Chemically bonded chelates as selective complexing sorbents for gas chromatography
V. Silica chemically modified by Cu(II) complexes via amino groups

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Abstract

The synthesis of packings for complexation gas chromatography was performed by bonding aminosilane with a silica surface, and then bonding it with Cu(II) using the complexation properties of amino groups. Packings obtained in such a way were used for elemental analysis and differential scanning calorimetry and some retention parameters were determined for hydrocarbons, nitroalkanes and ethers. The chromatograms of test mixtures are presented in order to illustrate the separation properties of the packings. The thermal stability of the packings was determined by the use of the differential scanning calorimetry (DSC) technique. It was concluded that the modification of amino groups of N-(2-aminoethyl)-3-amino-propyltrimethoxysilane by Cu(II) cations allows use of these packings in the chromatographic analysis of hydrocarbons, ethers and nitroalkanes.

Keywords: Stationary phases, GC; Complexation gas chromatography; Hydrocarbons; Ethers; Nitroalkanes

1. Introduction

Chemically bonded stationary phases containing amino groups in their structure are known since the 1970s. Haken et al. [1–4] were one of the first groups to prepare and test them. They concluded that polysiloxanes with an ethylenediamine moiety with both primary and secondary amino groups in their structure can be used to effectively extract aldehydes, lactones and most ketones by chemical reactions with carbonyl compounds through the formation of carbon–nitrogen double bonds [1–4]. The strong interactions also occur in the case of alcohols.

These interactions are caused by hydrogen bonding of the type (OH···NH−). A proton may be donated by the hydroxyl group while the nitrogen atoms in the polyamine are common proton acceptors [2]. Other applications of different stationary phases containing amino polysiloxanes, were pointed out by Haken et al. in their review papers [5,6]. In general, however, owing to the chemical reactivity of amino groups, general use of these stationary phases in gas chromatography is restricted to extraction columns (for carbonyl compounds). Silanes with 3-amino-propyl [7] and N-(2-aminoethyl-3-aminopropyl) groups are most commonly used for chemical modification of surfaces of inorganic solid supports. Amino stationary phases bonded via aliphatic chains

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and aromatic rings are much more frequently used in HPLC [8–12]. These packings are often modified by using compounds of transition metals, mainly Cu(II). In such a case, the ability of the amino group (having a lone electron pair) is used to form complex compounds with metals to separate series of mixtures (e.g. isomers of dimethylanilines, chloroanilines and some aromatic amines), which is not possible using packings with free amino groups on their surface [13–15].

2. Experimental

2.1. Reagents

Silica gel (Kieselgel 60) was purchased from Macherey, Nagel and Co. (Duren, Germany). N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane was purchased from Dow Corning (Midlands, MI, USA). 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 and were certified reagents or of analytical reagent grade.

2.2. Apparatus

All chromatographic measurements were carried out on a GCHF 18.3 gas chromatograph (Chromatron, Berlin, Germany), equipped with a flame ionisation detector (FID). Measurement of column temperature was realised using a digital thermometer (Slandi, Warsaw, Poland). Argon, deoxygenated (Supelpure-O-Trap, Supelco, Bellefonte, USA) and dried using molecular sieve 4A, was employed as a carrier gas. The gas flow-rate was measured by using

a digital flowmeter (J&W Scientific, Folsom, CA, USA). Stainless-steel columns of 1 m length and 0.3 cm I.D. were used. Elemental analysis of chemically bonded phases was performed on a 2400 C.H.N elemental analyzer (Perkin-Elmer, USA). Specific surface areas of the studied packings were determined using the BET method on a Gravimat Sorptometer (Sartorius, Gettingen, Germany). The obtained results are presented in Table 1. Differential scanning calorimetry (DSC) measurements were performed on a Shimadzu DSC-50 apparatus (Shimadzu, Japan).

2.3. Preparation of packing with chemically bonded N-(-2-aminoethyl)-3-aminopropyl-trimethoxysilane

A 50-g amount of silica was dried under vacuum at 170°C for 12 h and treated with 17 ml N-(-2-aminoethyl)-3-aminopropyltrimethoxysilane in 300 ml dry toluene. The whole mixture was heated under reflux in a dry atmosphere for 14 h. Subsequently, after washing with dry toluene, the material was transferred to a Soxhlet apparatus and extracted with toluene for 18 h. After the packing was dried, the unreacted silanol groups were deactivated by end-capping reaction with hexamethyldisilazane. Half of the resulting material was then treated with a solution of CuCl$_2$ in tetrahydrofuran (THF) under anhydrous conditions. The mixture was left standing for 7 days in order to reach equilibrium. Subsequently, the excess CuCl$_2$ was removed with THF.

3. Results and discussion

The use of packings with the surface amino groups

Table 1
Physico-chemical characterisation of the investigated packings

Packing	Elemental analysis (%)				Surface area (m^2/g)	Surface concentration of silane (μmol/m^2)
	C	H	N	Cu^{2+}		
Without metal	7.00	1.93	2.30	–	360	2.2
With Cu(II)	6.69	1.79	2.18	3.59	354	2.2

in gas chromatography is limited due to their high reactivity with compounds containing carbonyl groups, in contrast to HPLC where they are widely used. We have, therefore, investigated the modification of the amino groups by using their coordination properties. The results obtained by other authors who described chemically bonded complexes of transition metals in the HPLC were an additional encouragement [9–13].

The reported application of chemically bonded complexes to gas chromatography indicates a high selectivity of packings of these for a wide range of organic compounds having nucleophilic properties [16–20]. The Cu(II) complexes, formed on silica surface modified by aminosilane were analyzed and described by Leyden et al. [21–23] and other authors [24–27]. The complexes formed on the surface of the silica support are shown in Fig. 1.

Two forms of complexes are possible [23]: blocking of the active amino groups by Cu(II) (A) and the
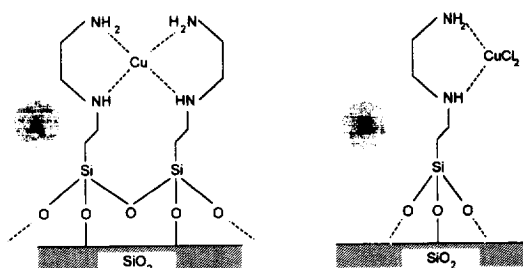

Fig. 1. Scheme of Cu(II) complexes chemically bonded with silica surface.

newly reported surface complex (B) which is capable of interacting specifically with compounds showing electron-donor properties. The chromatographic measurements were performed for a wide range of analytes (hydrocarbons, nitro compounds and ethers) for packings with free amino groups (reference system), and those with Cu(II) complexes.

Table 2
Values of retention factor, retention indices, molecular retention indices and specific retention volumes for aliphatic hydrocarbons at 130°C

Solutes	Packing without metal				Packing with CuCl$_2$			
	k	I	ΔM_c	V_g	k	I	ΔM_c	V_g
Pentane	1.88	500	0	3.73	3.91	500	0	8.02
1-Pentene	1.98	506	2.86	3.92	5.07	534	6.78	10.40
1-Pentyne	2.04	510	3.04	4.04	11.51	642	23.95	23.61
cis-2-Pentene	2.17	518	4.54	3.71	2.66	542	7.90	7.17
trans-2-Pentene	2.02	511	3.56	3.55	2.54	533	6.64	6.66
Hexane	4.18	600	0	8.30	8.34	600	0	17.11
1-Hexene	4.39	606	2.86	8.72	10.94	636	7.06	22.43
1-Hexyne	5.43	647	10.03	11.76	27.28	756	25.91	55.94
cis-2-Hexene	4.64	619	4.68	7.40	5.28	640	7.62	15.31
trans-2-Hexene	4.30	611	3.56	7.04	5.02	630	6.22	14.19
Heptane	8.94	700	0	16.42	17.81	700	0	36.52
1-Heptene	9.27	705	2.72	17.37	23.57	737	7.21	48.32
1-Heptyne	12.89	751	11.58	27.54	69.88	891	30.82	143.28
cis-2-Heptene	9.72	724	5.38	14.67	10.47	737	7.20	32.06
trans-2-Heptene	9.08	715	4.12	13.82	9.86	727	5.80	29.95
cis-3-Heptene	9.12	717	4.40	13.96	9.96	728	5.94	30.07
trans-3-Heptene	8.62	710	3.42	13.36	9.54	720	4.83	28.42
Octane	17.44	800	0	34.58	38.22	800	0	74.36
1-Octene	18.24	806	2.86	36.16	47.58	833	6.64	97.55
1-Octyne	26.31	855	12.29	56.11	169.07	1015	34.19	346.64
Nonane	36.12	900	0	74.59	74.37	900	0	152.48
1-Nonene	39.82	902	2.29	78.96	85.03	919	4.68	174.34
1-Nonyne	51.12	993	13.11	96.78	189.43	1165	30.45	215.78
Decane	78.12	1000	0	142.06	151.85	1000	0	311.33
1-Decene	87.89	1013	4.26	162.15	162.92	1018	3.42	334.03
1-Decyne	110.15	1109	12.78	197.89	245.98	1234	37.12	368.65

Table 3
Retention parameters for branched hydrocarbons at 130.1°C

Solutes	Packing without metal				Packing with CuCl₂			
	k	I	ΔM_e	V_g	k	I	ΔM_e	V_g
2,2-Dimethylbutane	3.59	566	-4.78	6.38	4.26	569	-4.34	12.03
2,3-Dimethylbutane	4.12	585	-1.96	7.40	4.94	586	-1.97	13.83
2,3-Dimethyl-1-butene	5.08	592	0.93	7.72	5.15	612	3.69	17.03
2,3-Dimethyl-2-butene	6.29	623	5.34	9.67	6.46	640	7.62	21.43
3,3-Dimethyl-1-butene	3.05	521	-9.06	4.57	3.84	577	-1.21	12.87
2-Methylpentane	6.26	578	-1.68	8.08	10.40	596	-1.24	16.55
3-Methylpentane	6.37	582	-1.12	8.85	10.69	588	-1.68	16.99
2-Methyl-1-pentene	7.02	604	2.61	9.07	14.06	626	5.66	22.34
3-Methyl-1-pentene	6.66	599	1.14	8.12	12.02	604	2.58	19.12
4-Methyl-1-pentene	6.27	588	0.37	8.09	12.31	608	3.14	19.59
2-Methyl-2-pentene	7.32	610	3.42	9.44	14.32	638	5.94	22.76
cis-3-Methyl-2-pentene	8.23	618	4.98	11.45	15.28	638	7.34	24.32
trans-3-Methyl-2-pentene	7.68	617	4.40	9.93	14.96	635	6.92	23.81
cis-4-Methyl-2-pentene	11.31	605	2.12	13.60	13.08	672	12.72	19.22
trans-4-Methyl-2-pentene	11.25	603	2.04	13.33	14.88	673	12.44	18.91
2,2,4-Trimethylpentane	18.47	743	-7.99	23.84	31.64	736	-8.98	50.35
2,4,4-Trimethyl-1-pentene	20.83	760	-3.59	26.88	41.96	772	-1.91	66.77
2,4,4-Trimethyl-2-pentene	20.69	759	-3.74	26.72	39.30	768	-3.03	62.54

The results obtained are reported in Tables 2–6.

The sample mixture chromatograms show separation capabilities of the tested packings. The presented chromatograms have symmetric peaks which points to homogeneity of surface adsorption centres. The retention measurements were performed for both packings at three different temperatures: 130, 140 and 150°C, which enabled calculation of the retention factor (k), retention indices (I), specific retention volume (V_g) and molecular retention index (ΔM_e) (for the definition of the latter, see Ref. [20]). The parameters mentioned above were determined for linear alkanes, alkenes and alkynes with an unsaturated bond near the first carbon atom and are juxtaposed in Table 2 for both packings. The sample chromatogram for the mixture of alkanes and alkenes is shown in Fig. 2. Following from earlier research, interactions of electron-donors (π bond) of such a type are very strong, due to easy access to the π bond located near the first carbon atom of the hydrocarbon chain. The results presented in Table 2 were obtained at 130°C. Similar values were observed at 140°C, while at 150°C the metal–alkene interactions were much weaker.

The analysis of the data listed in Table 2 shows that in the case of the metal free packing, differences are very small for an alkane–alkene or alkane–alkyne pair. However, the Cu(II) complex packing showed corresponding increases in the interactions with higher values of k, ΔM_e and $\Delta I = I_{alkene} - I_{alkane}$ due to an increase in the packing selectivity. Similar effects were observed for branched hydrocarbons (Table 3), although negative values of the molecular retention index were found with both packings due to the steric effect which made the interaction between analyte molecules and active centres more difficult, e.g. trisubstituted pentane and pentene derivatives, as well as branched alkanes, except for 3,3-dimethyl-1-butene.

In Table 4 retention parameters for cyclic and aromatic hydrocarbons are listed. In the case of the latter, k values were two and three times higher for the packing which contained the metal complex. In Fig. 3 a chromatogram of a mixture of aromatic hydrocarbons is presented.

In Tables 5 and 6 the results are presented for ethers whose oxygen lone electron pair is responsible for specific interactions. In nitro-compounds, the nitro group as a whole shows the electron-donor character. The separation of ethers and nitro-compounds has been reported for packings with complexes chemically bonded to the silica surface [29–

Table 4
Retention parameters for cyclic and aromatic hydrocarbons at 130.3°C

Solutes	Packing without metal				Packing with CuCl$_2$			
	k	I	ΔM_e	V_g	k	I	ΔM_e	V_g
Cyclopentane	3.25	512	3.69	4.80	2.96	510	−0.61	7.66
Cyclopentene	3.20	510	5.43	4.73	3.74	540	5.61	9.96
Cyclohexane	6.72	614	4.02	9.93	6.36	611	−0.44	17.73
Cyclohexene	7.54	630	6.24	11.13	9.06	655	7.71	25.74
Cycloheptane	16.09	738	7.35	23.76	15.82	726	1.83	45.74
Cycloheptene	16.16	705	4.73	23.87	21.40	766	7.26	62.29
Cyclooctane	35.25	848	8.75	52.06	36.76	835	2.89	107.78
Cyclooctene	34.65	845	10.34	51.17	47.30	866	9.26	138.24
1,3-Cyclohexadiene	8.33	645	12.36	12.29	15.47	724	19.41	44.72
1,4-Cyclohexadiene	9.63	665	15.17	14.21	14.28	713	17.86	41.19
Methylcyclopentane	5.28	596	−2.58	8.59	6.42	593	1.03	16.11
1-Methyl-1-cyclopentene	5.92	612	1.68	9.64	8.86	635	8.94	22.23
Methylcyclohexane	11.17	701	−1.88	18.20	13.69	691	0.75	34.36
1-Methyl-1-cyclohexene	13.50	727	3.78	22.00	20.51	744	10.19	51.47
4-Methyl-1-cyclohexene	12.36	715	2.09	20.14	19.68	739	9.49	49.39
Ethylcyclohexane	22.65	799	−2.16	36.90	29.32	791	0.75	73.58
1,3,5-Cycloheptatriene	19.06	775	18.58	31.04	44.12	834	28.54	110.72
1,3-Cyclooctadiene	32.06	846	8.46	52.22	50.72	864	15.02	127.32
1,5-Cyclooctadiene	42.18	884	13.79	68.73	105.66	963	28.91	265.19
Cyclooctatetraene	36.34	864	15.02	59.21	73.85	915	26.21	185.35
Benzene	10.41	668	17.60	14.83	26.81	726	25.74	46.91
Toluene	17.19	738	11.42	24.48	63.89	840	25.73	111.77
Ethylbenzene	45.46	871	10.02	64.14	123.51	929	26.16	216.09
o-Xylene	55.06	899	35.98	78.38	147.53	953	43.55	258.10
m-Xylene	48.53	881	33.45	69.08	157.13	962	44.81	274.90
p-Xylene	49.37	884	33.87	70.27	141.39	948	42.85	247.38
Styrene	59.39	910	25.51	84.55	180.75	980	35.33	316.22
Cumene	73.53	940	13.67	104.67	188.92	986	20.13	330.52
Propylbenzene	87.85	966	17.32	125.06	213.73	1003	22.51	373.93

31]. Nitroalkanes were characterised by high values of retention parameters and selectivity of the tested packings was lower than that shown in the case of hydrocarbons. However, it was possible to separate a mixture of four nitroalkanes (Fig. 4); the peaks were symmetric in spite of the long retention times.

Thermal analysis, performed for pure silica, packings with amino groups and packings with bonded complexes of Cu(II), show that the packings were stable at temperatures below 200°C. The amine-treated support, analyzed using the DSC method shows a characteristic peak at 250.6°C, which is

Table 5
Retention parameters for some nitroalkanes at 150°C

Solutes	Packing without metal				Packing with CuCl$_2$			
	k	I	ΔM_e	V_g	k	I	ΔM_e	V_g
Nitromethane	21.39	789	48.64	42.64	52.52	879	64.27	142.48
Nitroethane	31.58	834	44.92	62.99	65.67	909	54.45	178.15
1-Nitropropane	39.79	902	39.45	79.30	121.32	985	51.09	329.14
2-Nitropropane	34.91	852	36.64	75.58	109.65	973	49.40	297.48
1-Nitrobutane	92.08	1001	39.61	175.58	164.79	1091	51.93	618.38
2-Nitrobutane	78.12	972	38.32	157.14	147.39	981	48.53	571.14

Table 6
Retention parameters for ethers at 130°C

Solutes	Packing without metal				Packing with $CuCl_2$			
	k	I	ΔM_c	V_g	k	I	ΔM_c	V_g
Diethyl ether	4.91	574	8.41	5.39	53.1	809	41.37	7.90
Ethyl vinyl ether	4.18	548	6.78	4.58	–	–	–	–
Butyl methyl ether	10.07	698	11.77	11.04	96.3	902	40.39	14.32
tert.-Butyl ethyl ether	10.67	708	−0.85	11.69	102.15	912	27.76	15.19
Butyl vinyl ether	12.98	739	5.51	14.24	–	–	–	–
Dipropyl ether	13.45	745	4.34	14.74	120.81	940	31.69	17.97
Dibutyl ether	46.57	945	4.34	51.06	332.33	1099	25.94	59.43

ascribed to the effect of the siloxane layer melting [32,33]. The bonding of the metal with amine-treated support makes a new system of a higher thermal stability. The characteristic sharp peak at 330.2°C points to the high homogeneity of the system.

Elemental analysis of the packings showed that the surface concentration of the aminosilane is equal to 2.2 μmol/m^2 (calculated for nitrogen). This indicates that one atom of Cu(II) corresponds to approximately 2.8 atoms of nitrogen in the silane bonded to the silica surface, showing that Cu(II) is coordinated via one or two surface ligands (A and B in Fig. 1).

Similar conclusions were drawn by other authors [23,26] using photoacoustic spectroscopy and ESR. The Cu(II) ion is characterised by square planar and axial coordination bonds. Axial coordination of Cu(II) plays a very important role in the selectivity and ligand exchange [28,29]. Both complexes of Cu(II) with one amino ligand and those with two interact with electron donors; thus, they can be used in complexation gas chromatography. Therefore, aminated silica, modified by Cu(II) cations can be used in the separation of hydrocarbons, ethers and nitroalkanes.
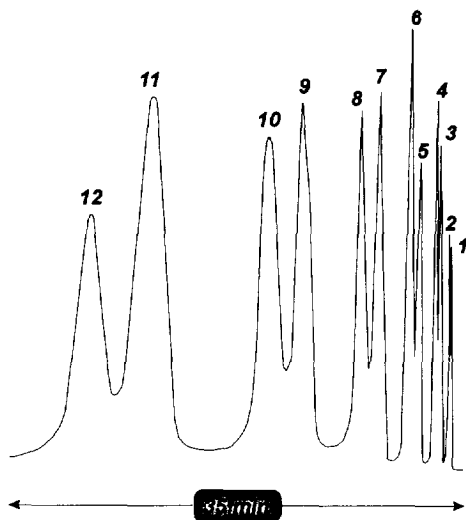

Fig. 2. Separation of mixture of alkanes and alkenes. Packing: with $CuCl_2$; column temperature: 150.9°C; argon carrier flow-rate: 21.4 ml/min. Peaks: 1=pentane; 2=pentene; 3=hexane; 4= hexene; 5=heptane; 6=heptene; 7=octane; 8=octene; 9=nonane; 10=nonene; 11=decane; 12=decene.

Fig. 3. Chromatogram of a mixture of aromatic hydrocarbons. Packing: as in Fig. 2. Column temperature: 150.2°C; argon carrier gas flow-rate: 20.7 ml/min. Peaks: 1=benzene; 2=toluene; 3= orto-xylene; 5=ethylbenzene; 6=propylbenzene.
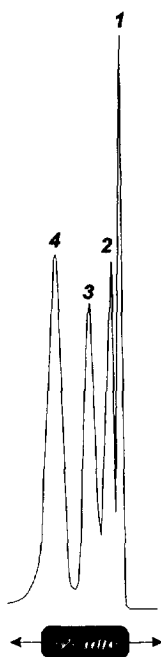
Fig. 4. Analysis of a mixture of nitroalkanes. Packing: as in Fig. 2. Column temperature: 150.8°C; argon carrier gas flow-rate: 22.7 ml/min. Peaks: 1=nitromethane; 2=nitroethane; 3=1-nitropropane; 4=2-nitropropane.

Acknowledgments

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