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# Chemically bonded chelates as selective complexing sorbents for gas chromatography

## VI<sup>1</sup>. Modification of silica with NiCl<sub>2</sub> and CoCl<sub>2</sub> via β-diketonate groups

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### Abstract

Results are presented of studies of new types of packings for gas chromatography which contain nickel(II) and cobalt(II) chlorides and nickel(II) acetylacetonate chemically bonded via β-diketonate groups to a silica surface. Taking into account the ability of the metals in the chlorides and acetylacetonate to interact with compounds showing electron-donor properties, the study was performed using such adsorbates as aliphatic linear and branched hydrocarbons. The study allowed the determination of the influence of structure and configuration of adsorbate molecules on their retention and the definition of the usefulness of thus prepared packings in chromatographic analysis. The obtained results point to selectivity of the packings to the compounds which contain π electrons. Moreover, to determine the influence of the type of functional group bonded with hydrocarbon chain of a given silane on charge-transfer interactions, the obtained results were compared with those for the packings in which nickel(II), cobalt(II) chlorides and nickel(II) acetylacetonate were bonded with silica via diphenylphosphine groups.

**Keywords:** Stationary phases, GC; Complexation gas chromatography; Metal complexes; Olefins; Hydrocarbons

### 1. Introduction

Complexation gas chromatography is based on the ability of packings to undergo specific π-type interactions with adsorbate molecules showing electron-donor properties. In this type of chromatography, the separation mechanism consists of the formation of metastable complexes either of organic type or with cations of transition metals. The cations of metals showing electron deficiency have at least one empty

valence orbital which can be involved in the coordinative interactions. The use of complex-forming properties of metals in gas chromatography was for the reported for the first time by Bradford et al. in 1955 in a paper describing the separation of olefins in the solution of silver nitrate in poly(ethylene glycol) [6]. Very good separation of these compounds was obtained by Schurig and coworkers [7–10] who employed β-diketonate complexes of rhodium(I) dicarbonyls dissolved in squalane as stationary phases.

In complexation gas chromatography the most commonly used modifiers of packings are salts and

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<sup>1</sup> For Parts I–V, see Refs. [1–5].

complexes of Ni and Co, and also Cu [11–13]. Such compounds were initially used either in the “coated on support” form, or dissolved in liquid stationary phase, or as pure metal salts {e.g.,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ , tetra-(4-methylpyridino)nickel dithiocyanate or tetra( $\gamma$ -picoline) dithiocyanate complexes of Co and Ni [14,15]}. Heavy metal salts ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ) of the higher fatty acids are, in the molten state, superselective for the separation of amines and N-heterocyclics, owing to the strong coordination forces that act between these solutes and the metal atoms [16].

In the 1960s Cartoni et al. described the application of N-dodecylsalicylaldehydes of nickel and the methyl *n*-octylglyoximes of nickel. These compounds also retain superselectively in the columns for which these solutes can be bound as ligands [17]. Similar properties are shown by the  $\beta$ -diketone complexes of Ni and others [18].  $\text{NiCl}_2$  and  $\text{CoCl}_2$  modified adsorbents (silica gel) were used for the separation of isomers of different families and aromatics [19–25]. In addition to unsaturated hydrocarbons, other soft bases containing N, O, or S heteroatoms (*n*-donors) have been separated on complexing stationary phases with  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  complexes [e.g., dimeric 3-trifluoroacetyl- or 3-heptafluorobutyl-(IR)-camphorates of  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$  or  $\text{Cu}^{+2}$ ] [25,26].

As mentioned above, chlorides are the most commonly used compounds of these two metals. Other simple salts used in the analysis of hydrocarbons were  $\text{CoSO}_4$  [27],  $\text{NiBr}_2$  [28],  $\text{NiSO}_4$  [27] and  $\text{Ni}(\text{ClO}_4)_2$  [27]. The salt concentrations were usually from 5 to 30%. Some examples of complexes of these two metals used as stationary phases are presented in Tables 15, 17 and 18 in Ref. [11]. Chemically bonded phases were the next stage in the development of the packings modified by metal compounds (including Co and Ni). They allowed researchers to decrease the amounts of used metals to 0.5–1.5%, while maintaining high selectivity towards donors of electrons. Metal complexes are chemically bonded with silica surface via appropriate functionalised silane.

Silanes in which hydrocarbon chain is terminated by diphenylphosphine or  $\beta$ -diketonate groups capable of forming complexes with transition metals including Co and Ni [29,30,1,2] are an example of such bonding agents. Studies of these packings [with

Ni(II) and Co(II) chlorides and Ni(II) acetylacetonate chemically bonded with silica via diphenylphosphine groups] have proven their high selectivity and efficiency in hydrocarbon analysis.

In this paper the results are presented of investigation of new packings with chlorides of Ni(II) and Co(II) chemically bonded to a silica surface via  $\beta$ -diketonate groups. Taking into account the ability of metals present in the used salts to interact with compounds showing nucleophilic properties, the study was carried out for the aliphatic hydrocarbons, both linear and branched. Due to the fact that some functional groups on the support surface are not bonded to the metals, the measurements were also performed for a packing with free acetylacetonate groups. The study allowed us to determine the influence of structure and configuration of the molecules of adsorbates on their retention as well as to define the usefulness of the obtained packings in the chromatographic analysis.

Some results are also included for packings in which Ni(II) and Co(II) chlorides as well as Ni(II) acetylacetonate were bonded to a silica surface via diphenylphosphine groups. It enabled us to determine the influence of the type of functional groups, bonded to hydrocarbon chain of silane, on the retention of nucleophilic compounds studied.

## 2. Experimental

### 2.1. Reagents

Silica (Porasil C, 80–100 mesh) was obtained from Waters (Milford, MA, USA). 3-(3-Trimethoxysilylpropyl)-pentanodione-2,4 (TMSPP) was obtained from the Laboratory of Organometallic Chemistry (AMU, Poznań, Poland). Xylene, hexane, tetrahydrofuran (THF), and nickel(II) and cobalt(II) chlorides were obtained from POCh (Gliwice, Poland). Chromatographic standards were purchased from different producers, including Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI, USA) and ICN (Plainville, USA).

### 2.2. Apparatus

Chromatographic measurements were performed on a gas chromatograph GCHF 18.3 (Chromatron,

Berlin, Germany) equipped with a flame-ionization detector. Temperature in the thermostat chamber was determined using a DT 200 thermometer (Digital Thermometer, Slandi, Warsaw, Poland), and the pressure at the column inlet was measured with a mercury manometer. Argon 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). Stainless steel columns were used (2 m×3 mm I.D.).

The obtained packings were characterised by performing: (i) elemental analyses on a 2400 CHN Elemental Analyzer (Perkin-Elmer, Norfolk, USA). The obtained results are presented in Table 1; (ii) measurement of nitrogen adsorption–desorption isotherms at liquid nitrogen temperature on a sorptometer ASAP 2010 (Micromeritics, Narcross, GA, USA). The latter measurements enabled calculation of silane surface concentration and surface coverage with silane (in %).

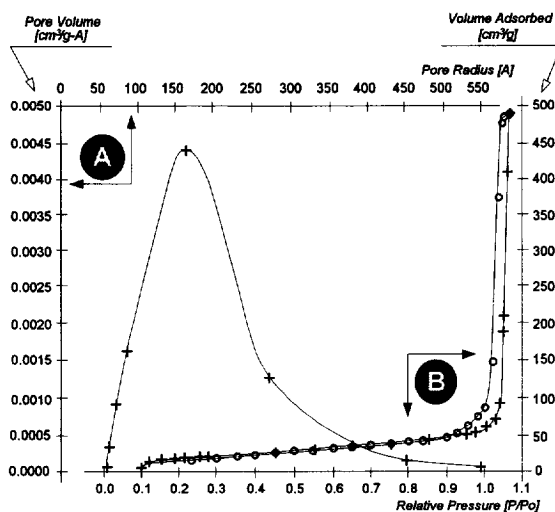


Fig. 1. Pore size distribution in silica support (A) and isotherms of adsorption–desorption of nitrogen for packings with bonded  $\text{NiCl}_2$  (B).

Table 1  
Physico-chemical parameters of the packings studied

No.	Packing	Elemental analysis (%)			Specific surface area ( $\text{m}^2/\text{g}$ )	Surface concentration of bonded silane ( $\mu\text{mol}/\text{m}^2$ )
		C	H or P <sup>a</sup>	Metal		
1	$\text{SiO}_2\text{-Si}-(\text{CH}_2)_3(\text{COCH}_3)_2$	2.54	0.61	–	85	3.33
2	$\text{SiO}_2\text{-Si}-(\text{CH}_2)_3(\text{COCH}_3)_2\cdot\text{NiCl}_2$	1.69	0.40	0.69	97	1.65
3	$\text{SiO}_2\text{-Si}-(\text{CH}_2)_3(\text{COCH}_3)_2\cdot\text{Ni}(\text{acac})_2$	2.46	0.47	0.11	91	2.88
4	$\text{SiO}_2\text{-Si}-(\text{CH}_2)_3(\text{COCH}_3)_2\cdot\text{CoCl}_2$	1.06	0.38	0.71	94	1.10
5	$\text{SiO}_2\text{-Si}-(\text{CH}_2)_2\text{PPh}_2\cdot\text{NiCl}_2$   OEt	1.79	0.30 <sup>a</sup>	0.27	75	1.27
6	$\text{SiO}_2\text{-Si}-(\text{CH}_2)_3\text{PPh}_2\cdot\text{CoCl}_2$   OCH <sub>3</sub>	5.95	1.50 <sup>a</sup>	0.82	91	3.67
7	$\text{SiO}_2\text{-Si}-(\text{CH}_2)_3\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2\cdot\text{Ni}(\text{acac})_2$	3.77	0.43 <sup>a</sup>	0.64	83	4.01

It is well-known that chromatographic materials should be possibly free of micropores, i.e., those below 20 Å [31], because their presence slows down mass transfer [32–35], and Fig. 1A shows that this is the case for packings studied by us. Moreover, the packings should be homogeneous as concerns the shape of pores. The latter is not easy to determine, but the analysis of the shape of hysteresis loop on the adsorption–desorption isotherm can give some information on the specific pore structure. The hysteresis loop shown in Fig. 1B has almost vertical with almost parallel branches and hence it belongs to type H1 according to the IUPAC classification [31]. The above type is usually associated with porous materials consisting of agglomerates or compacts of approximately uniform spheres in fairly regular array, therefore they have relatively narrow pore size distribution.

Pore volumes of the packings studied were: 0.86 cm<sup>3</sup>/g for the silica starting material, 0.83 cm<sup>3</sup>/g for the packings with bonded acetylacetonate, 0.80 and 0.79 cm<sup>3</sup>/g for packings with CoCl<sub>2</sub> and NiCl<sub>2</sub>, respectively. Surface areas determined by BET method are listed in Table 1.

### 2.3. Preparation of packings

The synthesis of the packings was performed by two stages. First, silane with β-diketonate group (TMSPP) was bonded to silica pre-dried at 180°C under vacuum. This reaction proceeded in anhydrous xylene. The system was heated to boiling under reflux for 12 h and the system protected against humidity at all times. The unreacted silane was extracted with xylene and then with hexane in a Soxhlet apparatus. The packing was then dried under

vacuum. At the second stage, silica with bonded silane was immersed into a saturated solution of anhydrous cobalt(II) chloride in THF. The system of reagents was allowed to stand at room temperature for 7 days and during that time, protected against humidity. Salt excess was removed by extraction with THF in the Soxhlet apparatus. The reaction with nickel(II) chloride was performed in the same way. Reactions proceeding during the synthesis are presented in Fig. 2.

The preparation of packings with nickel(II) and cobalt(II) chlorides, and nickel(II) acetylacetonate (acac) bonded to a silica surface by diphenylphosphine groups is described in Refs. [16–18].

### 3. Results and discussion

Electron-donor properties of transition metal complexes are of significant importance to the usefulness of the mentioned packings in complexation gas chromatography. Taking into account the ability of metal present in the used salts to interact specifically with compounds showing electron-donor properties, this chromatographic study was performed for linear and branched aliphatic hydrocarbons. The study was aimed at determining the influence of the structure and configuration of adsorbate molecules on their retention and the possibility of the application of such packings to analysis of hydrocarbons.

In Table 2 the values of the following parameters are presented for the packings investigated: retention factor (*k*), specific retention volume *V*<sub>g</sub> and molecular retention index Δ*M*<sub>e</sub> [24]. The molecular retention index enables determination of the influence of substituents on the retention of adsorbates. From this definition, the molecular retention index is equal to

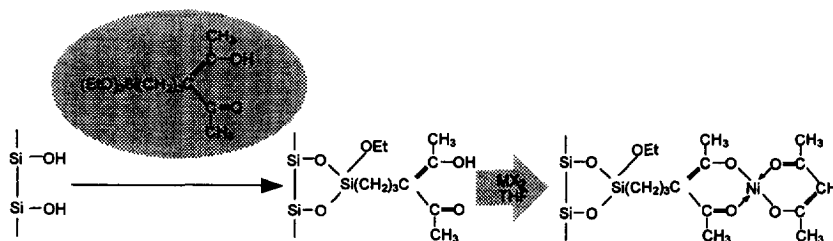


Fig. 2. Scheme of the preparation of the packings; MX<sub>2</sub> stands for CoCl<sub>2</sub>, NiCl<sub>2</sub> or Ni(acac)<sub>2</sub>.

Table 2

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

Adsorbate	-acac			-acacNiCl <sub>2</sub>			-acacCoCl <sub>2</sub>		
	$k$	$\Delta M_c$	$V_g$	$k$	$\Delta M_c$	$V_g$	$k$	$\Delta M_c$	$V_g$
Pentane	0.77	0.22	0.19	0.36	1.14	1.09	0.96	1.45	1.05
1-Pentene	0.80	2.86	0.75	1.39	6.53	2.40	1.92	8.39	3.29
<i>cis</i> -2-Pentene	0.87	4.96	0.82	1.65	8.21	2.63	2.16	12.22	3.65
<i>trans</i> -2-Pentene	0.84	4.12	0.79	1.58	7.20	2.52	2.06	11.12	3.48
1-Pentyne	1.14	14.27	1.07	2.46	21.78	4.25	4.28	28.60	7.32
Hexane	1.38	0.50	0.69	2.10	0.92	2.40	2.68	0.82	2.48
1-Hexene	1.44	2.30	1.35	2.59	6.84	4.46	3.64	8.88	6.22
<i>cis</i> -2-Hexene	1.56	4.96	1.47	3.01	8.33	4.79	3.98	12.15	6.75
<i>trans</i> -2-Hexene	1.50	3.98	1.41	2.85	7.04	4.54	3.74	10.74	6.34
1,3-Hexadiene	1.88	9.73	1.77	3.75	17.42	6.47	5.87	21.70	10.02
1,4-Hexadiene	1.55	4.82	1.46	3.47	15.63	5.99	5.47	20.12	9.35
1,5-Hexadiene	1.47	3.70	1.39	2.90	11.54	5.01	4.56	15.98	7.79
1,3,5-Hexatriene	1.48	7.73	1.40	4.91	23.85	7.82	6.89	28.69	11.68
1-Hexyn	2.06	14.13	1.94	4.76	22.96	8.21	8.38	29.83	14.31
Heptane	2.42	0.92	1.02	3.85	1.69	3.65	5.00	2.66	5.36
1-Heptene	2.53	3.14	2.38	4.76	6.92	6.80	6.80	9.04	11.62
<i>cis</i> -2-Heptene	2.73	5.10	2.57	5.56	8.69	8.84	7.51	12.57	12.72
<i>trans</i> -2-Heptene	2.66	4.40	2.50	5.24	7.31	8.34	7.11	11.34	12.05
<i>cis</i> -3-Heptene	2.73	5.24	2.57	5.23	7.28	8.33	7.14	11.40	12.09
<i>trans</i> -3-Heptene	2.57	3.56	2.42	5.01	6.24	7.97	6.68	10.52	11.63
2,3-Dimethylbutane	1.42	-2.24	1.22	2.16	-2.20	3.40	2.49	-2.35	4.04
2,2-Dimethylbutane	1.28	-4.92	1.10	1.98	-4.37	3.12	2.26	-4.57	3.67
2,3-Dimethyl-1-butene	1.48	0.75	1.26	2.63	4.42	4.14	3.68	8.66	5.96
2,3-Dimethyl-2-butene	1.76	5.38	1.51	3.34	10.16	5.26	5.10	16.20	8.16
3,3-Dimethyl-1-butene	1.26	-3.34	1.08	2.11	-0.79	3.33	2.80	2.42	4.55
2-Methylpentane	1.45	-1.68	1.24	2.17	-2.12	3.43	2.51	-2.14	4.08
2-Methyl-1-pentene	1.62	3.28	1.39	2.85	6.41	4.50	3.98	10.49	6.45
4-Methyl-1-pentene	1.48	0.89	1.27	2.48	3.02	3.91	3.20	5.46	5.19
2-Methyl-2-pentene	1.63	3.42	1.40	3.00	7.63	4.73	4.46	13.11	7.23
<i>cis</i> -3-Methyl-2-pentene	1.67	4.12	1.44	5.00	20.22	7.95	5.18	18.20	8.77
<i>trans</i> -3-Methyl-2-pentene	1.71	4.68	1.46	3.09	8.88	4.91	4.35	14.17	7.38
<i>cis</i> -4-Methyl-2-pentene	1.46	0.61	1.25	2.52	4.13	4.01	3.38	8.42	5.73
<i>trans</i> -4-Methyl-2-pentene	1.47	0.61	1.25	2.48	3.76	3.96	3.34	8.14	5.66

zero for *n*-alkanes [25,26]. Every additional function introduced to the *n*-alkane molecule (e.g., substituent, heteroatom, unsaturated bond) results in the appearance of a difference between molecular mass ( $M$ ) and effective molecular mass ( $M_c$ ). Positive values of the molecular retention index point to the occurrence of a positive interaction between a given functional group and a packing, while negative values indicate the occurrence of a repulsion between an adsorbate and a packing. Due to a possibility that some acetylacetonate groups on the support surface can be non-bonded to metal, the measurements of the retention of analysed compounds were carried out

also for a packing with free  $\beta$ -diketonate groups, and the latter was considered a reference. Table 3 contains values of retention index  $I$  and  $\Delta I$  for packings modified with nickel(II) and cobalt(II) chlorides as compared with the packing with free acetylacetonate groups ( $\Delta I = I_{\text{Ni(II) or Co(II)}} - I_{(\text{silica with acac})}$ ).

In Table 4 the retention parameters are presented for the packings with nickel(II) acetylacetonate bonded by diphenylphosphine and  $\beta$ -diketonate groups. Tables 5 and 6 show the retention indices and retention parameters, respectively, for those packings containing nickel(II) and cobalt(II) chlo-

Table 3

Retention indices  $I$  and  $\Delta I$  at 120.2°C for packings modified with nickel(II) and cobalt(II) chlorides and with free acetylacetonate groups

Adsorbate	-acac			-acacNiCl <sub>2</sub>		-acacCoCl <sub>2</sub>	
	$I$	$I$	$\Delta I$	$I$	$\Delta I$	$I$	$\Delta I$
1-Pentene	506	532	26	545	39		
<i>cis</i> -2-Pentene	521	544	23	573	52		
<i>trans</i> -2-Pentene	515	537	22	565	50		
1-Pentyne	573	627	54	675	102		
1-Hexene	607	634	27	649	42		
<i>cis</i> -2-Hexene	621	645	24	672	51		
<i>trans</i> -2-Hexene	614	636	22	662	48		
1,3-Hexadiene	655	695	40	726	71		
1,4-Hexadiene	620	682	62	715	95		
1,5-Hexadiene	612	654	42	685	73		
1,3,5-Hexatriene	612	727	115	761	149		
1-Hexyn	672	735	63	787	111		
1-Heptene	708	735	27	750	42		
<i>cis</i> -2-Heptene	722	748	26	775	53		
<i>trans</i> -2-Heptene	717	738	21	766	49		
<i>cis</i> -3-Heptene	723	738	15	767	44		
<i>trans</i> -3-Heptene	711	730	19	761	50		
2,3-Dimethylbutane	584	584	0	585	1		
2,2-Dimethylbutane	565	569	4	567	2		
2,3-Dimethyl-1-butene	591	617	26	647	56		
2,3-Dimethyl-2-butene	624	658	34	701	77		
3,3-Dimethyl-1-butene	562	580	18	603	41		
2-Methylpentane	588	589	1	590	2		
2-Methyl-1-pentene	609	631	22	660	56		
4-Methyl-1-pentene	592	607	15	625	33		
2-Methyl-2-pentene	610	640	30	679	69		
<i>cis</i> -3-Methyl-2-pentene	615	730	115	715	10		
<i>trans</i> -3-Methyl-2-pentene	619	649	30	687	68		
<i>cis</i> -4-Methyl-2-pentene	590	615	25	646	56		
<i>trans</i> -4-Methyl-2-pentene	591	612	21	644	53		

rides bonded via diphenylphosphine groups [29,30,1].

While discussing the influence of the structure and configuration of adsorbate molecules on specific interactions, attention was paid to the number, type and localisation of unsaturated bonds in a molecule, as well as to the number and type of the substituents in the main hydrocarbon chain. Comparing the values obtained for packings with and without metals, one can notice that in the case of linear olefins C<sub>5</sub>–C<sub>7</sub> the presence of a metal in a packing resulted in a significant increase in the retention parameters. In the case of mono-unsaturated olefins this increase was approximately by a factor of 2, while in the case of alkynes and dienes by a factor of

3 or more. This points to the existence of a  $\pi$ -type interactions and the extent of adsorbate molecule unsaturation.

How significant the effect of the availability of unsaturated bond is on values of specific interactions can be illustrated by using such compounds, as 1-heptene (terminal localisation of unsaturated bond) and *trans*-3-heptene (localisation of  $\pi$  bond inside the molecule) (Fig. 3).

The order of elution of the compounds is as follows: *trans*-3-heptene is eluted first, next comes 1-heptene, although the boiling point of 1-heptene is 2°C lower than that of *trans*-3-heptene. This is due to the steric effect of the substituents at unsaturated bond, which leads to blocking of the access to  $\pi$  bond in *trans*-3-heptene. The influence of the structure of adsorbate molecule on a value of  $\pi$ -type specific interactions can be observed also for geometric isomers. The *trans* isomer of 2-hexene is eluted before the *cis* one. This is also true for *trans*-2-heptene and *trans*-3-heptene, which are eluted earlier than *cis*-2-heptene and *cis*-3-heptene, because of different accessibility of unsaturated bonds in *cis* and *trans* isomers (Fig. 4).

Among branched hydrocarbons it is worth noting a pair of compounds: 2,3-dimethylbutane and 3,3-dimethyl-1-butene. The boiling points for both compounds are 57.98°C and 41.24°C, respectively. Despite a difference of as much as 16.74°C, the alkene was eluted after the alkane in agreement with the dependence discussed earlier. This observation concerns only the packings with bonded copper(II) and nickel(II) chlorides. In the case of the packing with free  $\beta$ -diketonate groups, the elution order followed the order of the boiling points, i.e., the alkene was eluted before the alkane. The presence of substituents in the main chain of alkenes can be discussed with regard to two aspects. On the one hand, they create an additional steric difficulty of hindrance which results in an increased direct contact between electron-acceptor centre and the adsorbate molecule. This is a negative influence. On the other hand, the alkyl substituent, due to its properties, leads to an increase in electron density of the unsaturated bond as a result of induction effect. Thus, the increase occurs in specific interactions in which  $\pi$  electrons play the main role.

The influence of substituents is the greater, the

Table 4  
Retention parameters of the studied packings modified with nickel(II) acetylacetonate bonded by diphenylphosphine and  $\beta$ -diketonate groups

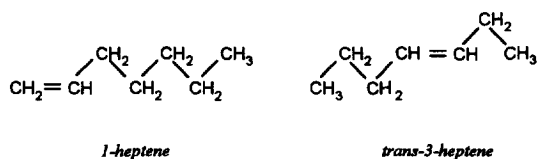
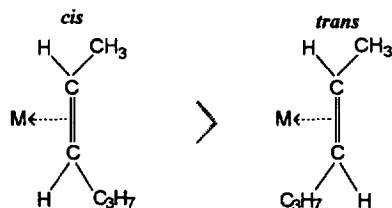
Adsorbate	acacNi(acac) <sub>2</sub>			PPh <sub>2</sub> Ni(acac) <sub>2</sub>		
	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>
Pentane	1.29	0.65	1.13	0.84	–	1.60
1-Pentene	1.44	4.82	1.27	1.02	6.19	1.93
<i>cis</i> -2-Pentene	1.59	7.21	1.40	1.20	10.01	2.26
<i>trans</i> -2-Pentene	1.56	6.78	1.37	1.13	8.58	2.14
1-Pentyne	2.31	18.34	2.07	2.19	26.79	4.14
Hexane	2.28	–	2.00	1.50	–	2.85
1-Hexene	2.52	4.40	2.21	1.88	7.00	3.55
<i>cis</i> -2-Hexene	2.90	7.77	2.55	2.09	9.61	3.95
<i>trans</i> -2-Hexene	2.74	6.36	2.41	2.01	8.70	3.81
1,3-Hexadiene	3.71	6.83	3.26	2.81	18.95	5.31
1,4-Hexadiene	3.20	10.15	2.81	2.43	15.41	4.60
1,5-Hexadiene	2.89	7.71	2.54	–	–	–
1,3,5-Hexatriene	4.51	22.32	3.96	3.63	27.06	6.86
Heptane	4.11	–	3.61	2.70	–	5.10
1-Heptene	4.58	4.54	4.02	3.44	7.66	6.49
<i>cis</i> -2-Heptene	5.25	7.91	4.61	3.78	9.98	7.15
<i>trans</i> -2-Heptene	–	–	–	3.74	9.74	7.07
<i>cis</i> -3-Heptene	5.01	6.78	4.40	3.80	10.12	7.19
<i>trans</i> -3-Heptene	4.83	5.94	4.24	3.58	8.62	6.76
2,3-Dimethylbutane	1.42	–2.67	1.50	1.37	–2.44	2.59
2,2-Dimethylbutane	1.29	–7.07	1.36	1.24	–5.11	2.35
2,3-Dimethyl-1-butene	1.74	4.26	1.84	1.91	7.49	3.62
2,3-Dimethyl-2-butene	2.27	19.15	2.40	2.52	14.28	4.76
3,3-Dimethyl-1-butene	1.38	–1.35	1.46	1.46	15.30	2.7
2-Methylpentane	1.43	–2.52	1.51	1.40	–1.88	2.65
2-Methyl-1-pentene	1.89	6.22	2.00	2.05	9.13	3.88
4-Methyl-1-pentene	1.62	2.72	1.71	1.69	4.59	3.20
2-Methyl-2-pentene	1.65	3.14	1.74	2.23	11.21	4.22
<i>cis</i> -3-Methyl-2-pentene	2.08	8.19	2.20	2.20	10.87	4.16
<i>trans</i> -3-Methyl-2-pentene	2.12	8.75	2.25	2.32	12.16	4.38
<i>cis</i> -4-Methyl-2-pentene	1.69	3.56	1.78	1.85	6.71	3.50
<i>trans</i> -4-Methyl-2-pentene	1.69	3.56	1.78	1.84	6.52	3.48

Table 5  
Retention indices *I* and  $\Delta I$  of the studied packings with nickel(II) and cobalt(II) chlorides bonded by diphenylphosphine groups

Adsorbate	-PPh <sub>2</sub>		PPh <sub>2</sub> NiCl <sub>2</sub>		PPh <sub>2</sub> CoCl <sub>2</sub>	
	<i>I</i>	$\Delta I$	<i>I</i>	$\Delta I$	<i>I</i>	$\Delta I$
1-Pentene	495	505	10	500	5	
1-Hexene	595	596	1	600	5	
<i>cis</i> -2-Hexene	606	611	5	610	4	
<i>trans</i> -2-Hexene	602	606	4	605	3	
1,3-Hexadiene	627	646	19	637	10	
1,4-Hexadiene	601	610	9	605	4	
1,5-Hexadiene	593	598	6	598	5	

Table 6  
Retention parameters of the studied packings with nickel(II) and cobalt(II) chlorides bonded by diphenylphosphine groups

Adsorbate	PPh <sub>2</sub> NiCl <sub>2</sub>			PPh <sub>2</sub> CoCl <sub>2</sub>		
	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>	<i>k</i>	$\Delta M_e$	<i>V<sub>g</sub></i>
Pentane	2.52	–	1.46	0.92	–	–
1-Pentene	2.58	2.72	1.49	0.90	2.02	–
Hexane	4.06	–	2.34	1.48	–	–
1-Hexene	4.99	1.45	2.30	1.49	2.02	–
<i>cis</i> -2-Hexene	4.27	3.56	2.46	1.55	3.42	–
<i>trans</i> -2-Hexene	4.17	2.86	2.40	1.52	2.72	–
1,3-Hexadiene	5.05	8.47	2.91	1.77	7.21	–
1,4-Hexadiene	4.26	3.42	2.45	1.52	2.72	–
1,5-Hexadiene	4.02	1.74	2.32	1.47	1.74	–

Fig. 3. Structure of 1-heptene and *trans*-3-heptene.Fig. 4. Elution order for *cis*-2-hexene and *trans*-2-hexene.

closer to double bond a substituent is located. 2,3-Dimethyl-1-butene, 2,3-dimethyl-2-butene and 3,3-dimethyl-1-butene are good examples of the relation between substituent position and its influence. The sequence of elution of such hydrocarbons is shown in Fig. 5.

Results presented in Tables 2–6 show that the interactions are stronger in the case of packings in which nickel(II) and cobalt(II) chlorides were bonded to a silica surface through acetylacetonate groups.

The comparison of the retention parameters for the packings with bonded nickel(II) chloride and nickel(II) acetylacetonate enables us to conclude that the modification of silica surface with silane ended with  $-\text{PPh}_2$  group and  $-\text{acac}$  group results in higher values of the retention parameters than in the case when chloride anion was bonded to the central cation of the complex.

In the absence of a factor capable of coordinatively interacting (e.g., metal), the retention parameters

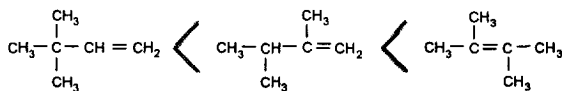


Fig. 5. Elution order for dimethylbutene isomers.

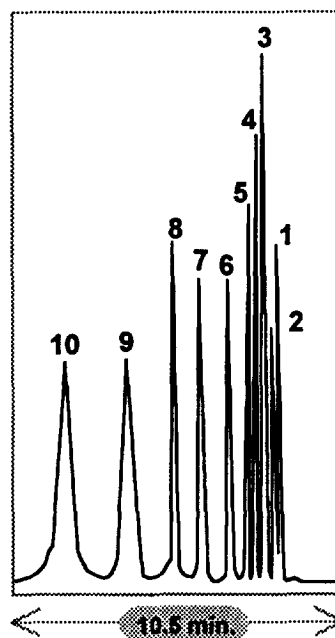


Fig. 6. Separation of five pairs alkane–alkene mixtures:  $V_{Ar}$  = 16.6 ml/min, temperature 140.7°C, column with *cis*-2-pentene packing, peaks: 1=pentane; 2=1-pentene; 3=hexane; 4=1-hexene; 5=heptane; 6=1-heptene; 7=octane; 8=1-octene; 9=nonane; 10=1-nonene.

are clearly lower as it is in the case of the reference packing, i.e., that with free diphenylphosphine or acetylacetonate groups.

The differences in the values of specific interactions between the bonded phases and the adsorbates with electron-donor properties were high enough to enable the separation of a mixture of the compounds studied. Chromatograms of the mixture are presented in Figs. 6 and 7. From Fig. 6 which shows the separation of a mixture of five alkane–alkene pairs it is clear that the elution order is strictly related to the presence of unsaturated bonds in adsorbate molecule.

Alkane is always eluted first, in spite of its higher boiling point as compared with that of the corresponding alkene, and this is due to  $\pi$ -type interactions. Some isomers were also present in the mixture, and their separation proves the selectivity of the packings. In Fig. 7 characteristics of the packing modified by nickel(II) chloride, which was used for the analysis of  $\text{C}_6$  hydrocarbons are presented.



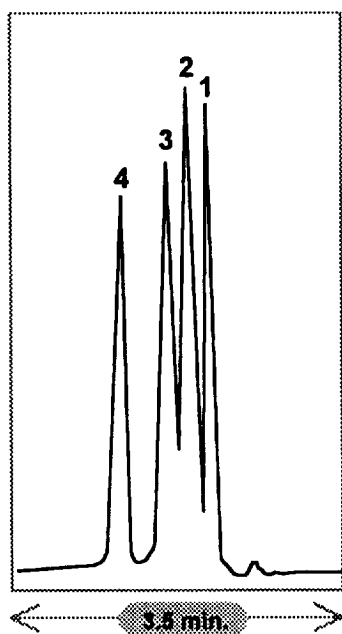


Fig. 7. Separation of  $C_6$  hydrocarbons:  $V_{Ar} = 17.9$  ml/min, temperature  $121.4^\circ C$ , column with 1-pentene packing. Peaks: 1= hexane; 2=1-hexene; 3=1,5-hexadiene; 4=1,3-hexadiene.

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