Chemically bonded chelates as selective complexing sorbents for gas chromatography
III. Silica chemically modified by N-benzoylthiourea groups

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Abstract

High stability and simple synthesis from inexpensive starting materials make it possible to use the N-benzoylthiourea groups as modifiers of silica for complexation gas chromatography. Taking advantage of the chelating properties of N-benzoylthiourea, copper(II) ions were bonded with SiO_2 to give a packing capable of entering into π-type interactions with adsorbates with electron-donor properties such as linear and branched alkenes and aromatic and cyclic hydrocarbons. The high selectivity of the packing obtained permitted the separation of complex mixtures (including isomers) of different classes of organic compounds.

1. Introduction

In general, complexation gas chromatography uses two types of packings. One employs phases bonded to the surface of the support, which include electron-donor or electron-acceptor groups capable of forming organic electron-donor–acceptor complexes with molecules of mixtures to be separated. The first attempt at using the formation of organic complexes in chromatography was made by Godlewicz [1]. He used silica gel impregnated with trinitrobenzene to separate the organic fraction of lubricating oils. In many instances the same molecule can act as an electron donor or acceptor, depending on the circumstances. It is only essential to ensure that the rate of formation of surface complexes and their dissociation are high. Phases

of this type are discussed in detail in Refs. [2–4].

The other type of packing employs electron-deficient species, such as many metal cations, which have at least an empty valence orbital available for extra coordination. These species are capable of complexing with electron-donating groups. Examples of packings of this type are those with transition metal complexes formed with such groups as diphenylphosphine, thiol, cyano, β-diketonate and iminoamine [5–10], bonded to the silica surface by a hydrocarbon chain.

The stability of the complexes which are formed by molecules of analyte compounds with a packing depends on at least six factors [2]: (1) valence, electronic structure and radius of the central metal ion; (2) spatial arrangement of

overlapping orbitals of central ion and ligands; (3) basicity of ligands; (4) "internal" electric effects of ligands transmitted through the central ion; (5) steric effects due to direct contact between the atoms of different ligands; and (6) "external" effects due to changes in the outer coordination sphere (e.g., solvent effect).

From the point of view of the complexation mechanism and stoichiometry, the following two cases can be distinguished: change in the number of ligands coordinated in the inner coordination sphere and displacement of a ligand coordinated in the inner coordination sphere. The fact that so many factors affect the process of complexation ensures a high sensitivity of complexation gas chromatography and permits its control. As the role of the ligand binding the metal ion with the support surface is of key importance, attempts are still made to determine the effects of using different groups as ligands.

This paper reports results obtained with the N-benzoylthiourea group applied as a binding ligand. A high affinity of this group to metals has been described by Koenig and co-workers [11–13] and others [14].

A sorption–spectrophotometric method was developed for determining silver using dithizone and silica chemically modified with N-propyl-N'-benzoylthiourea groups. The sensitivity and selectivity of the above method are better than those for the known methods based on organic reagents [15].

Complex formation between the N-benzoylthiourea group and metal ions on the surface of modified silica can be depicted as shown below; where $n = 1$, 2 or 3. A metal ion bonded in such a way is capable of entering into coordinative interactions with electron-donor molecules, so it can be used for modification of silica

for the purposes of complexation gas chromatography.

2. Experimental

2.1. Materials

In order to prepare the packings we used Porasil C, obtained from Waters (Milford, MA, USA), as a support. Its specific surface area was 89 m^2/g and the particle size was 177–149 μm (80–100 mesh). Hexamethyldisilazane and γ-aminopropyltriethoxysilane were purchased from Fluka (Buchs, Switzerland) and potassium thiocyanate, benzoyl chloride, toluene and acetone from POCh (Gliwice, Poland). The compounds used as sorbates were produced by different manufacturers and were either pure or of analytical-reagent grade.

2.2. Preparation of packings with N-benzoylthiourea groups

Synthesis of a packing was carried out in two stages. In the first stage, γ-aminopropyltriethoxysilane was bonded to the surface of silica dried at 180°C under reduced pressure. The reaction proceeded in anhydrous toluene under reflux. After washing and drying, an end-capping reaction was performed using hexamethyldisilazane. In the second stage, the reaction of the aminated silica with benzoyl isothiocyanate was carried out. The dry aminated silica was covered with a solution of benzoyl isothiocyanate in acetone. After 24 h, the packing was washed with dry acetone and then extracted with acetone in a Soxhlet extractor. Elemental analysis of the obtained dried packing gave N 1.16, C 5.43, H
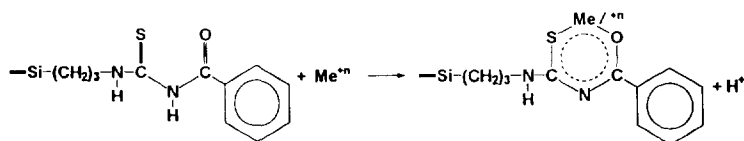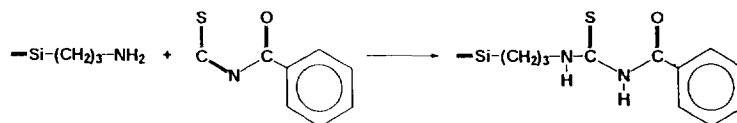
1.01, S 0.93%. This reaction can be represented schematically as shown above.

Part of the packing thus obtained was placed in a chromatographic column which was used as a reference for the packing subjected to reaction with copper(II) chloride. The reaction of isothiocyanate groups with copper(II) chloride was performed as follows: 9 g of the modified silica was covered with 50 ml of a saturated solution of $CuCl_2$ in acetone. The solution was light ochre in colour. At the moment of the contact with copper solution, the silica changed colour from light yellow to violet-ochre. After 12 h the packing was extracted with acetone in a Soxhlet extractor, dried and placed in a chromatographic column. The amount of bonded copper was 1.78% for the packing with a specific surface area of 81 m^2/g.

2.3. Apparatus

Chromatographic measurements were carried out on a GCHF 18.3 chromatograph (Chromatron, Berlin, Germany), equipped with a mercury manometer, digital thermometer and flame ionization detector with argon as the carrier gas. Stainless-steel columns of 1 m × 0.4 cm I.D. were used. The adsorbates were saturated and unsaturated linear and branched aliphatic hydrocarbons and cyclic and aromatic hydrocarbons. They were introduced by a Hamilton type syringe in doses of 0.01 μl or less.

3. Results and discussion

The measurements of retention time and calculations of retention parameters such as capacity factor (k'), retention index (I), molecu-

lar retention index (ΔM_e) and specific retention volume (V_g) were performed for both packings studied, i.e., that with Cu bonded via N-benzoylthiourea groups and that with free (without metal) N-benzoylthiourea groups, used as a reference. ΔM_e values can be calculated from $\Delta M_e = M_e - M$, where M = real molecular mass, $M_e = 0.14027I + 2.016$ and I = Kováts retention index. The results obtained for particular groups of adsorbates are given in Tables 1–4. The chromatographic measurements were carried out at three temperatures, 125, 135 and 145°C.

3.1. Aliphatic hydrocarbons

The presence of a metal capable of entering into coordinative interactions with additional ligands such as unsaturated hydrocarbons was responsible for the fact that the retention parameters determined under the same conditions were higher for the metal-containing packing. An increase in the strength of π-type specific interactions was accompanied by an increase in selectivity. A comparison of the differences in the capacity factors for alkene–alkane pairs obtained for the two packings (Table 2) provides clear evidence for the effect of a transition metal presence on specific interactions. Similar conclusions can be drawn from the retention indices (Table 1).

With the metal-containing packing, the difference (ΔI) between the extreme values of the retention indices for linear C_5 hydrocarbons ($\Delta I = I_{1\text{-pentyne}} - I_{\text{pentane}}$) was 110 u (u = unit of retention index), whereas with the packing free of metal, ΔI for the same compounds was only 39 u. This disproportion was much greater for subsequent hydrocarbons, C_6 and C_7. For C_6 hydrocarbons ΔI between an alkyne and alkane ($\Delta I = I_{1\text{-hexyne}} - I_{\text{hexane}}$) was 211 u with the metal-

Table 1
Values of capacity factors, retention indices, molecular retention indices and specific retention volumes for aliphatic hydrocarbons at 125°C

Solute	Packing with $-CuCl_2$				Packing without metal				B.p. (°C)
	k'	I	ΔM_c	V_g	k'	I	ΔM_c	V_g	
Pentane	1.73	500	0	1.27	1.74	500	0	2.14	36.07
1-Pentene	1.88	511	3.54	1.38	1.78	503	2.42	2.18	36.94
cis-2-Pentene	2.07	525	5.51	1.52	1.89	514	3.96	2.33	36.94
trans-2-Pentene	1.91	514	3.96	1.4	1.85	509	3.26	2.27	36.35
1-Pentyne	3.64	610	19.45	2.68	2.22	539	9.49	2.72	40.18
2-Methyl-1,3-butadiene	2.16	532	8.51	1.69	1.94	517	6.41	2.37	34.06
Hexane	3.41	600	0	2.5	3.22	600	0	3.95	68.74
1-Hexene	3.86	619	4.67	2.84	3.24	601	2.15	3.97	63.48
cis-2-Hexene	3.89	621	4.81	2.86	3.37	607	2.99	4.13	68.84
trans-2-Hexene	3.69	612	3.69	2.71	3.29	603	2.43	4.04	67.87
1,3-Hexadiene	5.14	662	12.71	3.78	3.96	613	5.85	4.85	73
1,4-Hexadiene	4.14	629	8.08	3.04	3.33	605	4.72	4.08	65
2,3-Hexadiene	4.68	647	10.61	3.44	3.78	626	7.66	4.63	68
2,4-Hexadiene	5.88	682	15.52	4.33	4.51	636	9.07	5.53	80
1-Hexyne	13.68	811	33.47	10.07	4.11	641	9.77	5.03	71.35
Heptane	6.61	700	0	4.86	5.85	700	0	7.17	98.42
1-Heptene	7.52	719	4.67	5.53	5.87	701	2.14	7.19	93.64
cis-2-Heptene	7.65	722	5.09	5.62	6.15	708	3.13	7.54	98.51
trans-2-Heptene	7.23	713	3.83	5.32	6.03	705	2.69	7.39	98.95
cis-3-Heptene	7.31	715	4.11	5.38	5.94	702	2.28	7.28	95.75
trans-3-Heptene	6.92	707	2.98	5.09	5.82	699	1.86	7.13	95.67
1-Heptyne	26.98	913	33.89	19.86	7.61	743	10.05	9.32	99.78
2-Methylpentane	2.97	581	−2.81	2.18	2.89	582	−2.53	3.54	60.27
3-Methylpentane	3.12	587	−1.83	2.29	3.04	594	−0.84	3.72	63.28
2-Methyl-1-pentene	3.53	605	2.71	2.6	2.94	586	0.05	3.85	60.7
4-Methyl-1-pentene	3.31	595	1.31	2.43	2.92	584	−0.23	3.58	53.88
2-Methyl-2-pentene	3.57	607	2.99	2.63	3.25	601	2.15	3.98	67.29
cis-3-Methyl-2-pentene	3.61	609	3.27	2.66	3.27	602	2.29	4.01	70.45
trans-3-Methyl-2-pentene	3.68	612	3.69	2.71	3.34	606	2.85	4.1	67.63
cis-4-Methyl-2-pentene	3.11	586	0.04	2.29	2.83	579	−0.93	3.47	56.3
trans-4-Methyl-2-pentene	3.12	587	0.18	2.3	2.88	582	−0.51	3.53	58.55
2,2-Dimethylbutane	2.59	559	−5.57	1.9	2.63	567	−4.63	3.22	49.7
2,3-Dimethylbutane	2.91	576	−3.33	2.14	2.86	580	−2.81	3.51	57.98
2,3-Mimethyl-1-butene	3.19	591	0.61	2.35	2.85	580	−2.79	3.41	55.67
2,3-Dimethyl-2-butene	6.15	615	4.11	2.78	3.42	611	3.41	4.19	73.21
3,3-Dimethyl-1-butene	2.29	559	−0.73	1.9	2.41	568	−4.72	2.95	41.24

containing packing and 41 u with the metal-free packing. For C_7 hydrocarbons these differences were 213 and 44 u for the packings with and without metal, respectively.

As far as the branched hydrocarbons are concerned, for which the steric effect must be taken into account, the effect of metal bonded on the packing surface on retention of the studied sorbates was much weaker. The differ-

ence in retention indices (ΔI) in the group of monosubstituted C_6 hydrocarbons calculated for 2-methylpentane and trans-3-methyl-2-pentene was 31 and 24 u for the packing with and without metal, respectively. For disubstituted derivatives of butene and butane, $\Delta I = I_{2,3\text{-dimethyl-2-butene}} - I_{2,3\text{-dimethylbutane}}$ was 39 and 31 u for the packing with and without metal, respectively. This indicates that the steric effect weakens the specific

Table 2
Values of $\Delta k' = k'_{alkene} - k'_{alkane}$ for the two packings investigated

Alkene–Alkane	125°C		136°C		145°C	
	Metal-containing packing	Metal-free packing	Metal-containing packing	Metal-free packing	Metal-containing packing	Metal-free packing
1-Pentene–pentane	0.18	0.04	0.13	0.01	0.09	−0.06
1-Hexene–hexane	0.45	0.02	0.29	0.03	0.24	0
1-Heptene–heptane	0.91	0.02	0.57	0.03	0.44	0.02
2-Methyl-1-pentene–2-methylpentane	0.56	0.05	0.29	0.14	0.27	0.11
2,3-Dimethyl-1-butene–2,3-dimethylbutane	0.28	−0.01	0.12	0.90	0.11	0

interactions between the bonded metal complex and the adsorbate, which, consequently, brings closer the selectivities of both kinds of packings towards the branched hydrocarbons. This conclusion is supported by the values of the molecular retention indices, which in a few cases are negative. According to the definition of this parameter, a negative value is evidence for repulsion between the electron-acceptor centre on the packing surface and the studied sorbate. The differences between the retention indices ($\Delta I = I_{cis\text{-isomer}} - I_{trans\text{-isomer}}$) obtained for the four pairs of geometric isomers of n-alkanes studied was within 9 u for the metal-containing packing, whereas for the metal-free packing the differences in the retention indices between these same pair of isomers were 3–5 u. The elution sequence of particular sorbates against their boiling temperatures also indicates the effect of π-type interactions on their retention parameters. Alkanes with higher boiling points were eluted first, before alkenes with lower boiling points (Table 1), e.g. pentane (b.p. = 36.07°C) was eluted before 2-methyl-1,3-butadiene (b.p. = 34.06°C), hexane before 1-hexene, trans-2-hexene and 1,4-hexadiene, etc.

3.2. Cyclic hydrocarbons

Similarly as for linear hydrocarbons, specific interactions were stronger in the case of the metal-containing packing (Table 3). The strength of the interactions increased with increase in the

number of unsaturated bonds in a molecule. This can be illustrated by the results for unsaturated cyclooctane derivatives. Lower values of the retention parameters of cyclooctatetraene than those of 1,5-cyclooctadiene, despite a larger number of unsaturated bonds in the former, are a consequence of its specific (tube-like) structure [16,17]:

Because of its unique structure, cyclooctatetraene is capable of interacting with metals only through two unsaturated bonds. It should also be noted that the interactions were stronger for dienes with isolated bonds than for dienes with conjugated bonds (1,4-cyclohexadiene and 1,3-cyclohexadiene or 1,5-cyclooctadiene and 1,3-cyclooctadiene). This is contrary to the situation observed for linear dienes (e.g., 1,3- and 1,4-hexadiene), for which the lowest values of k', I and ΔM_e were noted for the isomer with isolated unsaturated bonds (1,4-hexadiene). The presence of methyl or ethyl substituents resulted in a significant decrease in the molecular retention index (ΔM_e), even to negative values (with saturated cyclic hydrocarbons).

The strength of specific interactions can be judged from the values of the retention parameters obtained for four pairs of cycloalkanes–cycloalkenes using the metal-containing packing. Cyclopentene (b.p. 44.24°C) is eluted after

Table 3
Values of capacity factors, retention indices, molecular retention indices and specific retention volumes for cyclic hydrocarbons at 137°C

Solute	Metal-containing packing				Metal-free packing				B.p. (°C)
	k'	I	ΔM_e	V_g	k'	I	ΔM_e	V_g	
Cyclopentane	1.42	506	2.84	1.54	0.99	502	2.28	1.11	49.26
Cyclopentene	1.63	528	7.95	1.52	0.98	518	6.55	1.27	44.24
Methylcyclopentane	2.38	588	0.32	2.58	1.67	601	3.54	1.86	71.81
1-Methyl-1-cyclopentene	2.73	610	5.42	2.76	1.78	608	3.13	2.13	75.8
Cyclohexane	2.57	601	2.15	2.87	1.86	617	4.39	2.01	80.73
Cyclohexene	3.15	632	8.51	3.11	2.01	620	6.82	2.46	82.97
1,3-Cyclohexadiene	3.91	667	15.43	3.25	2.1	637	11.23	3.05	81.5
1,4-Cyclohexadiene	4.16	677	16.84	3.57	2.21	642	11.93	3.25	88.5
Benzene	4.02	671	11.97	3.5	2.16	640	13.67	3.14	80.1
Methylcyclohexane	4.41	687	0.18	4.7	3.04	697	1.58	3.46	100.93
Ethylcyclohexane	5.46	748	−3.26	8.67	5.61	802	2.28	6.61	131.78
Cycloheptane	5.48	720	4.81	5.9	3.82	736	7.05	4.28	118.79
Cycloheptene	7.06	760	12.44	5.96	3.86	738	9.35	5.51	115
1,3,5-Cycloheptatriene	7.96	779	19.13	6.68	4.33	757	16.05	6.21	116
Cyclooctane	10.94	829	6.07	11.31	7.33	848	8.73	8.55	151.14
Cyclooctene	12.66	852	11.31	10.92	7.08	842	9.91	9.89	138
1,3-Cyclooctadiene	12.17	846	12.49	10.94	7.09	842	11.93	9.51	141
1,5-Cyclooctadiene	26.26	962	29.61	12.93	8.38	871	16.01	20.51	148.4
Cyclooctatetraene	16.58	895	23.39	11.16	7.23	846	16.52	12.95	143

cyclopentane (b.p. 49.26°C). The situation is similar for cycloheptane and cycloheptene and for cyclooctane and cyclooctene. Only for C_6 cyclic hydrocarbons (cyclohexane and cyclohexene) is the sequence of elution according to increasing boiling point, because the boiling point of cyclohexane is lower than that of cyclohexene. For the packing free of metal the sequence of elution is according to increasing boiling points. However, the values of molecular retention indices, which are higher for cyclo-alkenes in the four pairs considered, are indicative of the fact that also in this case retention is affected by specific interactions.

3.3. Aromatic hydrocarbons

Interactions of aromatic hydrocarbons with the studied packings are strongly dependent on the size and structure of the adsorbate molecule. This is particularly well evidence when comparing molecular retention indices obtained for different adsorbates (Table 4).

Values of this parameter, reflecting the strength of specific interactions between the metal and π-electrons, increased from benzene to C_9H_{12}, and for the isomers of the studied group the highest values were obtained for trimethylbenzenes. The more branched were the substituents on the benzene ring, the weaker was the specific π-type interaction owing to growing steric hindrance. The ΔM_e values for 4-iso-propyltoluene, which are 0.61 and −2.60 (the only negative ΔM_e among the adsorbates in this group) for the packings with and without metal, respectively, provide a good example that confirms this observation. Low ΔM_e values were also obtained for sec.- and tert.-pentylbenzenes and for a pair of C_9H_{12} isomers, propylbenzene and cumene. A strong influence of π-electrons of the aromatic ring on specific interactions in the studied packing–sorbate systems is indicated by the values of the k'/k' ratio for pairs consisting of a halogenated benzene (chlorobenzene or bromobenzene) and an alkylbenzene (ethylbenzene or cumene) (Table 5).

Table 4
Values of capacity factors, retention indices, molecular retention indices and specific retention volumes for aromatic hydrocarbons at 145°C

Solute	Formula	B.p. (°C)	Metal-containing packing				Metal-free packing			
			V_g	k'	I	ΔM_e	V_g	k'	I	ΔM_e
Benzene	C_6H_6	80.1	2.49	3.24	672	18.16	2.7	1.82	643	14.09
Toluene	C_7H_8	110.62	4.9	6.38	786	20.1	4.93	3.32	753	15.49
Styrene	C_8H_8	145.2	12.13	15.79	939	29.57	9.97	6.72	882	21.57
Ethylbenzene	C_8H_{10}	136.18	8.49	11.05	879	19.13	8.28	5.38	848	14.78
p-Xylene	C_8H_{10}	138.35	9.41	12.25	896	21.51	8.73	5.88	857	16.04
o-Xylene	C_8H_{10}	144.41	10.38	13.51	913	23.9	9.69	6.53	877	18.85
m-Xylene	C_8H_{10}	139.1	9.33	12.15	895	21.37	8.79	5.92	859	16.32
α-Methylstyrene	C_9H_{10}	171.51	18.11	23.58	1006	33.55	15.28	10.3	962	18.76
Allylbenzene	C_9H_{10}	156.47	16.1	20.96	986	22.13	13.86	9.34	944	16.24
Propylbenzene	C_9H_{12}	159.21	14.86	19.35	973	18.28	14.03	9.46	946	14.5
Cumene	C_9H_{12}	152.39	12.56	16.35	944	14.22	12.44	8.38	923	11.27
1,2,3-Trimethylbenzene	C_9H_{12}	176.08	22.24	28.95	1038	27.4	18.53	12.48	999	21.93
1,2,4-Trimethylbenzene	C_9H_{12}	168.35	20.15	26.23	1023	25.3	16.53	11.13	977	18.8
1,3,5-Trimethylbenzene	C_9H_{12}	164.35	17.56	22.86	1001	22.21	14.92	10.05	958	16.18
2-Ethyltoluene	C_9H_{12}	165.15	16.91	22.02	994	21.23	15.4	10.38	964	17.02
3-Ethyltoluene	C_9H_{12}	161.3	14.77	19.22	972	18.14	14.3	9.63	950	15.06
n-Butylbenzene	$C_{10}H_{14}$	183.27	27.32	35.56	1071	18.01	25.9	16.45	1051	15.2
Isobutylbenzene	$C_{10}H_{14}$	172.75	23.2	30.2	1045	14.36	20.62	12.89	1019	10.8
tert.-Butylbenzene	$C_{10}H_{14}$	169.11	19.73	25.69	1019	10.72	18.54	12.49	999	7.81
sec.-Butylbenzene	$C_{10}H_{14}$	173.3	20.66	26.9	1027	11.84	19.52	13.15	1008	9.17
p-Diethylbenzene	$C_{10}H_{14}$	183.75	28.45	37.03	1078	18.99	24	16.17	1048	14.78
o-Diethylbenzene	$C_{10}H_{14}$	183.42	28.02	36.47	1075	18.57	23.87	16.09	1047	14.64
m-Diethylbenzene	$C_{10}H_{14}$	181.1	27.02	35.18	1069	17.73	23.1	15.56	1040	13.66
4-Isopropyltoluene	$C_{10}H_{14}$	177.1	23.47	30.54	1047	0.61	23.63	14.25	1024	−2.6
sec.-Pentylbenzene	$C_{11}H_{16}$	198.9	36.09	46.98	1116	10.29	31.91	21.5	1101	8.19
tert.-Pentylbenzene	$C_{11}H_{16}$	186	33.26	43.3	1102	8.33	30.04	20.24	1090	6.61
1,3,5-Triethylbenzene	$C_{12}H_{18}$	216.2	71.47	93.03	1224	11.41	55.53	37.42	1208	9.17
Fluorobenzene	C_6H_5F	85.1	3.01	3.92	704	4.65	3.17	2.13	672	0.17
Chlorobenzene	C_6H_5Cl	132.22	6.93	9.64	856	9.51	7.34	4.94	825	5.17
Bromobenzene	C_6H_5Br	156.43	9.73	15.27	933	−24.13	11.2	7.55	903	−25.62

The appropriate pairs of compounds (the first two) are characterized by similar boiling points (Table 5). In the case of alkylbenzenes, the electron density in the aromatic ring is increased as a result of the electron-donor character of the substituent. On the other hand, halogen sub-

Table 5
Values of k'/k' for selected pairs of adsorbates for the two packings investigated

Pairs of solutes	Metal-containing packing	Metal-free packing
Fluorobenzene–toluene	0.47	0.64
Chlorobenzene–ethylbenzene	0.62	0.91
Bromobenzene–cumene	0.59	0.9
Ethylbenzene–styrene	0.69	0.8
Propylbenzene–allylbenzene	0.95	1.01

stituents with electron-acceptor properties have a decreased electron density in the aromatic ring and thus reduce the ability of the ring to interact with metals. The presence of an unsaturated substituent increases the retention parameters, which is indicative of an increased strength of specific interactions. For example, for the pairs ethylbenzene–styrene or propylbenzene–allyl-benzene, stronger interactions were observed for styrene and allylbenzene. This is a consequence of the fact that for, e.g., styrene the double bond of the vinyl group conjugated with the benzene ring exhibits an electron-releasing tendency [18].

3.4. Separation properties of the studied packings

As the data presented in the form of tables do not give a clear illustration of the analytical usefulness of the packings, we performed a number of analyses of mixtures of standard hydrocarbons belonging to the studied groups. As follows from the chromatograms presented, the analysis can be performed in a short time and a complete separation of the analysed mixtures can be achieved. As the column used was only 1 m long, we can expect a further improvement of the separating abilities of the packings when the optimum conditions are found. Moreover, it should be emphasized that the peaks obtained were highly symmetrical and showed no tails. Fig. 1 illustrates a separation of four alkane–alkene pairs (from C_6 to C_9). Fig. 2 presents the result of the separation of a mixture of branched hydrocarbons including two alkane–alkene pairs. Because of the π-type interactions, the alkene is always eluted after the corresponding alkane, e.g., 2,3-dimethyl-2-butene is eluted after 2,2-dimethylbutane and 2,2,4-trimethyl-1-pentene after 2,2,4-trimethylpentane. Fig. 3 presents a chromatogram of a mixture of cycloalkanes and cycloalkenes. Also in this instance a cycloalkene is eluted after the corresponding cycloalkane. The chromatograms in Figs. 4 and 5 illustrate the separating power of the packing modified by $CuCl_2$ towards aromatic hydrocarbons. Both mixtures analysed included isomers. Fig. 4 shows the separation of three C_9H_{12} isomers (cumene,
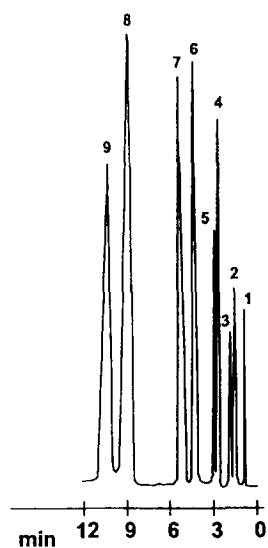

Fig. 1. Separation of a mixture of alkanes and alkenes on a Cu(II) complex-containing packing. Column temperature, 121°C; carrier gas flow-rate, 14 ml/min. Peaks: 1 = 1-pentene; 2 = hexane; 3 = 1-hexene; 4 = heptane; 5 = 1-heptene; 6 = octane; 7 = 1-octene; 8 = nonane; 9 = 1-nonene.
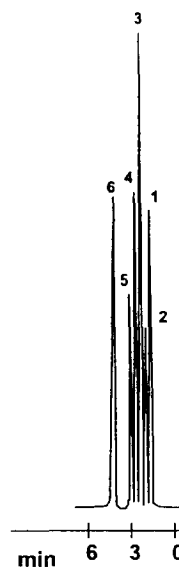

Fig. 2. Analysis of a mixture of branched hydrocarbons. Packing as in Fig. 1. Column temperature, 125°C; carrier gas flow-rate, 25.4 ml/min. Peaks: 1 = 2,2-dimethylbutane; 2 = 2,3-dimethyl-2-butene; 3 = 2,3-dimethylpentane; 4 = 2,2,4-trimethylpentane; 5 = 2,2,4-trimethyl-1-pentene; 6 = 2,2,5-trimethylhexane.
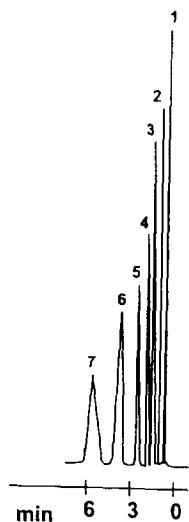
Fig. 3. Chromatogram of a mixture of cyclic hydrocarbons. Packing, column temperature and carrier gas flow-rate as in Fig. 2. Peaks: 1 = cyclopentane; 2 = cyclohexane; 3 = cyclohexene; 4 = cycloheptane; 5 = cycloheptene; 6 = cyclooctane; 7 = cyclooctene.

propylbenzene and *o*-ethyltoluene) and two $C_{10}H_{14}$ isomers (isobutylbenzene and *n*-butylbenzene), and Fig. 5 shows the separation
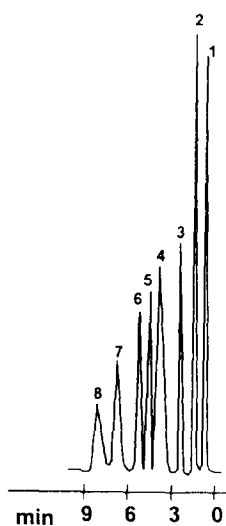

Fig. 4. Separation of a mixture of aromatic hydrocarbons. Packing as in Fig. 1. Column temperature, 147.5°C; carrier gas flow-rate, 18.8 ml/min. Peaks: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = cumene; 5 = propylbenzene; 6 = *o*-ethyltoluene; 7 = isobutylbenzene; 8 = *n*-butylbenzene.
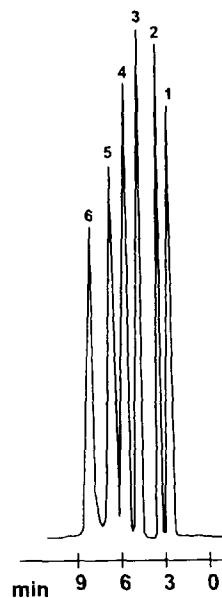

Fig. 5. Separation of a mixture of aromatic hydrocarbons. Packing, column temperature and carrier gas flow-rate as in Fig. 4. Peaks: 1 = *m*-xylene; 2 = styrene; 3 = allylbenzene; 4 = *tert.*-butylbenzene; 5 = isobutylbenzene; 6 = *n*-butylbenzene.

of three $C_{10}H_{14}$ isomers. Fig. 6 illustrates the separation of a mixture of three halogen derivatives of benzene and *p*-chlorotoluene. Also in this case the peaks are symmetrical.

4. Conclusions

Our earlier studies concerned packings capable of electron-donor–acceptor interactions obtained by modifying the silica support with chemically bonded simple functional groups such as cyano, thiol or diphenylphosphine [5–10]. The use of the N-benzoylthiourea group with chelating properties as a modifier has demonstrated that even spatially developed groups meet the requirements of complexation gas chromatography, in spite of the fact that their spatial structure may disturb the contact between the metal and electron donor. The packing modified with copper(II) chloride allowed the investigation of specific π-type interactions with unsaturated hydrocarbons. This packing can also be
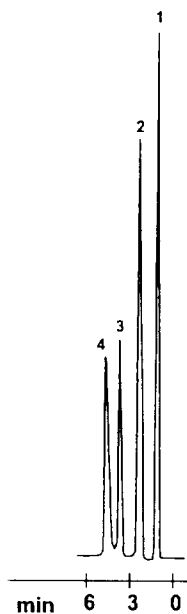
Fig. 6. Chromatogram of a mixture of halogen derivatives of benzene and toluene. Packing as in Fig. 1. Column temperature, 145°C; carrier gas flow-rate. 24 ml/min. Peaks: 1 = fluorobenzene; 2 = chlorobenzene; 3 = bromobenzene; 4 = p-chlorotoluene.

used in the chromatographic analysis of complex mixtures of hydrocarbons, including isomers. Its successful application to the separation of isomers confirms its high selectivity.

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