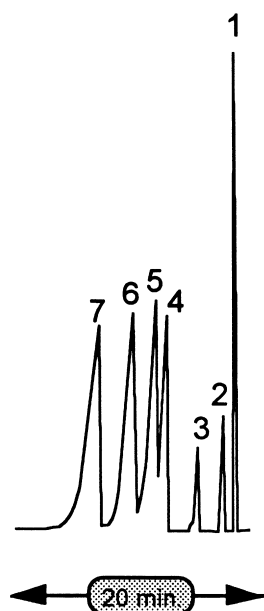


Fig. 4. Separation of a mixture of branched aliphatic hydrocarbons. Packing: as in Fig. 3; column temperature, 98°C; $V_{\text{helium}} = 23.1 \text{ ml min}^{-1}$. Peaks: 1=3-methylpentane; 2=3,3-dimethyl-1-butene; 3=2,3-dimethyl-2-butene; 4=3-methyl-1-pentene; 5=2,2,2-trimethylpentane; 6=2,4,4-trimethyl-2-pentene; 7=2,4,4-trimethyl-1-pentene.

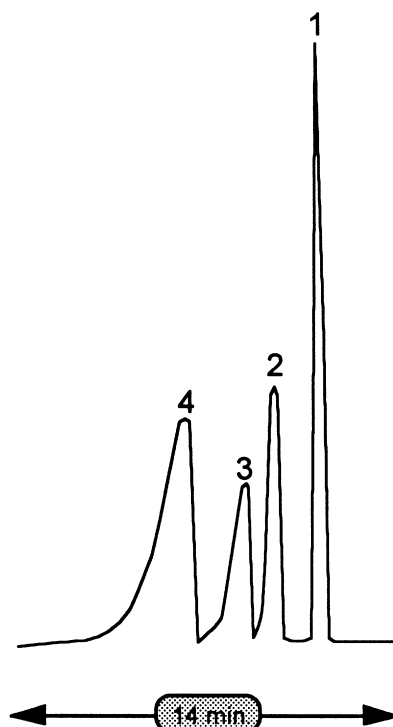


Fig. 5. Separation of a mixture of branched aliphatic hydrocarbons C_6 . Packing: as in Fig. 3; column temperature, 98°C; $V_{\text{helium}} = 23.1 \text{ ml min}^{-1}$. Peaks: 1=2-methylpentane; 2=4-methylpentene-2,*trans*; 3=4-methylpentene-2,*cis*; 4=4-methylpentene-1.

selectivity of the packings was also observed. This increase can be measured by growing difference of values of retention indices as a function of the type of packing. The greatest increasing of such difference was noted for a packing with bonded chlorine of Cu(II).

For the studied packings the differences in specific interactions between the bonded phases and the adsorbates of electron-donor properties are so significant that they allowed a separation of the compounds of the minimum differences in structure, e.g., geometric isomers (Fig. 5).

3.2.2. Aromatic and cyclic hydrocarbons

For aromatic hydrocarbons, the main type of interactions are those between the electrons from the ring and free orbitals of the complexed metal cation. This type of interaction can be described as the electron-transfer reaction between the acid and Lewis base. The retention parameter for aromatic com-

pounds used as adsorbates are given in Table 4. The results allowed a formulation of the relationship between the retention parameters and the type of chain as well as the site of its substitution in the ring. The chosen reference compound was benzene. It is widely known that, substituents may hinder the access to the ring, while as well, they can induce an increase of the electron cloud density in the ring. The results presented in Table 4 show that the presence of both the substituents with unsaturated and saturated chains is favourable for the adsorbate interaction with the electron-acceptor centre. Representatives of the substituents of saturated bonds were mono-, di- and trisubstituted benzenes. For both columns the sequence of elution of the isomers was as follows: 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene (Fig. 6). The position of the unsaturated bond in the substituent is also of great importance. When it is coupled with the aromatic ring, its effect is greater

Table 4

The retention parameters: retention factor (k), molecular retention index (ΔM_c), specific retention volume (V_g) for the studied packings at 120.2°C

No.	Adsorbate	Without metal				Modified with CuCl ₂				Modified with CrCl ₃			
		k	ΔM_c	V_g	I_R	k	ΔM_c	V_g	I_R	k	ΔM_c	V_g	I_R
1	Benzene	2.37	26.01	3.01	671	4.81	30.20	7.03	701	5.63	30.49	4.90	703
2	Toluene	3.77	-1.64	5.41	774	12.40	4.52	17.74	818	11.98	4.65	9.89	819
3	Ethylbenzene	7.67	40.64	9.77	875	20.44	45.07	29.87	907	23.01	46.72	20.02	919
4	Propylbenzene	13.31	40.64	16.96	975	37.32	42.88	54.55	991	40.65	44.93	35.36	1006
5	<i>para</i> -Xylene	6.95	28.88	9.97	877	26.15	35.44	37.40	924	23.83	35.58	19.67	925
6	<i>meta</i> -Xylene	6.99	29.00	10.02	878	28.89	37.34	41.31	937	23.38	35.17	19.30	922
7	<i>ortho</i> -Xylene	7.72	47.42	11.07	895	30.02	54.11	42.93	943	25.99	53.50	21.46	938
8	Styrene	8.69	50.35	12.46	916	n.a. ^a	n.a.	n.a.	n.a.	30.51	56.96	25.20	963
9	Cumene	9.72	29.16	13.94	936	35.48	33.29	50.74	965	25.49	36.76	32.52	990
10	1,3,5-Trimethylbenzene	11.32	23.09	14.89	952	45.04	32.50	65.83	1017	47.52	34.36	41.34	1031
11	1,2,4-Trimethylbenzene	14.20	28.27	18.09	987	55.14	36.42	80.59	1045	50.27	35.60	43.73	1039
12	1,2,3-Trimethylbenzene	16.71	62.32	21.28	1016	61.76	68.68	90.26	1061	59.80	69.50	52.02	1069
13	2-Ethyltoluene	12.69	57.90	18.19	984	56.08	64.17	80.19	1029	42.94	62.30	35.46	1015
14	2-Methylstyrene	15.55	66.97	22.30	1020	n.a.	n.a.	n.a.	n.a.	52.73	70.76	43.54	1047
15	3-Methylstyrene	15.68	53.14	22.48	1021	n.a.	n.a.	n.a.	n.a.	60.86	59.96	25.20	1069
16	4-Methylstyrene	16.56	37.77	23.75	1031	n.a.	n.a.	n.a.	n.a.	64.41	44.35	53.19	1078
17	3-Phenyl-1-propene	11.97	20.32	17.16	974	79.50	27.49	96.91	1025	32.38	7.74	41.31	1026
18	1-Phenyl-1-propene, <i>trans</i>	18.74	17.40	26.86	1052	n.a.	n.a.	n.a.	n.a.	51.69	23.74	66.30	1097
19	<i>meta</i> -Diethylbenzene	19.36	54.23	27.76	1058	112.15	58.63	136.71	1089	54.03	60.61	68.93	1103
20	<i>para</i> -Diethylbenzene	20.46	71.61	29.33	1067	116.15	59.55	141.58	1096	56.32	77.54	71.85	1110
21	<i>ortho</i> -Diethylbenzene	20.58	71.75	29.50	1068	114.50	59.17	139.57	1093	54.77	76.94	69.87	1105
22	<i>tert.</i> -Pentylbenzene	25.99	79.42	37.27	1109	n.a.	n.a.	n.a.	n.a.	65.86	82.93	84.02	1134
23	<i>sec.</i> -Pentylbenzene	28.22	67.34	40.45	1123	n.a.	n.a.	n.a.	n.a.	76.89	72.23	98.10	1157

^a n.a.=Non available.

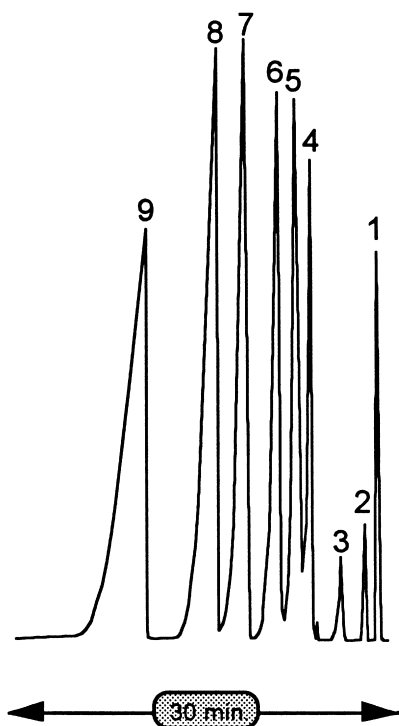


Fig. 6. Separation of a mixture of cyclic and aromatic hydrocarbons. Packing: as in Fig. 3; column temperature, 150°C; $V_{\text{helium}} = 22.3 \text{ ml min}^{-1}$. Peaks: 1=cyclohexane; 2=benzene; 3=toluene; 4=ethylbenzene; 5=*m*-xylene; 6=cumene; 7=propylbenzene; 8=1,3,5-trimethylbenzene; 9=1,2,3-trimethylbenzene.

than when it is isolated, which is clearly visible for 3-phenyl-1-propene and 1-phenyl-1-propene, *trans* as the latter compound was eluted later than the former.

In Table 5 the retention parameters are given for cyclic hydrocarbons. Their interactions with the packings investigated were stronger than those of the linear and branched hydrocarbons. The presence of a methyl or ethyl substituent in the ring resulted in decrease of interactions. For instance, the values of ΔM_e for methylcyclopentane and methylcyclohexane are lower than for cyclopentane and cyclohexane, which proves that the steric factor plays a substantial role in specific interactions between the adsorbates and adsorbents.

A change in the sequence of elution of cyclic compounds of more than one unsaturated bond was noted. For acyclic olefins the specific interactions increased in the sequence: isolated bond < cumulated

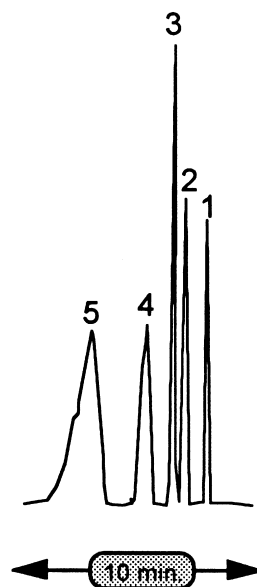


Fig. 7. Separation of a mixture of cyclic and aromatic hydrocarbons. Packing: as in Fig. 3; column temperature, 132°C; $V_{\text{helium}} = 22.3 \text{ ml min}^{-1}$. Peaks: 1=cyclohexane; 2=methylcyclohexane; 3=cycloheptane; 4=4-methyl-1-cyclohexene; 5=cycloheptene.

bond < coupled bonds. For cyclic olefins the strongest interactions were observed for those with isolated bonds (cyclohexadiene-1,3 was eluted before cyclohexadiene-1,4 and cyclohexadiene-1,3 before cyclohexane-1,5 (Fig. 7). A small difference between cyclooctadiene-1,5 and cyclooctatriene is implied by the structure of these compounds. Similar values of ΔM_e for benzene and 1,3,5-cycloheptatriene can also be explained by their structure and the interactions with the packings.

As follows from the above evidence, the packings studied can be used for analysis of a variety of organic compounds.

4. Conclusions

We have provided evidence for significant differences in the interactions of specific adsorbates with the packings studied. Analysis of the influence of the structure and configuration of aliphatic hydrocarbons has proved that the strength of charge-transfer interactions is substantially dependent on the unsaturation

Table 5

The retention parameters: retention factor (k), molecular retention index (ΔM_e), specific retention volume (V_g) for the studied packings at 130°C

No.	Adsorbate	Without metal				Modified with CuCl ₂				Modified with CrCl ₃			
		k	ΔM_e	V_g	I_R	k	ΔM_e	V_g	I_R	k	ΔM_e	V_g	I_R
1	Cyclopentane	1.23	3.60	1.30	511	1.91	2.48	2.16	503	1.24	2.14	1.41	501
2	Cyclohexane	2.20	4.57	2.33	618	3.77	1.51	4.25	596	2.55	1.55	2.92	597
3	Cycloheptane	4.55	6.59	4.83	733	8.64	3.13	9.75	708	5.92	3.82	6.79	713
4	Cyclooctane	8.74	7.56	9.27	840	18.67	3.87	21.06	813	12.02	4.30	13.78	816
5	1-Cyclopentene	1.23	5.74	1.31	512	2.77	11.65	3.13	554	1.40	6.47	1.60	517
6	1-Cyclohexene	2.44	8.87	2.59	635	5.68	11.25	6.41	651	3.30	8.51	3.78	632
7	1-Cycloheptene	4.78	9.74	5.07	741	16.71	17.76	18.85	798	7.06	9.44	8.09	739
8	1-Cyclooctene	8.74	9.59	9.27	840	37.81	19.63	42.67	911	13.72	9.02	15.73	936
9	Methylcyclopentane	1.99	2.42	2.11	603	3.46	-0.13	3.91	585	2.34	14.02	2.69	686
10	Methylcyclohexane	3.58	1.10	3.80	693	7.18	-0.37	8.11	683	4.80	-0.32	5.51	683
11	Ethylcyclohexane	6.51	0.82	6.91	791	14.83	-0.57	16.73	782	9.40	-0.74	10.77	780
12	1-Methyl-1-cyclopentene	2.67	10.81	2.83	648	5.03	8.95	5.67	635	4.92	7.98	5.01	633
13	1-Methyl-1-cyclohexene	4.32	7.41	4.58	724	9.16	6.26	10.34	716	6.23	6.87	7.14	720
14	4-Methyl-1-cyclohexene	3.98	5.52	4.22	711	10.52	8.90	11.87	735	6.10	6.44	6.99	717
15	1,3-Cyclohexadiene	2.67	12.85	2.84	649	8.35	20.54	9.43	703	4.17	15.01	4.78	664
16	1,4-Cyclohexadiene	3.03	15.58	3.22	668	9.00	21.96	10.16	713	4.77	17.62	5.47	683
17	1,3,5-Cycloheptatriene	5.87	18.53	6.23	775	19.21	10.48	21.67	717	11.31	23.13	12.97	808
18	Cyclooctadiene	13.40	7.39	14.21	814	87.09	36.98	98.27	999	20.22	18.31	23.18	892
19	Cyclooctatetraene	10.54	19.93	11.19	870	15.21	7.98	17.16	785	21.15	23.93	24.25	899
20	Decahydroxynaphthalene, <i>cis</i>	24.15	4.94	25.63	1006	56.94	-0.58	64.25	967	33.47	-1.05	38.38	964
21	Decahydroxynaphthalene, <i>trans</i>	20.85	1.55	22.13	982	53.38	-1.82	60.23	958	32.33	-1.74	37.07	959
22	Indane	22.64	9.49	24.02	996	34.99	-3.87	39.47	901	51.30	13.59	58.82	1025
23	Indene	35.31	23.79	37.47	1069	47.73	20.14	53.86	1043	77.72	26.11	89.11	1086

degree of adsorbate, the number of unsaturated bonds and their mutual positioning as well as the accessibility of an unsaturated bond. For aromatic hydrocarbons, the strength of the specific interactions between the bound metal complex and the adsorbate is mostly affected by the type of chain and the ring substituent. For the saturated substituents, the strongest interactions were observed for a trimethyl-substituted ring. The sequence of elution of these compounds is: 1,3,5-, 1,2,4-, 1,2,3-trimethylbenzene. A comparison of the effect of substituents with an unsaturated and saturated chain show that for the former ΔM_e is greater, e.g., ΔM_e for styrene is higher than for ethylbenzene. Moreover, the specific interactions are higher in the case when the unsaturated bond is coupled with the ring than when it is isolated. Results of the retention studies as well as the chromatographic analysis have proved that the packings investigated can successfully be used in complexation gas chromatographic analysis of mixtures of organic compounds including geometric isomers.

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