

Copper (II) Chelates of Tetradentate β -Ketomaines as Mixed Stationary Phases for Gas Chromatography

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Summary: Copper (II) chelates of tetradentate β -ketoamines bis(acetylacetonate) ethylenediimine (H_2AA_2en), bis (acetylacetonate)-propylenediimine (H_2AA_2Pr), bis(acetylacetonate) di-stilbenediimine (di- H_2AA_2S) and bis(acetylacetonate) meso-stilbenediimine (meso- H_2AA_2S) together with OV-101 have been examined as mixed stationary phase for gas chromatography (GC). The copper chelates (5%) and OV-101 (3%) were coated on Chromosorb G/NAW 60-80 mesh size. Thermoanalytical studies were carried out to ascertain the operating temperatures for stationary phases. The materials packed in stainless steel column s(3m x 3 mm i.d.) was examined for relative elution and separation of different organic compounds, including aliphatic hydrocarbons, aromatic hydrocarbons, heteroaromatic compounds, aldehydes, ketones and alcohols. The elution and resolution were compared with a column packed with OV-101 3% on Chromosorb G/NAW 60-80 mesh size. An increase in retention times, and kovats indices were observed with improvement in the resolution of alcohols, ketones and heteroaromatics on mixed stationary phases as compared to OV-101 using the same operating conditions. The mixed stationary phases OV-101, 3% with 5% AA_2enCu or di- AA_2SCu have high promise for the separation of alcohols, ketones, heteroaromatics.

Introduction

A number of attempts have been made to modify the stationary phases of gas chromatography (GC) with coordinatively unsaturated metal chelates. Some improvement in the column selectivity have been reported for electron donor compounds [1].

A number of metal chelates are used as GC phases including nickel, palladium, platinum chelates of N-dodecyl salicylaldimines; nickel, palladium and platinum complexes of n-octyl glyoximes [2]; beryllium, aluminum, nickel, and zinc complexes of n-nonyl- β -diketones [3],

transition metal phthalocyanine complexes in silicone oil [4], transition metals with 1,10-phenanthroline and 2,2'-bipyridines [5] nickel (II) bis(3-trifluoroacetyl) 1R camphorate in squalane; nickel (II) bis (α -heptafluorobutyryl) terpeneketonates in squalane [6], molybdenum (VI) (oxo-diperoxo) complexes [7], triphenylphosphine complexes of rhodium (I) and ruthenium(II) [8] and copper, nickel complexes of Schiff bases in squalane [9,10].

Wasiak has examined chemically bonded copper (II) and nickel complexes as selective complexing sorbent for GC [11-13] and Wasiak and Szczepaniak [14] have examined high temperature treated chemically bonded metallo-phenylsiloxane for complexation GC.

In the recent years, nickel (II) chelates of bis (acetylacetonate)ethylenediimine (H_2AA_2en), bis (acetylacetonate)propylenediimine H_2AA_2Pn , bis (acetylacetonate) dl-stilbenediimine (dl- H_2AA_2S) and bis (acetylacetonate) meso-stilbenediimine (meso- H_2AA_2S) individually and together with OV-101 have been examined as stationary phases for GC [15]. In the present work the copper (II) chelates of H_2AA_2en , H_2AA_2pn dl- H_2AA_2S and meso- H_2AA_2S with OV-101 have been examined as mixed stationary phases for the separation of hydrocarbons, alcohols, aldehydes, ketones and heteroaromatics.

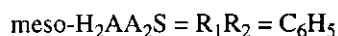
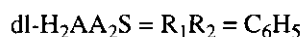
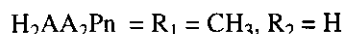
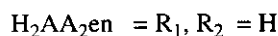
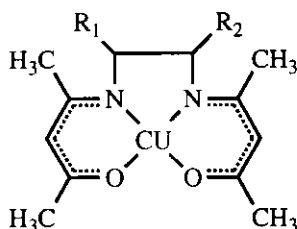


Fig. 1: Structural diagram of Metal Chelates.

Results and Discussion

DTA and TG of the GC column packing materials were recorded to evaluate the maximum operating temperatures. In case of AA_2enCu , dl- AA_2SCu and meso- AA_2SCu loss in weight started at 180°C, 220°C, and 220°C respectively and loss of 5% owing to metal chelates occurred at 390°C, 390°C and 350°C respectively. This was followed by 3% loss corresponding to OV-101 upto 450°C (Fig. 2).

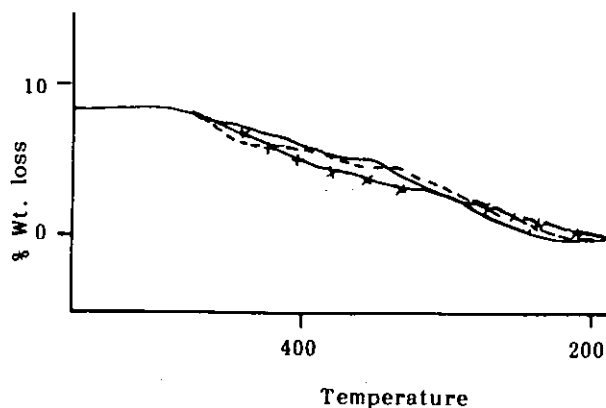


Fig. 2: TG AA_2enCu 5% + OV-101 3%, meso AA_2SCu 5% + OV-101 3% ----- dl- AA_2SCu 5% + OV-101 3% ----- on Chromsorb G/NAW 60-80 mesh size. Heating rate 10°C/min and nitrogen flow rate of 45 ml/min.

Each of the column was injected 10-20 times different compounds, before their analytical responses were measured. The elution of different saturated and aromatic hydrocarbons, heteroaromatic, aldehydes, ketones, and alcohols was examined on these columns. The retention times, theoretical plates and capacity factors were calculated. It was observed that their retention times and theoretical plates on mixed stationary phases increase as compared to OV-101, 3% (Table-1). The relative retention time increases on mixed stationary phase column OV-101 3% + 5% dl- AA_2SCu for saturated hydrocarbons, aromatic hydrocarbons, heteroaromatics, aldehydes, ketones and alcohols. They were higher in the range of 2-6%, 42-51%, 8.0-13.5%, 28-35%, 41-46% and 34-43% as compared to OV-101, 3%. Theoretical plates for hexanol on OV-101, 3% column observed as 600

Table-1: Total number of theoretical plates on each phase packed in column (3m x 3mm ID) experiment conditions are as described under experimental.

S.No.	Compound	3% OV-101	5% AA ₂ PnCu +3% OV-101	5% AA ₂ enCu +3% OV-101	3% meso- AA ₂ SCu +3% OV-101	5% dl-AA ₂ SCu +3% OV-101
1.	Pentanol	437	1270	1465	1503	1751
2.	Hexanol	601	2668	3136	3265	3738
3.	Pyridine	417	746	1024	940	935
4.	2-Picoline	655	875	1296	1158	1094
5.	3-Picoline	676	1015	1451	1388	1336
6.	2,6-dimethyl- pyridine	690	1362	1991	1960	1885
7.	Toluene	661	1008	1089	1024	1201
8.	MIBK	846	956	1542	1354	1111
9.	3,3-Dimethyl-2- butanone	1156	1366	2025	1788	1521
10.	Paraldehyde	595	1085	1209	1230	1296
11.	Cyclohexanone	876	1252	1637	1530	1528

increased to 3740 on OV-101, 3% + 5% dl-AA₂SCu using same operating conditions. A straight line correlation was obtained, on calculating log of adjusted retention time of straight chain hydrocarbon from C7 to C11 with *n*-hexane, was plotted against hundred times the carbon number (Fig. 3). The graphs were used to calculate relative retention or kovats indices. Table 2 shows that kovats indices of alcohols, aromatic, hydrocarbons, aldehyde, ketones and amines on the mixed stationary phases increase as compared to OV-101, 3%. The maximum kovats indices were

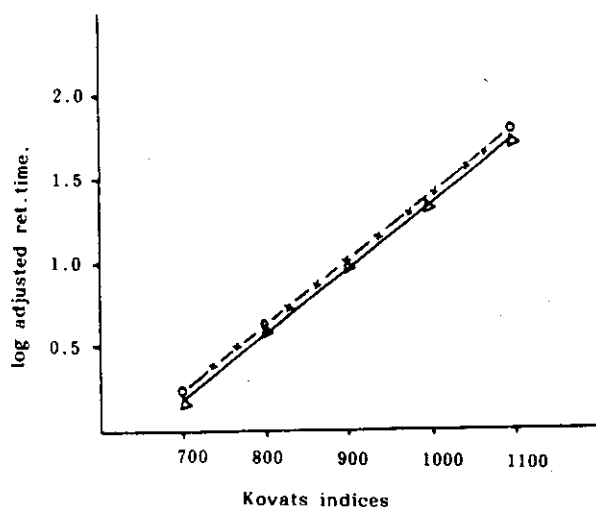


Fig. 3: Variation of log adjusted retention time with kovats indices OV-101 3%, O-x-x-O dl-AA₂SCu 5% + OV-101 3% on Chromosorb G/NAW 60-80 mesh size. Column (3 mx 3 mm i.d.) temperature column 80°C and injection port 100°C, nitrogen flow rate 12 ml/min.

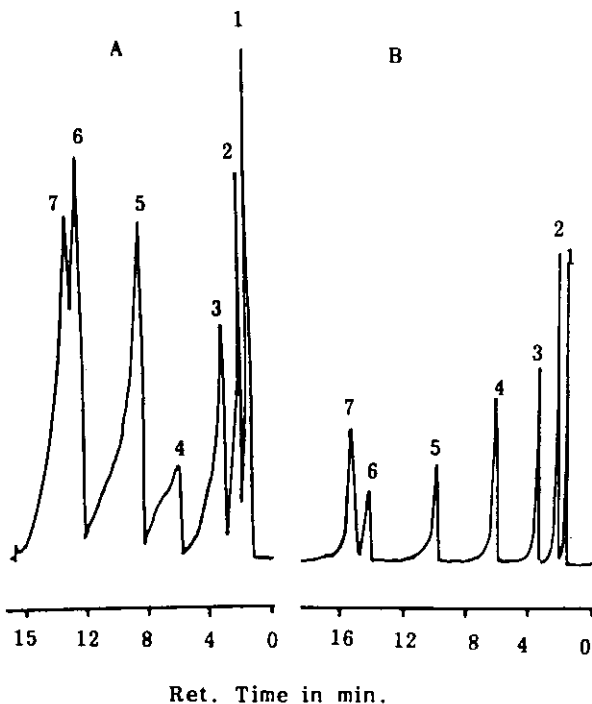


Fig. 4: Separation of alcohols (1) Ethanol 2) 1-propanol 3) 1-butanol 4) 1-pentanol 5) 1-hexanol 6) 1-heptanol (7) octan-2-ol. Column (3 m x 3 mm i.d) packed with A) OV-101 3% B) dl-AA₂SCu 5% + OV-101 3% on Chromosorb G/NAW 60-80 mesh size. Column temp. 80°C for 4.80 min. followed by programmed heating rate 4°C/min upto 120°C/injection port 130°C, nitrogen flow rate 12 ml/min. Detection FID.

observed on 3% OV-101 + 5% dl-AA₂SCu on Chromosorb G/NAW 60-80 mesh size. Kovates indices of hexanol were observed 915 on 3% OV-101 + 5% dl-AA₂SCu as compared to 870 on OV-101, 3%. It is also observed that alcohols showed pronounced peak tailing on the column 3% OV-101, however, their peak shape improved substantially using mixed stationary phases. The resolution factor (*R_s*), between pentanol and hexanol calculated on (1) 3% OV-101 was 0.96, which improved on mixed stationary phases (2) 3% OV-101 + 5% AA₂enCu (3) 3% OV-101 + 5% meso-AA₂SCu and (4) 3% OV-101 + 5% dl-AA₂SCu to 3.16, 3.08 and 3.33 respectively (Fig. 4). The Resolution factor (*R_s*) between 3-

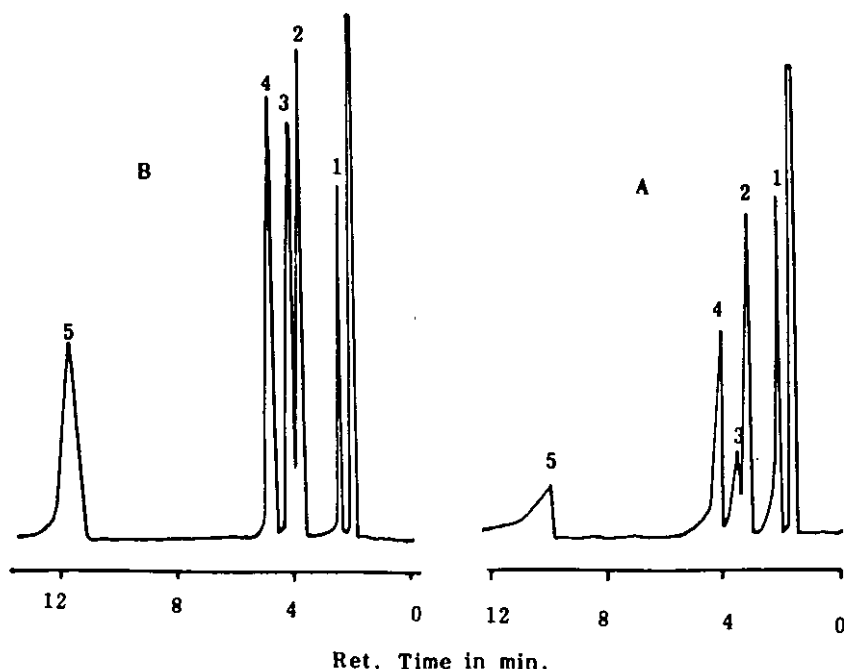


Fig. 5: Separation of ketones 1) 2-butanone 2) 3-pentanone 3) 3,3-dimethyl-2-butanone 4) 4-Methyl-2-pentanone 5) cyclohexanone. Column (3 m x 3 mm id) packed with A) OV-101 3% b) AA₂SenCu 5% + OV-101. Column temp. 80°C, injection port 100°C, nitrogen flow rate 12 ml/min. Detection FID.

Table-2: Comparison of kovats indices observed on different stationary phase packed in column (3m x 3mm x 1.D). Experiment conditions are as described under experimental.

S.No.	Compound	3% OV-101	5% AA ₂ PnCu +3% OV-101	5% AA ₂ enCu +3% OV-101	3% meso- AA ₂ SCu +3% OV-101	5% dl-AA ₂ SCu +3% OV-101
1	Toluene	745	766	780	783	785
2	O-xylene	870	880	892	903	903
3	P-Xylene	844	850	876	882	885
4	Aniline	940	955	993	981	1000
5	Benzaldehyde	926	929	938	954	959
6	Paraldehyde	755	757	769	775	785
7	Pentanol	770	785	798	795	814
8	Hexanol	875	882	891	900	915
9	Heptanol	970	978	985	990	1008
10	Octanol	990	991	1002	1010	1020
11	Pyridine	725	728	738	735	734
12	2-Picoline	795	800	816	810	805
13	3-Picoline	820	826	856	854	848
14	2,6-dimethyl- pyridine	855	859	872	870	866
15	Cyclohexanone	870	882	896	895	894
16	MBK	710	720	738	730	735

Pentanone and 3,3-dimethylbutane observed on column (1) 0.98 improve to 1.30, 1.28 and 1.27 on column 2, 3 and 4 respectively (Fig. 5) with a significant improvement in the peak shape of the compounds. Cyclohexanone indicated a pronounced peak tailing with theoretical of 876 on OV-101, 3%, column, however a better elution

with theoretical plates of 1637 was observed on OV-101, 3% + 5% AA₂enCu. Similarly, the Rs calculated between o-xylene and p-xylene on column 1,2,3 and 4 was 1.52, 1.68, 1.62 and 1.64 respectively.

On separating hetro-aromatic compounds pyridine, 2-picoline, 3-picoline and 2,6-dimethylpyridine on the columns, 3-picoline and 2,6-dimethylpyridine co-eluted on the column (1), however the separation was improved on mixed stationary phases (Fig. 6). In conclusion the improvement achieved on mixed stationary phases is attributed to selective adsorption due to donor acceptor complexation.

Experimental

All the reagents H₂AA₂en, H₂AA₂Pn, dl-H₂AA₂S and meso-H₂AA₂S and their copper chelates were prepared as previously reported [16,17] Fig. 1).

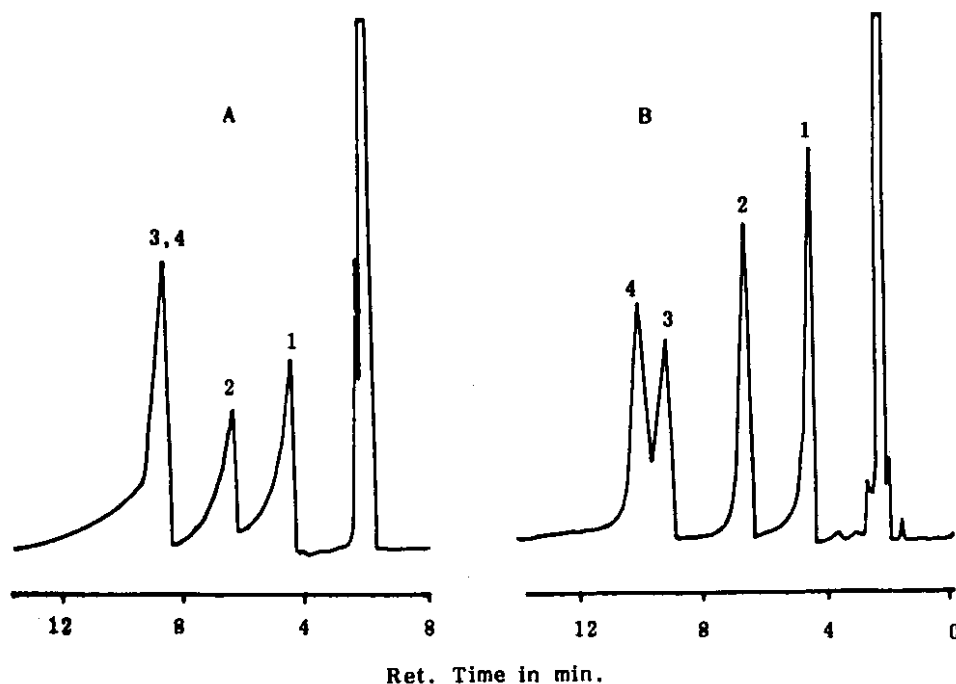


Fig. 6: Separation of 1) Pyridine 2) 2-picoline 3) 3-picoline 4) 2,6-dimethylpyridine. Conditions same as Fig. 5.

Preparation of stationary phase for GC

The copper(II) complexes of H_2AA_2en , H_2AA_2Pn , $dl-H_2AA_2S$ or $meso-H_2AA_2S$ (0.70 g) dissolved in chloroform (10 ml) and OV-101 (BDH, England) (0.42 g) dissolved in chloroform (15 ml) were mixed together. The solution was added to Chromosorb G/NAW 60-80 mesh size (14.0 g) with constant shaking. The solvent from the well mixed contents was removed on rotavapor at $60^\circ C$. The dried material were packed in stainless steel column (3m x 3mm id) following usual procedure [18]. The column was coiled and attached with injection port of GC and were conditioned by programmed heating rate of $1^\circ C/min$ from ambient temperature to $150^\circ C$ and maintained at this temperature for 24 hours.

A column packed with OV-101, 3% on Chromosorb G/NAW 60-80 mesh size was also prepared following the above procedure, except the addition of copper chelate was omitted.

Hitachi 163 gas chromatograph connected with FID detection system and recorder 056 was used.

Thermogravimetry (TG) and differential thermal analysis (DTA) of the GC packing material was recorded on Shimadzu TG30 Thermal analyzer from room temperature to $500^\circ C$ at a heating rate of $10^\circ C/min$ and nitrogen flow rate of 45 ml/min.

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