

Comparative Studies of Gas Chromatographic Properties of New Packings with Chemically Bonded Complexes

I. Rykowska* and W. Wasiak

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 60-780 Poznań, Poland

Abstract

Specific interactions of aliphatic linear and branched hydrocarbons as well as cyclic and aromatic hydrocarbons with new packings containing chemically bonded complexes of transition metals are studied. The possibility of using these packings to separate these compounds is also discussed. The packings under study contain complexes of Cu(II) and Cr(III) chemically bonded to the silica surface. Chlorides of these metals are bonded to the silica surface by the use of the ketoimine group originally from 2-(3-triethoxysilylpropylimino)-3-(*n*-butyl)-pentanon-4. In order to determine an influence of the performed modification to gas chromatographic properties of the packings, such retention parameters as retention factor, retention index, molecular retention index, and specific retention volume are measured for these compounds. Based on the obtained values, a trial is taken to determine an influence of the nature of the bonded metal from the complex on the retention of the adsorbates under study and a dependence between a structure of an adsorbate molecule and values of charge-transfer interactions with the bonded metal complexes.

Introduction

Although new materials (such as porous polymers, carbons, and composite adsorbents-carbosiles) are continuously developed, silica-based adsorbents (silica gel and porous glass) are still fundamentally important as column packings used for high-performance liquid chromatography, gas chromatography (GC), and solid-phase extraction (1-4).

Chemically bonded chelates acting as selective sorbents of complexing reactions in capillary GC were used many times to separate such groups of compounds as hydrocarbons, halogeno- and nitro- derivatives of hydrocarbons, ketones, ethers, and thioethers (5-9). The factors having influence on the stability of the electron donor/acceptor (EDA) complexes under creation depend on the structure of both the sorbate molecule and the bonded complex of a metal. Also, the following factors must be taken into consideration: ligand structure, its stability, complexation ability

of a metal, and steric effects.

The packings under study contain complexes of Cu(II) and Cr(III) chemically bonded to the silica surface. The chlorides of these metals were bonded to the silica via a ketoimine group, originally from 2-(3-triethoxysilylpropylimino)-3-(*n*-butyl)-pentanon-4.

In this study, a comparison of some retention parameters (retention factor, retention index, specific retention volume, and molecular retention index) was made for the packings under study. It allowed for the ability to estimate the observed specific interactions as well as determine dependencies among a structure of an adsorbate molecule, retention time, and a type of packing. Aliphatic linear hydrocarbons as well as linear and branched, aromatic, and cyclic hydrocarbons were used as adsorbates. When discussing an influence of the adsorbate structure and configuration on the specific interactions, particular attention was given to the quantity, type, and location of unsaturated bonds in a molecule and the quantity and types of substituents in the basic hydrocarbon chain. In the case of aromatic hydrocarbons, an influence of the type of a chain and a place of substitution of this chain in a ring was also discussed.

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.

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

Experimental

Apparatus

Chromatographic measurements were carried out on a GC CHROM 5 (Laboratory Instruments, Praha, 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 that was dried on molecular sieve 4A was used as the carrier gas. The flow rate of the carrier gas was measured with a digital flowmeter (J&W Scientific, Folsom, CA). Stainless steel columns were used (2-m length, 3-mm i.d.).

This work is dedicated to Prof. Walenty Szczepaniak (Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland) for his 70th birthday.

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

Elemental analysis was performed on a 2400 CHN Elemental Analyzer (PerkinElmer, Norfolk, VA). The obtained results are presented in Table I.

The measurement of nitrogen adsorption/desorption isotherms at the liquid nitrogen temperature was performed on an ASAP 2010 sorptometer (Micrometrics, Nacross, GA). 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). Figure 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 the hysteresis loop on the adsorption/desorption isotherm can give some information on the pore structure. The hysteresis loop shown in Figure 1B is almost vertical with almost parallel branches, thus it belongs to type H1 according to the IUPAC classification (10). This type of hysteresis is usually associated with porous materials consisting of agglomerates or compacts of approximately uniform spheres in a fairly regular array; therefore, they have a relatively narrow pore-size distribution.

Pore volumes of the packings studied were 0.83 cm³/g for the

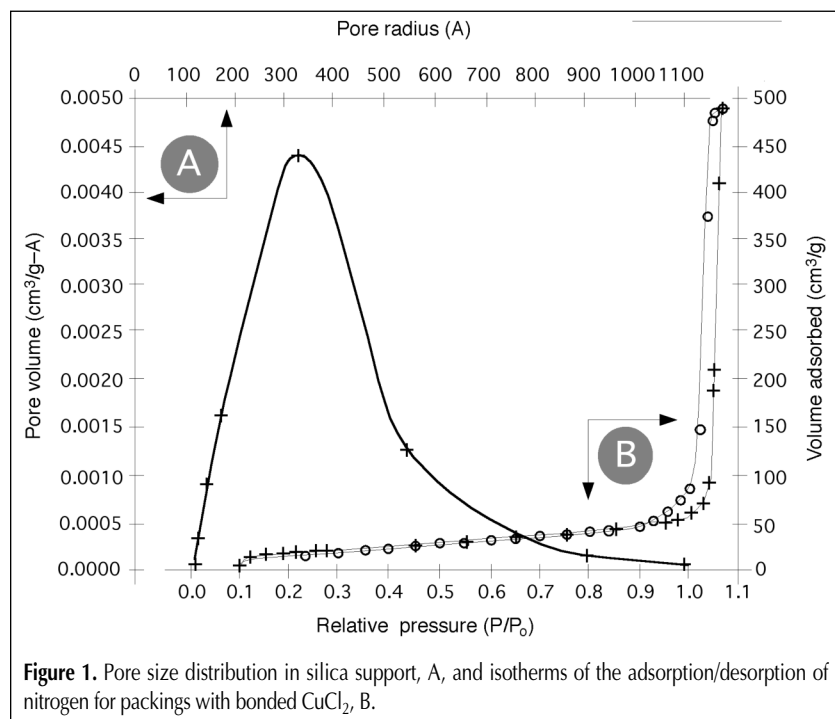


Figure 1. Pore size distribution in silica support, A, and isotherms of the adsorption/desorption of nitrogen for packings with bonded CuCl₂, B.

Table I. Physicochemical Characteristics of the Investigated Packings

Packing	Elemental analysis (%)				Surface area (m ² /g)
	C	H	N	Metal	
without metal	5.51	1.10	1.07	–	87
modified with CuCl ₂	5.62	1.87	1.00	1.71	88
modified with CrCl ₂	8.19	1.59	1.66	0.05	83

starting material, 0.72 cm³/g for packing with bonded 2-(3-triethoxysilylpropylimino)-3-(*n*-buthyl)-pentanon-4, and 0.68 cm³/g and 0.57 cm³/g for packings with CuCl₂ and CrCl₃, respectively. Surface areas determined by the BET method are listed in Table I.

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

Preparation of columns

Approximately 50 mL of dry silica (Porasil C) was immersed in a mixture consisting of 100 mL anhydrous xylene and 5 mL 3-aminopropyltriethoxysilane. The mixture was boiled in a vessel provided in which a reflux condenser was under continuous stirring and careful protection against moisture. Unreacted silane was extracted with xylene and hexane in a Soxhlet apparatus. After this operation, silica was subjected to drying under vacuum and then a so-called “endcapping” reaction with hexamethyldisilazane in order to deactivate free silanol groups remaining on the silica surface. The next step was then the reaction aiming at bonding amino groups with *n*-buthylpentanon-4. The reaction proceeded in xylene for 6 h under continuous stirring and was followed by the removal of the excess on a rotary evaporator. Dry silica was immersed in an anhydrous tetrahydrofuran solution of Cu(II) or Cr(III) chloride and allowed to stand for 7 days at room temperature. The system was protected against the access of moisture. Then, the silica was filtered off, the excess of CuCl₂ extracted with tetrahydrofuran in a Soxhlet apparatus, and eventually the silica was subjected to drying. The stages of the modification of silica are shown in Figure 2.

Results and Discussion

One of the most important parameters of packings for GC is its thermal stability. Thermograms obtained by the use of classical thermogravimetric 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 allow for the precise characterization of the changes for other packing components (remaining 10%). Because of this fact, the DSC method (15) was used to obtain more detailed information about energetic changes at the silica surface at different temperatures. Besides 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. However, it should be noted that the DSC analysis was not used to precisely characterize physicochemical properties of the packings under study, but only to determine their thermal stability.

The results of the DSC analysis of the packings bonded with CuCl₂, CrCl₃, and no metal are presented in Figure 3. As can be seen, the bonding of Cu(II) and Cr(III) chlorides was practically com-

plete, 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 were considerably more stable than the free ligand.

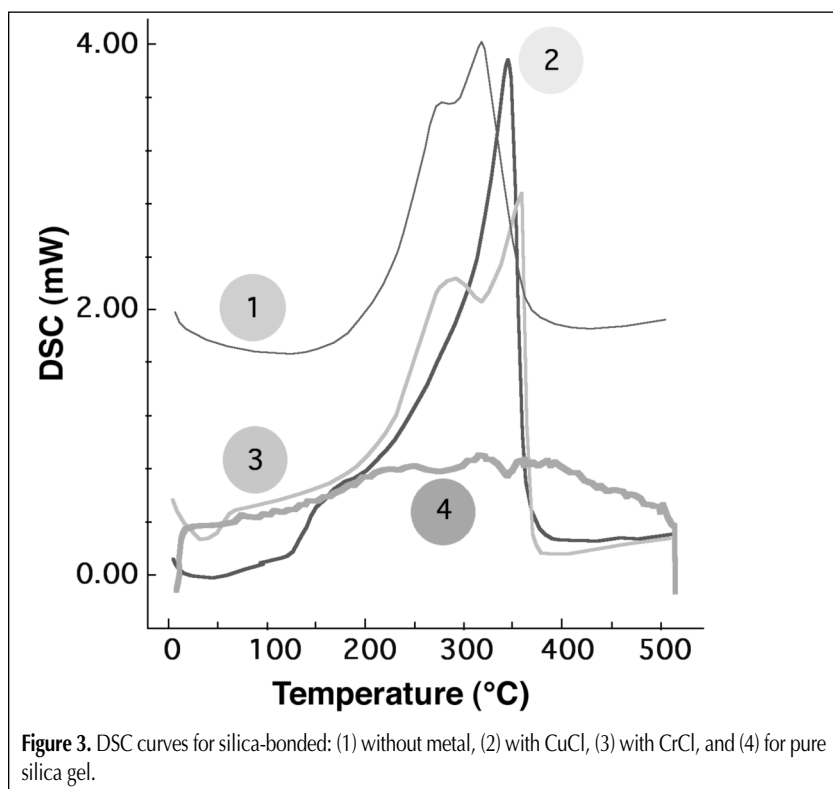
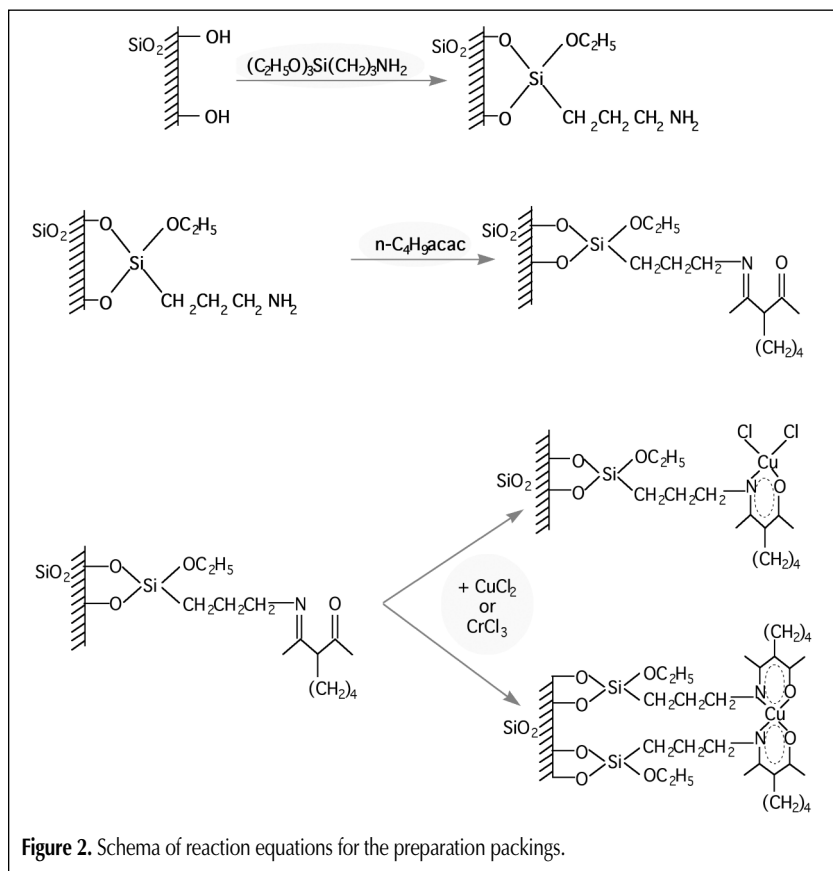
The main advantage of packings with complexes of transient metals chemically bonded to the silica surface is that, on one hand, they make it possible to separate compounds showing EDA properties, and on the other, they allow for the study of interactions among sorbates and complexes of transient metals.

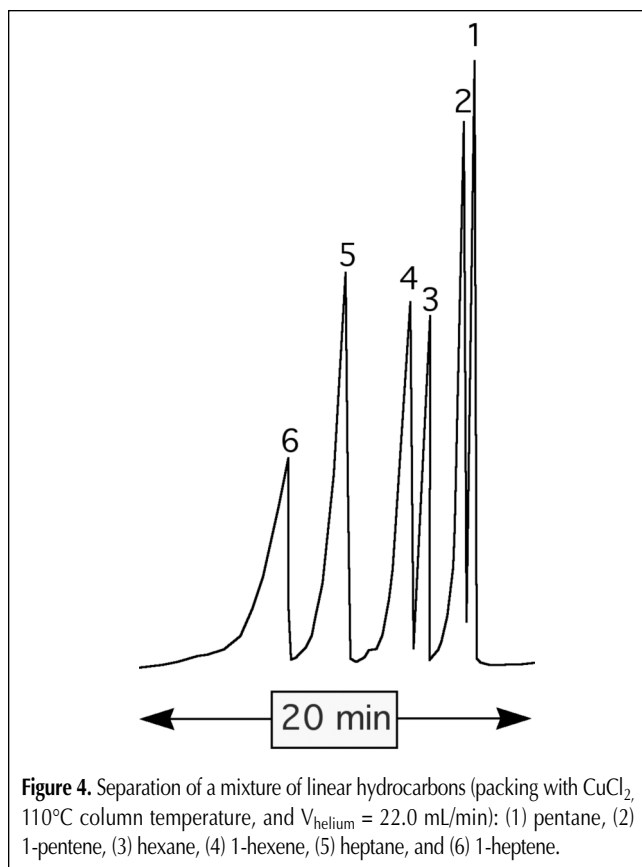
The charge-transfer interactions of the metal in complexes with electron-donor properties have been assessed on the basis of such parameters as the retention factor (k), retention index (I), specific retention volume (V_g), and molecular retention index (ΔM_e) (16). The ΔM_e (17,18) provides information about an influence of substituents on the retention of particular adsorbates. Its positive values testify to the attraction, whereas negative ones explain the repulsion between a given functional group and the packing. The interactions between the adsorbate and the packing modified by transition metal complexes are a mix of the specific and nonspecific ones. The former depend on the π -electron character of the adsorbate and its conformation, and they are responsible (among others) for different retention properties of aromatic hydrocarbons with electron-donor ($-\text{CH}_3$) or electron-acceptor ($-\text{Cl}$) substituents.

The chromatographic measurements were performed for a wide range of analytes (linear and branched aliphatic hydrocarbons and aromatic and cyclic hydrocarbons) for packings with Cu(II) and Cr(III) complexes and a packing without a metal (reference system). The obtained results are reported in Tables II–V.

The sample mixture chromatograms show separation capabilities of the tested packings. The presented chromatograms have symmetric peaks, which points to the homogeneity of surface adsorption centers.

In the case of linear hydrocarbons the presence of unsaturated bonds (π -electrons) in the hydrocarbon chain of olefins that are capable of specific interactions with the transition metal complexes bonded to the silica surface is responsible for an increase in the retention of these compounds relative to the corresponding alkanes. This situation is illustrated in Figure 4. The sequence of elution is directly related to the presence of unsaturated bonds in the adsorbate molecule. The first compound eluted is always an alkane, despite having a higher boiling point than that of the corresponding alkene. A comparison of the results obtained for the packing with and without a metal (Table II) has shown that for linear mono-olefins the presence of metal caused an approximate two-fold increase in the retention parameters, and for alkynes and diens it was three-fold and higher. This fact indicates the dependence of π -type interactions on the degree of the adsorbate unsaturation. For hexadiens it was observed that the specific





interactions depend not only on the degree of unsaturation but also on the number of unsaturated bonds and their mutual arrangement. For this group of compounds the values of the parameters of retention decreased with increasing distance between the unsaturated bonds; therefore, the sequence of elution of the compounds is as follows: 1,3-hexadiene > 1,4-hexadiene > 1,5-hexadiene.

An influence of the steric effect of substituents near a saturated bond (i.e., blocking an access to the π bond) on the values of charge-transfer interactions has been observed in the case of such compounds as 1-heptene (extreme position of an unsaturated bond) and *trans*-3-heptene (position of the π bond inside a molecule). Although the boiling point of 1-heptene is 20°C lower than that of *trans*-3-heptene, the latter is eluted before the former (Table II).

The interactions of the branched aliphatic hydrocarbons were weaker than those of linear olefins, as indicated by the frequently obtained negative values of ΔM_e (Table III). In the group of branched hydrocarbons, an interesting phenomenon that was observed was the influence of substituents on the retention. The presence of substituents in the main chain of alkenes should be considered in at least two ways. On the one hand, they provoke an additional steric hindrance obstructing a direct contact of the adsorbate with the electron-donor center, and on the other, the alkyl substituent (because of its specific properties) induces an increase in the electron density of the unsaturated bond. Consequently, the specific interactions in which the π -electrons

Table II. Retention Parameters for Studied Packings at 133°C

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-Pentene	1.26	2.24	1.13	502	1.69	3.62	1.55	511	2.32	3.62	1.68	511
<i>cis</i> -2-Pentene	1.38	4.33	1.23	516	1.78	4.78	1.63	520	2.49	5.15	1.80	522
<i>trans</i> -2-Pentene	1.26	2.27	1.13	502	1.66	3.26	1.52	509	2.32	3.65	1.68	512
1-Pentyne	1.46	7.78	1.31	527	3.34	20.85	3.06	620	3.61	15.11	2.61	579
Hexane	2.25	0.00	2.01	600	2.94	0.00	2.69	600	4.14	0.00	2.99	600
1-Hexene	2.28	2.27	2.03	602	3.25	4.22	2.97	616	4.39	3.32	3.17	609
<i>cis</i> -2-Hexene	2.31	2.63	2.07	604	3.43	5.45	3.15	624	4.67	4.69	3.38	619
<i>trans</i> -2-Hexene	2.26	2.08	2.02	600	3.17	3.71	2.91	612	4.45	3.62	3.22	611
1,3-Hexadiene	2.76	6.81	2.47	634	4.26	10.19	3.91	658	6.25	11.09	4.52	665
1,4-Hexadiene	2.29	2.40	2.05	603	3.69	7.00	3.38	636	5.11	6.65	3.69	633
1,5-Hexadiene	2.34	2.89	2.09	606	3.63	6.67	3.33	633	4.60	4.38	3.33	617
1,3,5-Hexatriene	3.20	14.39	2.86	659	n.e.*	n.e.	n.e.	n.e.	9.04	23.19	6.54	722
1-Hexyne	2.77	8.97	2.48	635	6.99	23.00	6.40	735	6.96	15.47	5.03	682
2-Hexyne	3.15	11.99	2.82	657	6.99	23.02	6.41	735	7.37	16.74	5.33	691
3-Hexyne	2.96	10.49	2.64	646	6.81	22.43	6.24	731	6.66	14.52	4.82	675
1-Heptene	4.08	2.06	3.65	700	6.26	4.57	5.74	718	8.61	4.09	6.23	715
<i>cis</i> -2-Heptene	4.38	3.72	3.92	712	6.47	5.27	5.92	723	8.97	4.97	6.49	721
<i>trans</i> -2-Heptene	4.22	2.86	3.77	706	5.83	3.02	5.34	707	8.32	3.33	6.02	709
<i>cis</i> -3-Heptene	4.18	2.61	3.74	704	6.23	4.46	5.71	717	8.70	4.31	6.30	716
<i>trans</i> -3-Heptene	4.08	2.07	3.65	700	5.68	2.42	5.20	703	8.18	2.96	5.91	707
1-Heptyne	5.26	10.06	4.70	743	15.04	25.75	13.78	855	14.32	17.08	10.36	793
1-Octene	7.47	2.26	6.67	802	11.32	3.47	10.37	810	16.30	3.84	11.79	813
1-Octyne	9.60	10.18	8.58	844	n.e.	n.e.	n.e.	n.e.	26.63	16.46	19.26	889
4-Octyne	9.67	10.35	8.64	845	n.e.	n.e.	n.e.	n.e.	24.08	14.28	17.41	873
1-Nonene	13.49	2.15	12.06	901	24.68	6.65	22.61	933	30.87	3.66	22.33	912
1-Decene	24.63	1.53	22.02	997	40.47	3.11	37.08	1008	59.52	4.33	43.05	1016

* n.e., not eluted.

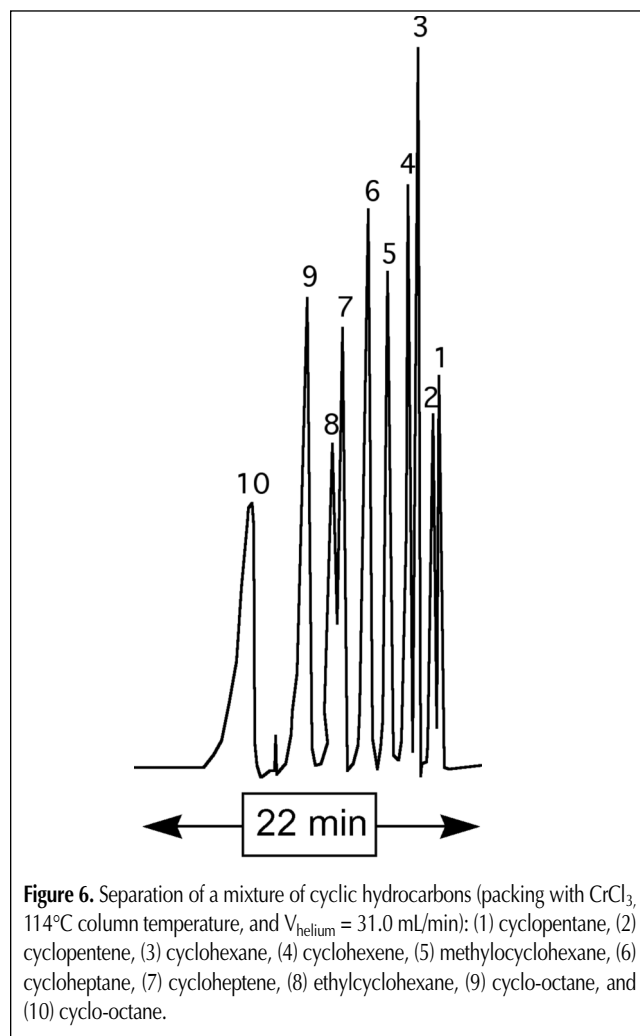
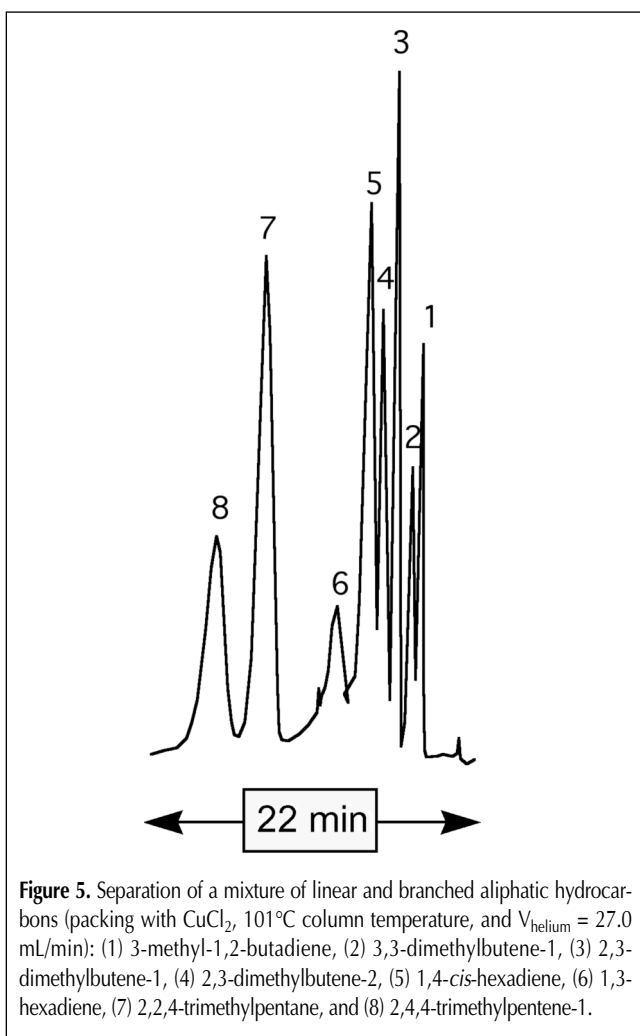


Table III. Retention Parameters for Studied Packings at 133°C

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
2-Methyl-1,3-butadiene	1.45	4.85	1.50	506	1.87	7.82	1.68	527	2.44	9.77	1.82	541
3-Methyl-1,2-butadiene	1.44	4.72	1.49	505	1.82	7.26	1.64	523	2.30	8.52	1.72	532
2,3-Dimethylbutane	2.19	-3.00	2.27	579	2.57	-2.91	2.32	579	3.05	-3.51	2.28	575
2,2-Dimethylbutane	1.71	-9.05	1.77	535	2.36	-4.90	2.12	565	2.68	-6.25	2.01	555
2,3-Dimethyl-2-butene	1.28	-9.65	1.62	516	2.98	-8.12	2.21	545	3.33	0.36	2.49	588
2,3-Dimethyl-1-butene	2.68	3.96	2.77	614	3.22	4.14	2.90	615	4.02	4.32	3.01	616
3,3-Dimethyl-1-butene	1.81	-5.64	1.88	545	2.27	-3.76	2.04	559	2.73	-3.84	2.04	558
2-Methylpentane	2.19	-3.00	2.27	579	2.59	-2.76	2.33	580	3.23	-2.29	2.42	584
3-Methylpentane	2.22	-2.62	2.30	581	2.76	-1.30	2.49	591	3.31	-1.78	2.48	587
2-Methyl-1-pentene	2.31	0.40	2.40	588	3.20	4.02	2.88	614	3.79	3.08	2.83	608
3-Methyl-1-pentene	2.15	-1.41	2.23	576	2.73	0.40	2.45	589	3.29	0.12	2.46	586
4-Methyl-1-pentene	2.16	-1.34	2.23	576	2.75	0.61	2.47	590	3.40	0.82	2.54	591
2-Methyl-2-pentene	2.50	2.30	2.59	602	3.06	2.99	2.75	607	3.88	3.60	2.90	611
<i>cis</i> -3-Methyl-2-pentene	2.49	2.28	2.59	601	3.05	2.97	2.75	607	3.87	3.54	2.89	611
<i>trans</i> -3-Methyl-2-pentene	2.56	2.85	2.65	606	3.03	2.78	2.72	605	3.83	3.30	2.86	609
<i>cis</i> -4-Methyl-2-pentene-2	2.18	-1.02	2.26	578	2.70	0.16	2.43	587	3.30	0.16	2.47	587
<i>trans</i> -4-Methyl-2-pentene	2.19	-0.99	2.26	579	2.64	-0.30	2.38	583	3.29	0.08	2.46	586
2,2,4-Trimethylpentane	5.43	-9.21	5.63	734	6.71	-9.73	6.03	731	8.33	-10.62	6.23	724
2,4,4-Trimethyl-1-pentene	5.85	-5.41	6.07	747	7.95	-3.98	7.15	757	10.30	-4.22	7.70	756
2,4,4-Trimethyl-2-pentene	5.90	-5.22	6.12	748	7.29	-5.88	6.56	744	9.53	-5.82	7.13	744

play the most important role increase. The influence of substituents is greater as the substitution becomes closer to the double bond. This can be particularly seen for dimethylbutens, for which the sequence of elution is 3,3-dimethylbutene-1 < 2,3-dimethylbutene-1 < 2,3,2,3-dimethylbutene. The separation of these compounds (among others) is presented in Figure 5.

When comparing the values obtained for the packings with and without a metal, it can be seen that in the case of all the adsorbates under study the presence of a metal forces an increase of the retention parameters.

In the case of cyclic and aromatic hydrocarbons, such an increase is greater by two and even three times (Tables IV and V).

Table IV. Retention Parameters for Studied Packings at 133°C

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
Cyclopentane	1.55	4.09	1.19	515	1.89	3.78	1.50	513	1.74	3.93	1.56	514
Cyclohexane	2.86	4.66	1.89	619	3.57	3.77	2.83	612	3.42	3.54	3.07	611
Cycloheptane	5.90	8.11	3.91	743	7.56	6.40	5.98	731	6.92	4.17	6.20	715
Cyclo-octane	11.33	9.60	7.50	854	15.01	7.44	11.88	839	14.72	6.59	13.20	833
1-Cyclopentene	1.50	5.48	1.00	510	2.07	7.79	1.64	527	1.77	6.36	1.59	517
1-Cyclohexene	3.01	7.93	1.99	628	4.25	9.64	3.36	640	3.94	8.48	3.53	632
1-Cycloheptene	5.77	9.62	3.82	740	9.25	12.82	7.32	763	7.99	9.34	7.16	738
1-Cyclo-octene	10.80	10.47	7.15	846	19.28	15.00	15.26	878	15.90	10.26	14.26	844
Methylcyclopentane	2.55	1.89	1.69	599	3.29	1.96	2.61	600	3.09	1.45	2.77	596
Methylcyclohexane	4.61	2.28	3.06	702	6.25	2.24	4.95	702	6.02	1.20	5.40	694
Ethylcyclohexane	8.42	2.55	5.58	804	11.94	2.37	9.45	803	11.83	1.89	10.60	799
1-Methyl-1-cyclohexene	5.31	7.64	3.52	726	7.38	7.88	5.84	727	7.55	8.11	6.77	729
4-Methyl-1-cyclohexene	4.91	5.77	3.25	712	6.96	6.59	5.50	718	6.91	6.17	6.20	715
1,3-Cyclohexadiene	3.13	10.92	2.08	635	5.14	15.91	4.06	670	4.55	13.48	4.08	653
1,4-Cyclohexadiene	3.51	13.70	2.33	655	5.21	16.25	4.13	673	5.14	15.97	4.61	671
1,3,5-Cycloheptatriene	6.48	16.40	4.29	759	9.57	17.60	7.57	768	11.38	21.12	10.20	793
1,5-Cyclo-octadiene	12.88	16.02	8.53	876	27.66	24.50	21.89	936	21.02	17.61	18.85	887
Indane	24.18	7.67	16.01	983	37.27	7.93	29.50	985	48.59	10.94	43.57	1006
Indene	28.85	15.89	19.11	1013	45.48	16.28	35.99	1015	87.54	21.26	78.49	1051

Table V. Retention Parameters for Studied Packings at 133°C

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
Benzene	3.09	-2.11	3.34	571	4.57	5.67	4.21	626	4.67	13.66	4.94	683
Ethylbenzene	3.09	8.52	3.34	646	4.57	10.14	4.21	658	4.67	14.60	4.94	690
Propylbenzene	10.55	23.61	11.41	854	17.54	24.68	16.16	862	18.70	28.48	19.79	889
1,3,5-Trimethylbenzene	10.55	9.58	11.41	854	17.54	10.65	16.16	862	18.70	14.46	19.79	889
1,2,4-Trimethylbenzene	18.18	22.34	19.67	945	31.39	23.42	28.92	953	34.09	26.95	36.08	978
1,2,3-Trimethylbenzene	20.95	55.73	22.67	969	38.24	57.82	35.23	983	35.53	57.76	37.59	983
tert-Buthylbenzene	24.53	45.40	26.54	995	44.47	47.09	40.96	1007	48.27	49.25	47.05	1022
sec-Buthylbenzene	25.09	31.90	27.15	999	43.14	32.40	39.74	1002	49.34	35.68	48.10	1026
izo-Buthylbenzene	26.51	59.25	28.69	1008	43.73	58.73	40.28	1004	53.07	63.23	51.73	1036
n-Buthylbenzene	27.80	46.35	30.08	1016	50.94	48.04	46.93	1028	56.08	50.34	54.67	1045
Toluene	33.52	36.76	36.28	1048	63.18	38.44	58.20	1060	62.96	38.09	66.63	1057
4-Ethyltoluene	5.85	25.83	6.33	755	9.45	27.15	8.70	765	9.53	30.50	10.09	789
2-Ethyltoluene	18.65	53.00	20.18	949	31.17	53.33	28.71	951	33.92	56.91	35.89	977
para-Xylene	20.50	41.29	22.18	966	36.27	42.35	33.40	973	35.77	43.61	37.85	982
meta-Xylene	10.61	25.69	11.48	854	17.88	27.25	16.47	866	18.08	29.86	19.13	884
ortho-Xylene	10.74	42.04	11.63	857	18.47	43.98	17.01	870	18.33	46.12	19.40	886
Styrene	12.07	44.80	13.06	876	20.43	46.08	18.82	885	20.57	48.52	21.76	903
3-Methylstyrene	12.74	17.39	13.79	886	24.14	21.08	22.24	912	25.65	23.94	27.14	932
4-Methylstyrene	21.88	30.05	23.68	976	49.35	36.70	45.46	1023	46.07	36.75	48.75	1024
Cumene	21.76	34.62	23.55	975	51.33	42.26	47.28	1029	47.64	41.98	50.41	1027
3-Phenyl-1-propene	15.00	-8.20	16.23	913	27.19	-5.78	25.04	930	28.51	-2.81	30.17	951
trans-1-Phenyl-1-propene	16.92	0.67	18.31	933	32.57	4.26	30.00	958	41.15	9.92	40.12	999

In Figures 6 and 7, chromatograms of a mixture of cyclic hydrocarbons is presented. Their interactions with the packings investigated were stronger than those of linear and branched hydrocarbons. The presence of a methyl and ethyl substituent in the ring resulted in a decrease of interactions. For instance, the values of ΔM_e for methylcyclopentane and methylcyclohexane were lower than for cyclopentane and cyclohexane, which proves that the steric factor plays a substantial role in specific interactions between the adsorbates and the adsorbents. A change in the sequence of elution of cyclic compounds with more than one unsaturated bond was noted. For acyclic olefins the specific interactions increased in the following sequence: isolated bond < cumulated 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.

The results have proven that the strength of specific interactions between the bonded metal complex and aromatic hydrocarbons (with benzene as a reference compound) depends on the type of chain and the position of its substitution in the ring. For substituents with saturated chains the strongest interactions were observed for the trisubstituted ring (Table V). The sequence of elution for these compounds was 1,3,5-trimethylbenzene < 1,2,4-trimethylbenzene < 1,2,3-trimethylbenzene. Figure 8 illustrates a separation of an aromatic hydrocarbon mixture of the previously mentioned isomers. For a styrene built of an unsaturated chain an increase of ΔM_e values was noted with respect to the value obtained for ethylbenzene from the saturated chain. In regards to the position of the unsaturated bond in the sub-

stituent, when it was coupled with the ring (*trans*-1-phenyl-1-propene), the specific interactions of the adsorbate were stronger than when it was isolated (3-phenyl-1-propene).

Conclusion

In this presented work some retention parameters were compared with linear and branched, aliphatic, and cyclic as well as aromatic hydrocarbons using packings with chemically bonded complexes of Cu(II) and Cr(III). The obtained results allowed for the packings under study to be ordered taking into account the following increasing values of retention parameters: packing with no metal < Cu(II) < Cr(III).

It was proved that values of specific interactions between a metal complex and a nucleophilic adsorbate are determined not only by factors related to the packing, but also by a structure and a configuration of an adsorbate molecule (i.e., unsaturation factor, number of unsaturated bonds and their mutual positions, as well as number and types of substituents).

Besides an increase of adsorbent/adsorbate reactions, all the packings modified with metals were characterized by higher selectivity in comparison with a reference packing. It created a possibility of separate compound mixtures belonging to the same class, with slightly different molecule structures. The presented chromatograms proved to be great possibilities for the analytical use of the presented packings.

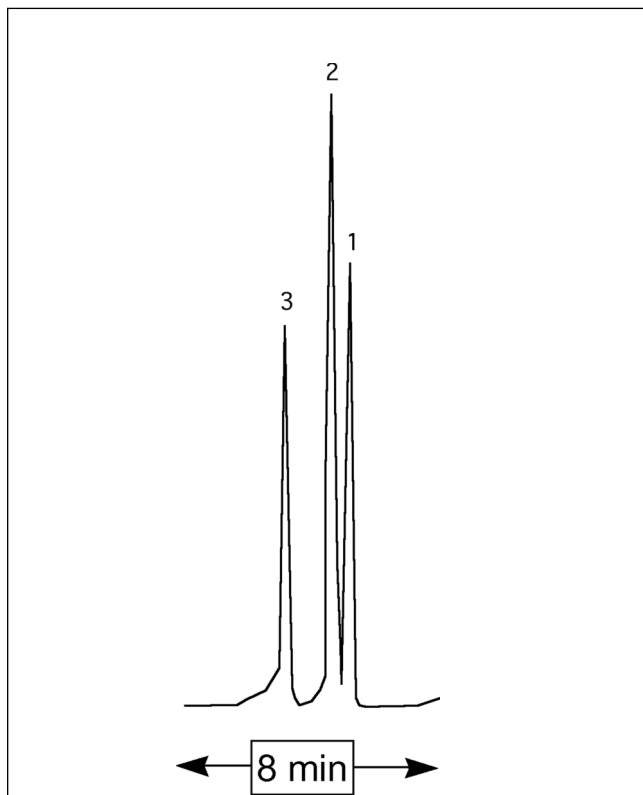


Figure 7. Separation of a mixture of cyclic C7 hydrocarbons (packing with CrCl_3 , 114°C column temperature, and $V_{\text{helium}} = 31.0$ mL/min): (1) methylcyclohexane, (2) 1-methyl-1-cyclohexene, and (3) cycloheptene.

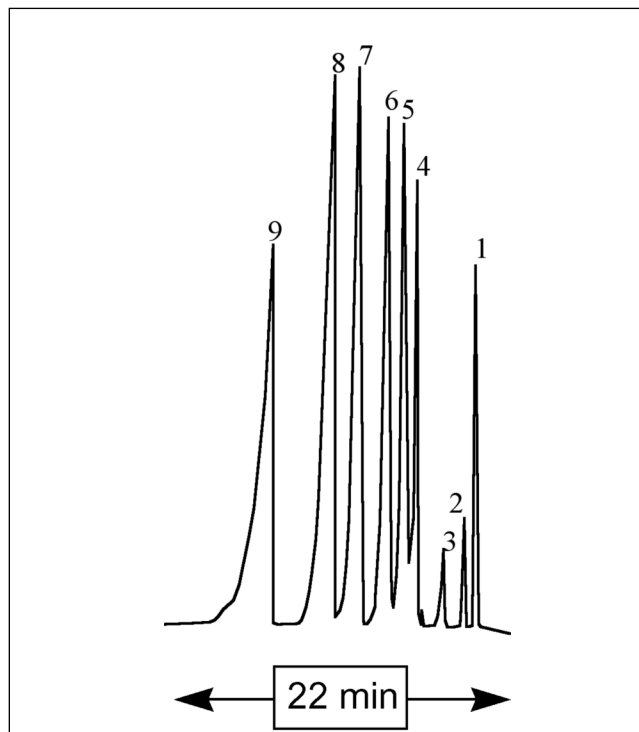


Figure 8. Separation of a mixture of aromatic and cyclic hydrocarbons (packing with CrCl_3 , 140°C column temperature, and $V_{\text{helium}} = 23.0$ mL/min): (1) cyclohexane, (2) benzene, (3) toluene, (4) ethylbenzene, (5) *m*-xylene, (6) cumene, (7) propylbenzene, (8) 1,3,5-trimethylbenzene, and (9) 1,2,3-trimethylbenzene.

References

1. B. Buszewski, M. Ligor, T. Ligor, and N. Tanaka. Determination of hazardous compounds isolated from environmental samples utilizing various stationary phases and columns for chromatographic techniques. *Chemia Analityczna* **44(3A)**: 327 (1999).
2. B. Buszewski, M. Jezierska, M. Welniak, and D. Berek. Survey and trends in the preparation of chemically bonded silica phases for liquid chromatographic analysis. *J. High Resolut. Chromatogr.* **21**: 267 (1998).
3. C.F. Pool and S.K. Pool. *Chromatography Today*. Elsevier, Amsterdam, The Netherlands, 1992.
4. K.K. Unger. *Packings and Stationary Phases in Chromatographic Techniques*. Marcel Dekker, Inc., New York, NY, 1990.
5. Chia-Fu Yeh, Sun-Dsong Chyuch, and Wei-Shi Chen. Application of dithiocarbamate resin-metal complexes as stationary phases in gas chromatography. *J. Chromatogr.* **630**: 275 (1993).
6. W. Wasiak and W. Urbaniak. Chemically bonded chelates as selective complexing sorbents for gas chromatography. V. Silica chemically modified by Cu(II) complexes via amino groups. *J. Chromatogr.* **757**: 137 (1997).
7. I. Rykowska, S. Smyka, W. Urbaniak, and W. Wasiak. Chemically bonded chelates as selective complexing sorbents for gas chromatography. VII. *N*-[3-(trimethoxysilyl)propyl] diethylenetriamine complexes with CuCl₂ and CrCl₃. *J. Chromatogr.* **844**: 239 (1999).
8. S.O. Akapo. Evaluation of transition metal complexes of amino-propylsilyldithioamide bonded phases for gas chromatography. *Anal. Chim. Acta* **341**: 35 (1997).
9. I. Rykowska and W. Wasiak. Polyamine complexes of copper(II) and chromium(III) for the analysis of nucleophilic compounds by complexation gas chromatography. *Chromatographia* **51**: 623 (2000).
10. IUPAC recommendations 1984. *Pure Appl. Chem.* **57**: 603 (1985).
11. K.K. Unger. *Porous Silica*. Elsevier, Amsterdam, The Netherlands, 1979.
12. J. Nawrocki and B. Buszewski. Influence of silica surface chemistry and structure on the properties structure and coverage of alkyl-bonded phases for high-performance liquid chromatography. *J. Chromatogr.* **449**: 1 (1988).
13. I. Novak, B. Buszewski, and D. Berek. Characterization of C18 chemically modified silica gel and porous glass phases by high-resolution solid state NMR spectroscopy and other physicochemical method chromatography. *Chromatographia* **29**: 233 (1990).
14. B. Buszewski and R. Lebeda. Testing of columns for high-performance liquid chromatography. *Appl. Chem. (Warsaw)* **34**: 196 (1990).
15. G. Widman and R. Riesen. *Thermoanalyse*. Hüthig, Heidelberg, Germany, 1984.
16. N.H.C. Cooke, E.F. Barry, and B.S. Salomon. Use of transition metal chlorides as salt modifiers in gas-solid chromatography. *J. Chromatogr.* **109**: 57 (1975).
17. V. Schurig. Resolution of enantiomers and isotopic compositions by selective complexation gas chromatography on metal complexes. *Chromatographia* **13**: 263 (1980).
18. V. Schurig and R. Weber. Manganese(II)-bis (3 heptafluorobutyl-*R*-camphorate): a versatile agent for the resolution of racemic cyclic ethers by complexation gas chromatography. *J. Chromatogr.* **217**: 51 (1981).

Manuscript accepted April 20, 2001.