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## POLYCOMPLEXONATES OF METALS BASED ON VINYL PYRIDINE DERIVATIVES AS SELECTIVE SORBENTS FOR GAS CHROMATOGRAPHY

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### SUMMARY

Polycomplexonates of copper, mercury and silver based on vinyl derivatives of pyridine have been studied as potential selective sorbents for gas chromatography. The specificity of the sorbents and their high selectivity towards halogen-, sulphur- and nitrogen-containing compounds, aromatics and olefins have been evaluated. Recommendations are given for the practical usage of the polycomplexonates investigated in gas chromatography.

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### INTRODUCTION

The chemical modification of known polymeric sorbents and the use of macroporous ion-exchange resins has resulted in sorbents of higher selectivity for gas chromatography (GC)<sup>1-3</sup>. Metal polycomplexonates based on porous polymers possessing complexing power are of great interest from this standpoint. The use of different metal ions and porous polymeric matrices of different natures makes it possible to control, over a wide range, the chemical nature of the polymer surface and thereby to obtain selective sorbents capable of efficient separation.

### EXPERIMENTAL

The polycomplexonates of copper, silver and mercury were based on a pyridine-containing macroporous polymeric sorbent, namely, a copolymer of 2-methyl-5-vinylpyridine, divinylbenzene and glycidyl methacrylate (83:12:5, w/w/w). This copolymer is obtained by suspension copolymerization of the monomers in the presence of an inert solvent (grade PT-2 petrol).

The copolymer was treated first with a 5% solution of sodium hydroxide and then with a 5% solution of hydrochloric acid. To obtain the copper polycomplexonate, copper ions were sorbed from a methanol solution of copper(II) chloride under static conditions for 24 h, with periodic stirring. The sample saturated with copper ions was removed from the solution, washed with methanol and air-dried. To obtain the polycomplexonates of silver and mercury, silver and mercury(II) ions were sorbed from methanol solutions of the corresponding nitrate salts under static conditions

until a given degree of saturation was reached. The polycomplexonates obtained were removed from the solutions, washed with water and ethanol and then with a 5% solution of sodium chloride under dynamic conditions until free from nitrate ions. They were then washed with ethanol to remove the sodium chloride.

The following sorbents were investigated: sample 1, copolymer containing 83% of 2,5-methylvinylpyridine (2,5-MVP), 12% of divinylbenzene (DVB) and 5% glycidyl methacrylate (GMA); sample 2, copolymer of 83% 2,5-MVP, 12% DVB and 5% GMA, 100% saturated with  $\text{Cu}^{2+}$ ; sample 3, the same copolymer, 100% saturated with  $\text{Ag}^+$ ; sample 4, the same copolymer, 100% saturated with  $\text{Hg}^{2+}$ .

GC investigations were carried out on a Tsvet-132 gas chromatograph equipped with a thermal conductivity detector and  $1\text{ m} \times 3\text{ mm}$  I.D. columns, at  $150^\circ\text{C}$  and a carrier gas (helium) flow-rate of 30 ml/min. The columns packed with the sorbents were conditioned before experiments in a flow of helium at 150 and  $180^\circ\text{C}$  for 8 h.

The retention indices for various compounds were determined. The results obtained are presented in Tables I–IV and compared with the corresponding data for the 2,5-MVP, DVB and GMA copolymer.

## DISCUSSION

As is seen from Table I, the polycomplexonates of silver, mercury and copper exhibit higher selectivity towards unsaturated and aromatic compounds. The silver polycomplexonate is the most selective towards olefins: the difference in the retention indices for linear olefins and paraffins is 230–250 units, compared to 130–160 and 80–10 units in the cases of the mercury and copper polycomplexonates, respectively.

TABLE I  
RETENTION INDICES OF PARAFFIN, OLEFIN AND AROMATIC HYDROCARBONS

<i>Sorbate</i>	<i>Basic copolymer</i>	<i>Polycomplexonate</i>		
		<i>Copper</i>	<i>Mercury</i>	<i>Silver</i>
Pentane	500	500	500	500
2-Methylbutene-2	539	576	614	698
Methylbutadiene-1,3	566	600	603	644
Hexane	600	600	600	600
Hexene-1	624	678	730	830
2-Methylpentene-2	619	640	707	769
Cyclohexane	731	643	602	620
Cyclohexene	756	750	700	728
Benzene	826	875	942	693
Heptane	700	700	700	700
Heptene-1	732	780	842	954
2-Methylhexene-2	729	753	801	940
Toluene	948	996	956	872
Octane	800	800	800	800
Octene-1	840	900	965	1051
Ethylbenzene	1041	1036	993	1000
<i>p</i> -Xylol	1027	1039	973	988

For branched olefins the differences are less, namely 200–240 units on the silver polycomplexonate and 114–110 and 76–53 units on the mercury and copper polycomplexonates, respectively. Olefins with two double bonds are retained on the polycomplexonates of mercury and silver somewhat less strongly than olefins with one double bond.

The mercury polycomplexonate was the most selective towards aromatics, the difference in the retention indices for benzene and cyclohexane being 340 units, compared with 232 and 73 units on the copper and silver polycomplexonates, respectively.

The observed selectivity of these polycomplexonates with respect to olefins and aromatics is connected with the formation of complex compounds between the metal polycomplexonate and the organic substrates during GC which determine the order of elution of the substrates from the column. The heats of adsorption of a number of compounds (see Table II) on the silver polycomplexonate were determined gas chromatographically from the  $\lg V_R$  vs.  $1/T$  dependence. The values for olefins (cyclohexene, *n*-heptene) are much larger than those for paraffins (*n*-hexane, *n*-heptane). This can be explained by an additional contribution of the unsaturated compounds to the sorbate–sorbent intermolecular interaction.

The data listed in Table III reveal the high selectivity of the polycomplexonates investigated with respect to halogen-, sulphur- and nitrogen-containing compounds. For the polycomplexonates of copper, mercury and silver, the order of elution of chlorine-substituted derivatives of methane is  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , which differs from that observed on the basic sorbent and other polymeric sorbents without metal ions. This order of elution and the high retention indices of these compounds on the polycomplexonates testify to the formation of complex compounds in the process of GC separation. Further evidence in support of this is provided by the considerable retention of chlorobenzene as compared to benzene and ethylbenzene. The difference  $I_{\text{chlorobenzene}} - I_{\text{ethylbenzene}}$  is 120–200 units on the polycomplexonates investigated, indicating the stability of the complexes formed between the polycomplexonates and chlorobenzene.

The polycomplexonates, in particular that of mercury, exhibit high selectivity towards sulphur-containing compounds. This is likely to be connected with the formation of stable complexes due to charge transfer by displacement of *d*-electrons from the  $\text{Hg}^{2+}$  to a free orbital of sulphides.

The high selectivity of the copper polycomplexonate towards sulphur-containing compounds provides the uncommon ( $\text{SO}_2$  before  $\text{H}_2\text{S}$ ) order of elution in a GC

TABLE II

HEATS OF ADSORPTION,  $Q_{\text{ads}}$ , OF SOME COMPOUNDS ON SILVER POLYCOMPLEXONATE

<i>Sorbate</i>	$Q_{\text{ads}}$ (kcal/mol)
<i>n</i> -Hexane	6.3
<i>n</i> -Heptane	7.1
Benzene	9.0
Cyclohexane	8.6
Cyclohexene	9.8
Heptene-1	14.4

TABLE III

RETENTION INDICES OF SOME HALOGEN-, SULPHUR- AND NITROGEN-CONTAINING COMPOUNDS

<i>Sorbate</i>	<i>Basic copolymer</i>	<i>Polycomplexonate</i>		
		<i>Copper</i>	<i>Mercury</i>	<i>Silver</i>
Dichloromethane	778	1112	952	901
Chloroform	857	1000	917	814
Carbon tetrachloride	71	961	659	776
Chlorobenzene	1061	1181	1197	1121
Ethylbenzene	1041	1036	993	1009
Thiophene	865	1016	1118	946
Dimethyl sulphide	664	785	816	739
Diethyl sulphide	783	896	938	849
Tributylamine	1203	1600	1332	1358
Dibutylamine	1289	1600	1456	1476
Acetonitrile	792	1040	1065	843
Propionitrile	857	1112	1103	886
Butyronitrile	1019	1151	1152	992
Nitromethane	897	1066	1176	931

analysis of a mixture of air, sulphur dioxide and hydrogen sulphide (Fig. 1), as well as a greater retention of  $H_2S$  as compared with  $SO_2$ . For this reason the copper polycomplexonate can be used as a sorbent for concentrating trace amounts of hydrogen sulphide.

The very strong retention of amines by the polycomplexonates due to the formation of complexes with the coordinatively unsaturated metal ions allows these sorbents to be recommended for the removal of ammonia and amines from air, and in the elimination of amines.

Table IV presents the retention indices for a number of polar compounds on the polycomplexonates and on the basic copolymer. It is seen that the investigated sorbents possess high specificity of molecular interaction.

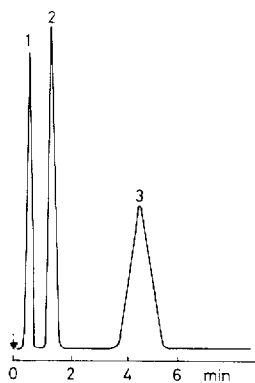


Fig. 1. Chromatogram of a mixture of air (1), sulphur dioxide (2) and hydrogen sulphide (3). Sorbent: copper polycomplexonate based on the copolymer of 2-methyl-5-vinylpyridine, divinylbenzene and glycidyl methacrylate. Column: 1 m  $\times$  3 mm I.D. Temperature: 140°C. Carrier gas (helium) flow-rate: 30 ml/min.

TABLE IV  
RETENTION INDICES FOR POLAR COMPOUNDS

<i>Sorbate</i>	<i>Basic copolymer</i>	<i>Polycomplexonates</i>		
		<i>Copper</i>	<i>Mercury</i>	<i>Silver</i>
Ethanol	803	934	1000	814
Benzene	826	875	942	693
Methyl ethyl ketone	795	930	1017	793
Dioxane	648	738	1003	925
Acetic acid	1600	1225	1352	1187
Water	779	1060	1127	804
Ethyl acetate	739	727	883	765

The results presented suggest a change in the nature of the intermolecular interaction in the sorbate-sorbent system on passing from a sorbent containing pyridine rings to sorbents containing silver, mercury and copper ions coordinated to the nitrogen atoms of pyridine rings. They also testify to the higher selectivity of the metal polycomplexonates and, therefore, to their higher specific interaction energy with molecules capable of donor-acceptor interactions. The sorbents investigated differ in their selectivities towards particular classes of compounds, which is connected with the type of metal linked to the polymeric matrix.

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