

## Ketoimino groups as silica surface modifiers

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### Abstract

The presented work is devoted to Porasil C silica, with organic compounds bonded to its surface and capable of electron-donor–acceptor (EDA) interactions. These packings are a good base for studying interactions among stationary phases and the adsorbate molecules showing electron-donor properties. The presented work concentrates on the phases containing ketoimino groups at their surface. Copper and chromium chlorides were bonded through these to the surface. Physicochemical characteristics of the obtained packings were determined by the use of elemental analysis, differential scanning calorimetry (DSC) and inverse gas chromatography. We examined the influence of the surface modification on the retention parameters of the nucleophilic compounds.

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*Keywords:* Stationary phases, GC; Metal complexes; Hydrocarbons; Halogenated compounds; Ketoimines

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### 1. Introduction

Silica gel is a base material for chromatography, extraction, filtration, etc. Its surface may be modified in different ways. The presented work is devoted to Porasil C silica, with organic compounds bonded to its surface and capable of electron-donor–acceptor (EDA) interactions. Such modified silica may be used as a packing in complexation gas chromatography (CGC). Such packings are characterized by the high selectivity, thermal stability and resistance to different external factors [1–5]. These packings form a good base to study interactions between stationary phases and the adsorbate molecules showing electron-donor properties. A possibility of influencing

the above parameters in a simple way, by changing the composition of the chemically bonded phase, makes these packings important from both analytical and physicochemical points of view.

The complexes of transition metals with  $\beta$ -ketoimine are characterized by the use of high volatility and this fact enables their efficient use in the analysis of metals by gas chromatography [6,7]. Due to the high values of the stability constants of the above complexes, these ligands were also employed for the separation of metals by the use of the liquid chromatography [8].

Due to co-ordinative unsaturation, additional ligands can be inserted in the unoccupied co-ordinative positions of metal iminoketonates. They form adducts with Lewis bases through intermolecular bonds. In the presented work, pyridinium bases were separated by the use of nickel(II) *N,N'*-ethylene-, *N,N'*-trimethylene, and *N,N'*-phenyl-bis(acetyl-

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acetimine) dissolved in squalane [9]. It was concluded that strong electrostatic interactions occur between copper and nickel chelates with  $\beta$ -ketoimines and  $\sigma$ -type electron-donating molecules containing an oxygen atom. The stability of adducts decreases in the following order: cyclic ethers > ketones > esters > aldehydes > ethers.

The presented work concentrates on the phases containing ketoimino groups at their surface. Copper and chromium chlorides were bonded through these to the surface. Retention parameters (retention index, separation factor, specific retention volume, molecular retention index) for packing with bonded metal and packing with no metal were compared. The latter was regarded as a reference. On the basis of the retention parameters obtained, we have performed an evaluation of the specific interactions observed and a determination of the effect of adsorbate molecule structure and retention time depending on a packing was investigated. Adsorbates used in the study were the following nucleophilic compounds: aliphatic halogenated hydrocarbons.

Physicochemical characteristics of the obtained packings were determined by the use of elemental analysis and differential scanning calorimetry (DSC).

## 2. Experimental

### 2.1. Reagents

Silica gel (Porasil C, 80–100 mesh) was purchased from Waters Associates, Milford, MA, USA. Silane [2-(3-triethoxysilylpropylimino)-3-(*n*-butyl)-pentanone-4)], which was used for the modification

of the silica surface, was obtained from the Metalorganics Department of the Adam Mickiewicz University, Poznań, Poland. Hexamethyldisilazane, which was used to deactivate free silanol groups in the “end capping” reaction, was purchased from Riedel–De Haen (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 Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI, USA) and ICN (Plainview, TX, USA). 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 4A, was used as carrier gas. The flow-rate of the carrier gas was measured with a digital flowmeter (J&W Scientific, Folsom, CA, USA). Stainless steel columns were used (2 m  $\times$  3 mm I.D.).

The obtained packings were characterized by performing: (1) elemental analysis, and (2) DSC.

Elemental analysis was performed on a 2400 CHN Elemental Analyzer (Perkin–Elmer, Norfolk, USA). The obtained results are presented in Table 1. Surface areas determined by the BET method are listed in Table 1.

Table 1  
Physicochemical characteristics of examined packings

No.	Packing	Elemental analysis (%)				Surface area (m <sup>2</sup> g <sup>-1</sup> )
		C	H	N	Metal	
I	R = <i>n</i> -Buacac, without metal	5.51	1.10	1.07	–	87
II	R = <i>n</i> -Buacac, metal = Cu(II)	5.62	1.87	1.00	1.71	88
III	R = <i>n</i> -Buacac, metal = Cr(III)	8.19	1.59	1.66	0.05	83
IV	R = Hacac, without metal	1.78	0.45	0.53	–	85
V	R = Hacac, metal = Cu(II)	3.38	0.60	0.51	1.60	83

R = H, *n*-Bu.

The packings were also subjected to analysis by DSC. DSC analyses were performed on a DSC-50 calorimeter (Shimadzu, Japan).

### 2.3. Preparation of columns

The modification of the silica was performed in three stages.

#### 2.3.1. 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 to so-called “end capping” reaction with hexamethyldisilazane (HMDS), in order to deactivate free silanol groups remaining at its surface.

#### 2.3.2. Stage II

The second step was the bonding of amino groups with 2,4-pentanodione or 3-*n*-butyl-2,4-pentanodione.

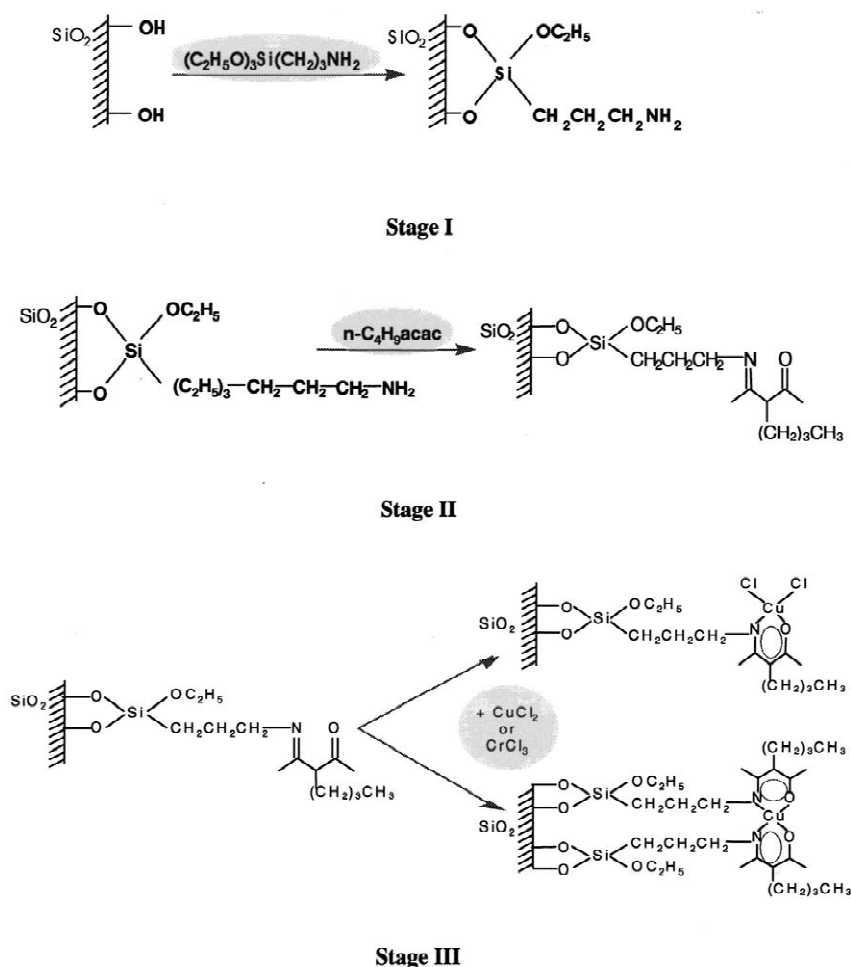


Fig. 1. Stages of reaction for the preparation of the packings.

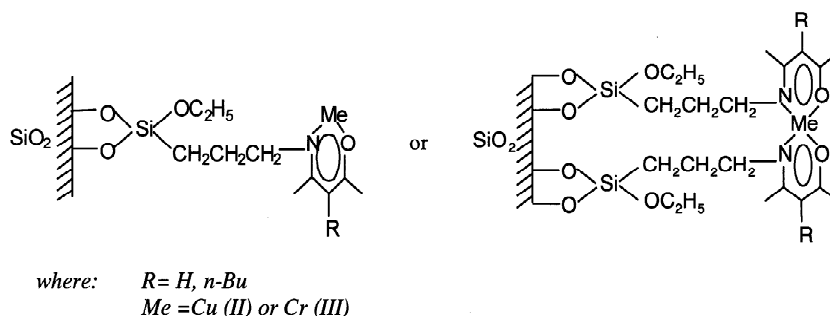


Fig. 2. Final complexes formed at the silica surface.

As the previous one, this reaction was also performed in anhydrous xylene for 12 h under continuous stirring. The system was protected against humidity during all the reaction time. The final product (Hacac or *n*-Buacac) of the reaction was extracted by the subsequent use of xylene and hexane in a Soxhlet apparatus. Finally, the silica was dried under vacuum.

### 2.3.3. Stage III

During the third stage, the last reaction was performed—bonding of copper(II) and chromium(III). Dry, partially modified, silica from 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 at room temperature. The system was protected against moisture. Finally, the silica was filtered off, the excess of  $CuCl_2$  was extracted with tetrahydrofuran in a Soxhlet apparatus and the silica was dried.

The above stages as well as the complexes formed at the surface of the silica support are shown in the Figs. 1 and 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 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 precise characterization of changes for other packing components (remaining 10%). Due to this fact, DSC [10] 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 physicochemical properties of the packings under study, but only to determine their thermal stability.

The results of the DSC analysis are shown in Fig. 3. As it can be seen, in both cases bonding of the metal was practically complete, as the peak, being characteristic for the free ligand (curve 1), disappeared completely after introducing copper (curve 2) and chromium (curve 3). The complexes formed at the surface are considerably more stable than the free ligand.

The influence of the modification on the chromatographic properties of the obtained packings was determined by the injection of several test compounds to the columns. These compounds belong to a wide group of different classes of organic compounds differing by electron-donor properties as well as their configuration. Particular attention was paid to include the high number of isomers, as their separation proves a high selectivity of a stationary phase. Among others, *cis*- and *trans*-isomers of alkenes  $C_6$  and  $C_7$  were separated on the examined

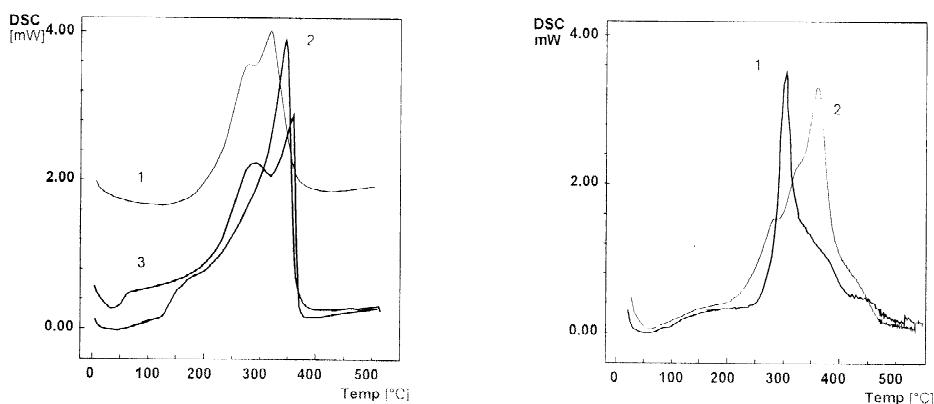


Fig. 3. DSC results for examined packings (the left figure: packing I from Table I—curve 1, packing II—curve 2, packing III—curve 3; the right figure: packing IV—curve 1, packing V—curve 2).

packings (Fig. 4). Other test compounds were as follows: aliphatic hydrocarbons, both linear and branched (including monomethylpentenes, dimethylbutenes and trimethylpentenes), and

halogenohydrocarbons (including dichlorobutenes and trichloroethanes) (Figs. 5–7).

The following retention parameters were deter-

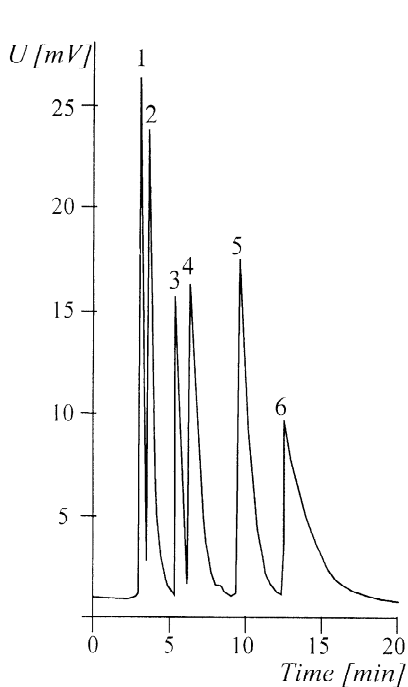


Fig. 4. Separation of  $C_5$ – $C_7$  alkenes; column:  $CuCl_2$ ;  $V_{He} = 21.5$  ml/min, column temperature:  $110^\circ C$ ; peaks: (1) *trans*-pentene-2, (2) *cis*-pentene-2, (3) *trans*-hexene-2, (4) *cis*-hexene-2, (5) *trans*-heptene-2, (6) *cis*-heptene-2.

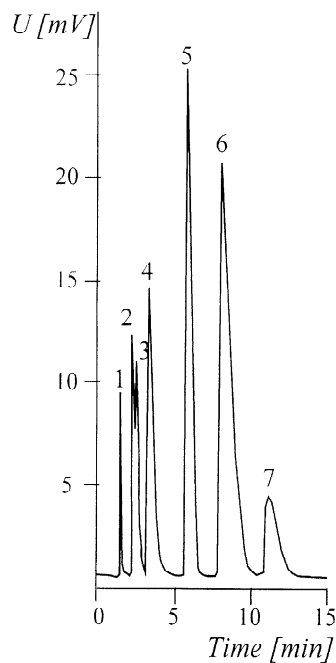


Fig. 5. Separation of branched aliphatic hydrocarbons; column:  $CrCl_2$ ;  $V_{He} = 23.1$  ml/min, column temperature:  $98^\circ C$ ; peaks: (1) 3-methylpentane, (2) 3,3-dimethylbutene-1, (3) 2,3-dimethylbutene-2, (4) 3-methylpentene-1, (5) 2,2,2-trimethylpentane, (6) 2,4,4-trimethylpentene-2, (7) 2,4,4-trimethylpentene-1.

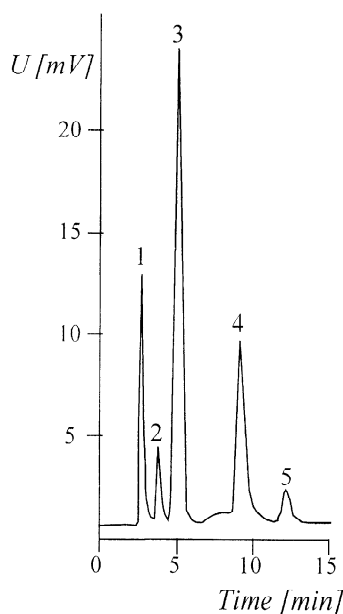


Fig. 6. Separation of halogenohydrocarbons; column:  $\text{CuCl}_2$ ;  $V_{\text{He}} = 19.1$  ml/min, column temperature:  $135^\circ\text{C}$ ; peaks: (1) 2-dichlorobutane, (2) 1-chlorobutane, (3) 1,1-dichlorobutane, (4) 1,2-dichlorobutane, (5) 1,4-dichlorobutane.

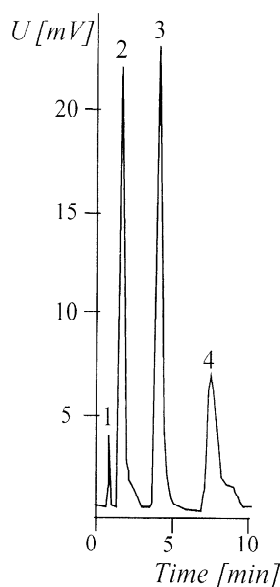


Fig. 7. Separation of aromatic halogenohydrocarbons; column:  $\text{CuCl}_2$ ;  $V_{\text{He}} = 22.3$  ml/min, column temperature:  $150^\circ\text{C}$ ; peaks: (1) benzyl chloride, (2) *n*-amyl bromide, (3) chlorobenzene, (4) bromobenzene.

mined: capacity factor ( $k$ ), retention index ( $I$ ), specific retention volume ( $V_g$ ), and molecular retention index ( $\Delta M_c$ ). For the definition of the latter see Ref. [11]. Results for some packings are given in Tables 2–5.

Significant differences in the interactions of the adsorbates with the packings were found. The absence of an element capable of co-ordinative interactions, such as a metal, lead to lower values of particular retention parameters (see the results in Tables 2–6 for the reference packings I and IV without a metal).

Results of the studies on the effect of the structure and configuration of linear and branched aliphatic hydrocarbons show that the strength of the charge-transfer interactions is mostly affected by: the level of the adsorbate saturation, number of unsaturated bonds and their mutual positions, and accessibility of an unsaturated bond.

#### 4. Conclusions

The series of chromatographic packings, showing the high ability to specific interactions was prepared and examined. The introduction of metal complexes chemically bonded to the stationary phase significantly increased the values of retention parameters in comparison to the reference packings.

Retention parameters of linear and branched aliphatic hydrocarbons, as well as halogenohydrocarbons, determined on the packings with chemically bonded complexes of  $\text{Cu(II)}$  and  $\text{Cr(III)}$  were compared. The obtained results arrange the studied packings, taking into account increasing values of retention parameters, in the following way:

*packings with no metal*

< *packings with bonded  $\text{CuCl}_2$*

< *packings with bonded  $\text{CrCl}_3$*

It was proven that values of specific interactions between a metal complex and a nucleophilic adsorbate are determined, not only by the 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

Table 2  
Retention parameters for halogenated aromatic hydrocarbons

No.	Adsorbate	Packing without metal (I)				Packing modified with CuCl <sub>2</sub> (II)				Packing modified with CrCl <sub>3</sub> (III)			
		<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>
1	Chlorocyclohexane	10.98	4.76	10.67	865	17.46	6.45	18.31	877	21.30	11.51	21.72	913
2	Fluorobenzene	5.81	4.42	5.65	752	6.44	8.16	6.75	729	5.87	6.92	5.98	720
3	Chlorobenzene	3.51	-15.88	3.41	675	4.72	-14.50	4.95	685	6.16	-8.49	6.29	728
4	Bromobenzene	9.15	-37.91	8.89	835	13.24	-35.81	13.88	845	17.09	-31.44	17.43	881
5	<i>para</i> -Chlorotoluene	14.61	3.48	14.21	913	21.03	4.32	22.04	915	29.14	9.99	29.71	959
6	<i>meta</i> -Chlorotoluene	16.71	6.60	16.24	935	26.22	6.95	27.49	938	34.42	13.42	35.09	984
7	<i>ortho</i> -Chlorotoluene	16.38	6.14	15.92	932	25.56	6.42	26.80	934	31.01	11.27	31.61	968
8	1,2-Dichlorobenzene	34.41	3.14	33.45	1056	57.67	2.97	60.46	1055	70.47	8.24	71.85	1092
9	1,3-Dichlorobenzene	26.10	-3.40	25.37	1009	41.91	-3.66	43.93	1008	57.68	3.95	58.82	1062
10	1,4-Dichlorobenzene	21.02	-8.46	20.44	973	30.65	-10.21	32.13	961	40.55	-3.59	41.35	1008

Retention factor (*k*), retention index (*I*), molecular retention index ( $\Delta M_e$ ), specific retention volume (*V<sub>g</sub>*); column temperature *T* = 130 °C.

mutual positions, as well as number and types of substituents.

Beside an increase of adsorbent–adsorbate interactions, all the packings modified with metals were characterized by higher selectivity in comparison to a reference packing. It created a possibility to separate mixtures of compounds belonging to the same class, with slightly different molecular structures. The presented chromatograms show great possibilities for the analytical use of the presented packings.

Analysis of the influence of the structure and configuration of aliphatic hydrocarbons has proven that the strength of charge–transfer interactions substantially depends on the adsorbate unsaturation degree, the number of unsaturated bonds and their mutual positioning, as well as the accessibility of an unsaturated bond.

Results of the retention studies, as well as the chromatographic analysis, have proven that the packings studied may be successfully used in complex-

Table 3  
Retention parameters for halogenated aromatic hydrocarbons

No.	Adsorbate	Packing without metal (IV)				Packing modified with CuCl <sub>2</sub> (V)			
		<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>
1	Chlorocyclohexane	8.22	7.56	11.13	885	8.25	12.57	23.24	921
2	Fluorobenzene	2.11	2.83	3.76	691	2.27	9.01	6.38	735
3	Chlorobenzene	5.64	7.98	8.89	845	6.01	12.08	16.91	874
4	Bromobenzene	9.36	-25.40	13.87	924	9.80	-22.10	27.58	947
5	<i>p</i> -Chlorotoluene	12.09	8.87	16.19	951	13.52	15.23	38.06	997
6	<i>m</i> -Chlorotoluene	11.75	8.17	15.73	946	13.14	14.61	36.98	992
7	<i>o</i> -Chlorotoluene	10.38	6.14	14.91	932	13.00	15.42	26.80	934
8	1,2-Dichlorobenzene	18.04	-0.28	25.49	1032	18.73	1.68	52.73	1046
9	1,3-Dichlorobenzene	12.99	-6.24	20.07	987	13.53	-5.17	38.09	997
10	1,4-Dichlorobenzene	13.24	-5.40	20.76	995	14.24	-4.10	40.07	1004

Retention factor (*k*), retention index (*I*), molecular retention index ( $\Delta M_e$ ), specific retention volume (*V<sub>g</sub>*); column temperature *T* = 120.1 °C.

Table 4  
Retention parameters for halogenated hydrocarbons

No.	Adsorbate	Packing without metal (I)				Packing modified with CuCl <sub>2</sub> (II)				Packing modified with CrCl <sub>3</sub> (III)			
		<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>
1	1-Chloropropane	1.87	0.35	2.13	548	2.51	1.34	2.03	555	3.46	8.20	3.14	604
2	2-Chloro-1-propene	1.88	0.36	2.14	549	2.52	1.35	2.04	557	3.47	8.19	3.15	605
3	1-Chlorobutane	1.25	-23.13	1.42	481	1.53	-23.28	1.24	480	1.89	-18.11	1.71	516
4	2-Chlorobutane	3.57	1.78	4.07	658	5.02	2.74	4.06	665	6.98	8.81	6.33	708
5	3-Chloro-1-butene	2.96	-1.66	3.37	627	4.12	-0.56	3.34	634	5.48	4.55	4.96	671
6	1-Chloropentane	2.83	-17.79	3.22	619	1.23	-42.06	0.99	446	1.80	-35.38	1.64	493
7	2-Chloropentane	6.83	3.10	7.79	768	10.16	4.17	8.23	775	15.23	10.84	13.80	823
8	Dichloromethane	1.07	-19.46	1.22	452	2.08	-8.92	1.68	528	1.73	-12.67	1.57	501
9	1,1-Dichloroethane	2.35	-14.51	2.68	588	3.98	-8.72	3.22	629	4.11	-8.66	3.72	629
10	1,2-Dichloroethane	2.63	-11.84	3.00	607	3.68	-10.41	2.98	617	5.14	-3.88	4.66	663
11	1,1-Dichlorobutane	2.35	-42.60	2.68	587	3.98	-37.11	3.22	627	3.48	-33.48	3.94	652
12	1,2-Dichlorobutane	8.31	-12.55	9.48	802	12.55	-11.94	10.16	806	13.82	-5.98	15.64	849
13	1,3-Dichlorobutane	9.92	-8.35	11.31	832	24.45	3.23	19.80	914	17.49	-1.36	19.79	881
14	1,4-Dichlorobutane	12.75	-2.54	14.53	873	34.89	10.71	28.25	967	30.01	11.07	33.97	970
15	2,2-Dichlorobutane	12.75	-2.36	14.53	874	34.89	10.71	28.25	967	30.01	8.67	33.97	953
16	2,3-Dichlorobutane	6.07	-20.03	6.92	748	8.47	-20.35	6.86	746	3.46	-33.58	3.92	652
17	1,1,1-Trichloroethane	8.29	-19.33	9.45	800	12.57	-18.15	10.18	809	15.35	-15.77	13.91	826
18	1,1,2-Trichloroethane	3.40	-40.27	3.88	651	4.29	-41.48	3.47	642	4.54	-41.32	4.12	644
19	1,1,1,2-Tetrachloroethane	2.97	-77.87	3.39	627	3.76	-79.20	3.05	618	3.41	-74.72	3.86	650
20	1,1,2,2-Tetrachloroethane	4.41	-68.48	5.03	694	16.09	-47.13	13.03	846	15.94	-45.96	18.03	855

Retention factor (*k*), retention index (*I*), molecular retention index ( $\Delta M_e$ ), specific retention volume (*V<sub>g</sub>*); column temperature *T* = 130 °C.

Table 5  
Retention parameters for halogenated hydrocarbons

No.	Adsorbate	Packing without metal (IV)				Packing modified with CuCl <sub>2</sub> (V)			
		<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>
1	1-Chloropropane	1.48	2.16	1.90	561	1.93	11.51	3.74	628
2	2-Chloro-1-propene	0.98	-2.31	1.08	507	1.10	-1.56	2.12	527
3	1-Chlorobutane	2.59	2.91	3.34	666	3.53	10.68	6.83	722
4	2-Chlorobutane	2.22	-1.07	2.86	638	3.05	7.34	5.89	698
5	3-Chloro-1-butene	2.12	-1.23	2.73	630	3.73	12.92	7.21	730
6	1-Chloropentane	4.69	3.86	6.04	773	6.99	11.90	13.51	830
7	2-Chloropentane	3.81	-1.41	4.90	736	5.68	7.31	10.98	798
8	Dichloromethane	1.63	-1.58	2.09	580	1.82	3.82	3.52	618
9	1,1-Dichloroethane	4.00	-5.94	5.15	644	5.84	-0.69	7.43	735
10	1,2-Dichloroethane	7.09	-1.20	9.14	847	9.44	1.60	14.93	907
11	1,1-Dichlorobutane	6.10	-9.87	7.85	821	8.99	-2.94	17.37	870
12	1,2-Dichlorobutane	7.04	-6.14	1.06	847	11.55	2.60	22.32	910
13	1,3-Dichlorobutane	9.32	1.16	12.00	899	16.34	10.23	31.58	964
14	1,4-Dichlorobutane	13.11	9.32	16.88	8958	24.56	19.24	47.47	1028
15	2,2-Dichlorobutane	4.38	-18.30	5.64	761	5.61	-13.39	10.84	796
16	2,3-Dichlorobutane	5.94	-10.53	7.65	816	9.96	-0.66	19.25	886
17	1,1,1-Trichloroethane	2.44	-39.69	3.14	655	2.65	-36.68	5.13	677
18	1,1,2-Trichloroethane	6.93	-15.56	8.92	827	9.80	-7.62	18.94	884
19	1,1,1,2-Tetrachloroethane	8.51	-42.02	10.97	883	10.45	-40.43	20.20	894
20	1,1,2,2-Tetrachloroethane	4.99	-55.82	6.43	784	27.73	-18.90	53.59	1048

Retention factor (*k*), retention index (*I*), molecular retention index ( $\Delta M_e$ ), specific retention volume (*V<sub>g</sub>*); column temperature *T* = 130 °C.



Table 6  
Retention parameters for hydrocarbons

No.	Adsorbate	Packing without metal (I)				Packing modified with CuCl <sub>2</sub> (II)				Packing modified with CrCl <sub>3</sub> (III)			
		<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>I<sub>R</sub></i>
1	<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
2	<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
3	<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
4	<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
5	1,3-Hexadiene	2.76	6.81	2.47	634	4.26	10.19	3.91	658	6.25	11.09	4.52	665
6	1,4-Hexadiene	2.29	2.40	2.05	603	3.69	7.00	3.38	636	5.11	6.65	3.69	633
7	1,5-Hexadiene	2.34	2.89	2.09	606	3.63	6.67	3.33	633	4.60	4.38	3.33	617
8	<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
9	<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
10	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
11	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
12	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
13	2-Methyl-pentane	2.19	-3.00	2.27	579	2.59	-2.76	2.33	580	3.23	-2.29	2.42	584
14	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
15	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
16	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
17	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
18	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
19	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
20	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

Retention factor (*k*), retention index (*I*), molecular retention index ( $\Delta M_e$ ), specific retention volume (*V<sub>g</sub>*).

ation gas chromatography for the analysis of mixtures of organic compounds, including geometric isomers.

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