CHAPTER - IV

CUPROUS SALTS IN GAS-LIQUID CHROMATOGRAPHY

CONTENTS

ABSTRACT

The effect of cuprous halides on the resolution of olefinic mixtures in gas-liquid chromatography has been investigated. It has been shown that impregnation of a polyester stationary phase with cuprous halides provides an effective column for the resolution of higher boiling olefinic mixtures eg:- terpenes.

A. INTRODUCTION

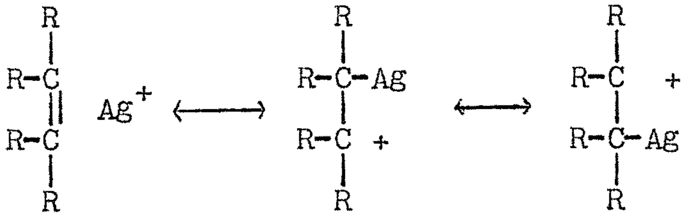
Gas-liquid chromatography, after the first rudimentary application by Brunschwig and subsequent enunciation of the guiding principles by Martin and Synge has in the last forty years grown to become an indispensible tool in analytical chemistry[1]. It has also been used on a preparative scale through it becomes inconvenient for large quantities. A tube packed with an inert powder(the support) coated on the surface with a film of a non-volatile liquid(the stationary phase) constitutes the chromatographic column. The dimensions of the tube may range from 2 to 30 mm in diameter and 1 to 20 m in length and is usually made of glass, copper or aluminium. The vapourized sample is carried by an inert gas(carrier gas) through the column and separation of its constituents is achieved by virtue of a competitive partition of the sample between the moving carrier gas and the stationary liquid phase. This technique makes use of the fact that when two or more components are present in the sample each usually behaves independantly of the other so that for a given carrier gas flow rate the speed of each component through the column will depend on the extent of its interaction with the stationary phase.

Various stationary phases have been employed to effect the separation of a variety of classes of organic compounds. The separation of olefinic mixtures may also be achieved by this approach though often the results are not satisfactory[2]. This is particularly true in the case of a mixture of isomers, geometric or structural. In this connection modified stationary phases have been used to enhance the resolution. Modification usually involves the impregnation of the stationary phase with metal ions known to form loose complexes with olefins[3].

(I) Separation of olefins by metal ion impregnated stationary phases:

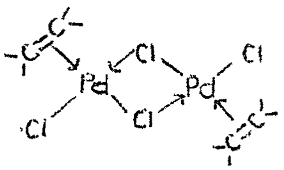
The separation of olefins by gas-liquid chromatography with the use of modified liquid phases which form loose complexes with the components of the sample has not received much attention. The earliest and to date the most widely exploited columns of this type contain stationary phases incorporated with silver nitrate[4]. Silver nitrate dissolved in a non-volatile polar substrate usually ethylene glycol, propylene glycol or benzyl cyanide[4,5,6] constitutes a stationary phase specific for olefins[7]. More recently a variety of thermally stable aromatic nitriles have been used as solvent[8].

The use of silver nitrate in the separation of olefins in column[9], paper[10] and thin layer[11] chromatography is well-known. The specificity of the silver(I) ion for olefins is due to its electronic configuration ($4d^{10}$, $5S^{0}$). The silver(I) ion forms a complex with the olefin where the electron density is transferred from the π-orbital of the olefin to the empty 5S orbital of Ag(I) and also a back bonding where the filled 4d orbital of the Ag(I) overlaps with the empty antibonding π-orbital of the olefin[12]. This can be represented as a resonance hybrid.



The complex-formation is a reversible process the strength of the complex being dependent on the nature of olefin[13]. In chromatographing mixed hydrocarbons the unsaturated hydrocarbons are adsorbed on these columns while non-olefinic compounds behave as if the silver nitrate were not there. Acetylenic compounds are strongly adsorbed whereas ethylenic compounds are less strongly adsorbed[14]. The strength of Ag(I)-olefin complex and consequently the retention of olefin on the column being dependent on the steric environment of the unsaturated site these columns have been used to assign the stereochemistry in some cases[15]. The underlying principle here is that the more hindered olefin is less strongly retained on the column and consequently eluted faster than the less hindered one. Siler trifluoromethane sulphonate may also be used in place of silver nitrate[16].

Though the use of Ag(I) incorporated columns has been particularly effective in the separation of olefins in g.l.c it is severely handicapped by the fact that these columns must invariably be operated at temperatures below 65° and preferably below 40°[6]. They cannot be exploited for mixtures of higher boiling olefins such as terpenes[2] as the solutions of silver nitrate in stationary phase are unstable at higher temperatures. Other metal ions known to form complex with olefins, particularly those of the platinum group have been studied. The results, with the exception of thallium, were not very promising[17,18]. Thallium nitrate dissolved in ethylene glycol has successfully been used as stationary phase in the separation of β-pinene and sabinene[19]. Though initial results were not encouraging Kraitr and coworkers succeeded in using solutions of $PdCl_2$ in N-methyl acetamide(NMA) as a stationary phase for lower boiling monoalkenes[20]. These columns were used to separate a mixture of hexene isomers at an optimum operation temperature of 30°. While for monoalkene--Ag(I) complexes a metal to alkene ratio of [1:1] is generally anticipated, the authors found that the whole molecule of $PdCl_2$ took part in forming the complex with olefin and the ratio was also [1:1][20c]. These complexes were found to be of a relatively higher stability than the corresponding ones of Ag(I) and have a dimeric structure.



The decrease of π-complex stability due to steric hindrance around the C=C was found to be more significant with the alkene-$PdCl_2$ complexes than with similar complexes of Ag(I). These columns also cannot be used at temperatures above 50° due to the irreversible formation of π-allyl complexes of the general formula $[PdCl(CnH_{2n-1})]_2$ with olefins at higher temperatures.

A number of dicarbonyl-Rh(I)-β-diketonates which show marked selectivity in their interaction with olefins have been incorporated in the stationary phase (Squalene) to effect the separation of C_2-C_6 alkenes and some cyclic olefins[29]. These columns have been operated upto 50°. The Rhodium(I)-olefin complexes are characterized by the following features:-

(i) In common with Ag(I), Rh(I) shows higher interaction with the *cis*- than with the *trans*- isomer though Rh(I) forms stronger complexes than Ag(I).

(ii) Substitutions at the double bond considerably decreases the interaction with Rh(I). The reduction is far greater than that of Ag(I).

(iii) The chain length of normal chain-1-olefins ($RCH=CH_2$) does not have much effect on the Rh(I)-olefin complex while chain branching decreases complexation.

(iv) With cyclic olefins the extent of interaction with Rh(I) is strongly dependent on ring size.

(II) Summary:-

Though metal ion impregnated columns have been used for the gas-liquid chromatography of olefins their utility is restricted to the lower boiling olefin mixtures and cannot be used for higher boiling olefins such as terpenes. Need for improved resolution of terpene mixtures is acutely felt in view of the large number of isomers possible within each group and the known propensity of terpenes to occur along with their isomeric counterparts in nature[2].

B. Use of cuprous salts

The copper(I) ion which has an electronic configuration($3d^{10},4s^{0}$) similar to that of Ag(I) is also known to form loose π-complexes with olefins[21,22]. An industrial method for the separation of olefins uses the differing stabilities of their cuprous chloride complexes[23]. The formation of these complexes is reversible and the olefins are not chemically affected. Thus it was envisaged that analogous to Ag(I), Cu(I) could also be used to enhance the separation of olefins in g.l.c. and the present study was undertaken to verify this.

Preliminary investigations with 12′ columns prepared by the incorporation of some 10 percent CuCl in diethylene glycol succinate(DEGS) as stationary phase(10 percent) gave a much improved resolution of some two component olefin mixtures[24]. Moreover these columns could be operated at temperatures upto 190° without detriment. Table-I gives a comparison of retention times(RT) of some olefins on DEGS(diethylene glycol succinate) and DEGS-CuCl columns operated under exactly identical conditions. As can be seen RT for a given olefin is higher on the DEGS-CuCl column suggesting some sort of an interaction with CuCl, presumbaly π-complexation. Table-2 summarizes the resolution data[25] for the two columns for a number of two component pairs; better performance of DEGS-CuCl is clearly evident for most of the pairs(see also Fig.1 to 4).

TABLE- I

GLC[a] Retention time (RT) of some compounds on DEGS and DEGS-CuCl columns

No	Compound	RT[b] (minutes)		ΔRT
		DEGS	DEGS-CuCl	
1	Methylcyclopentene	0.28	0.39	0.11
2	Cyclohexene	0.39	0.51	0.12
3	α-Pinene	1.50	2.05	0.55
4	Camphene	2.01	2.83	0.82
5	β-Pinene	2.52	3.54	1.02
6	Car-3-ene	3.23	4.57	1.34
7	Myrcene	3.94	5.20	1.26
8	Terpinolene	7.40	10.24	2.84
9	*p*-Cymene	7.40	10.87	3.47

[a] GLC conditions: Al columns, 360 cm x 0.6 cm; support, 60-80 mesh Chromosorb W; stationary phase, 10% DEGS/10% DEGS + 1% CuCl; carrier gas, H_2, 60 ml/min; temp., 80°; instrument, Hewlett-Packard 7624A.

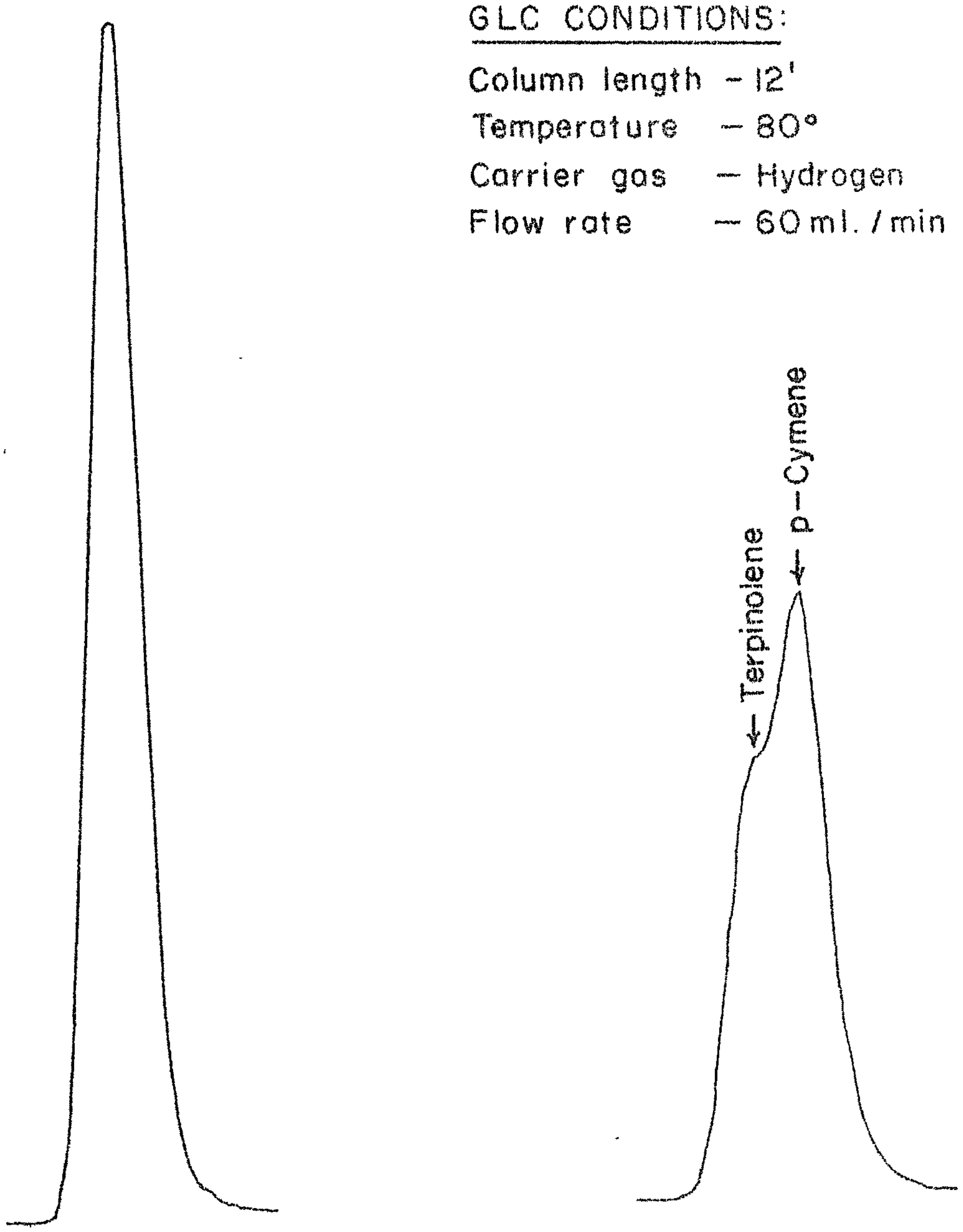
[b] Relative to air peak, measured in minutes from peak maxima.

TABLE - II

Relative performance of DEGS and DEGS-CuCl columns in the GLC resolution of some two-component mixtures.

No.	Components		Column temp. [°C]	R_s [a] (Peak resolution)	
	A	B		DEGS	DEGS-CuCl
1	Methylcyclopentene	Cyclohexene	80	0.40	0.46
2	α-Pinene	Camphene	80	1.08	1.43
3	α-Pinene	β-Pinene	80	1.92	2.17
4	β-Pinene	Car-3-ene	80	1.24	1.37
5	Car-3-ene	Myrcene	80	1.37	0,95
6	Terpinolene	*p*-Cymene	80	0	0.37
7	Isolongifolene	Longifolene	140	0.87	1.25
8	*cis*-ψ-Ionone	*trans*-ψ-Ionone	170	2.58	2.90
9	*cis*-Geranylacetone	*trans*-Geranylacetone	170	0.46	0.50
10	Methyl stearate	Methyl oleate	190	0.64	1.16

a) Peak resolution was calculated by the formula $R_s = 2\,\frac{t_2 - t_1}{w_1 + w_2}$

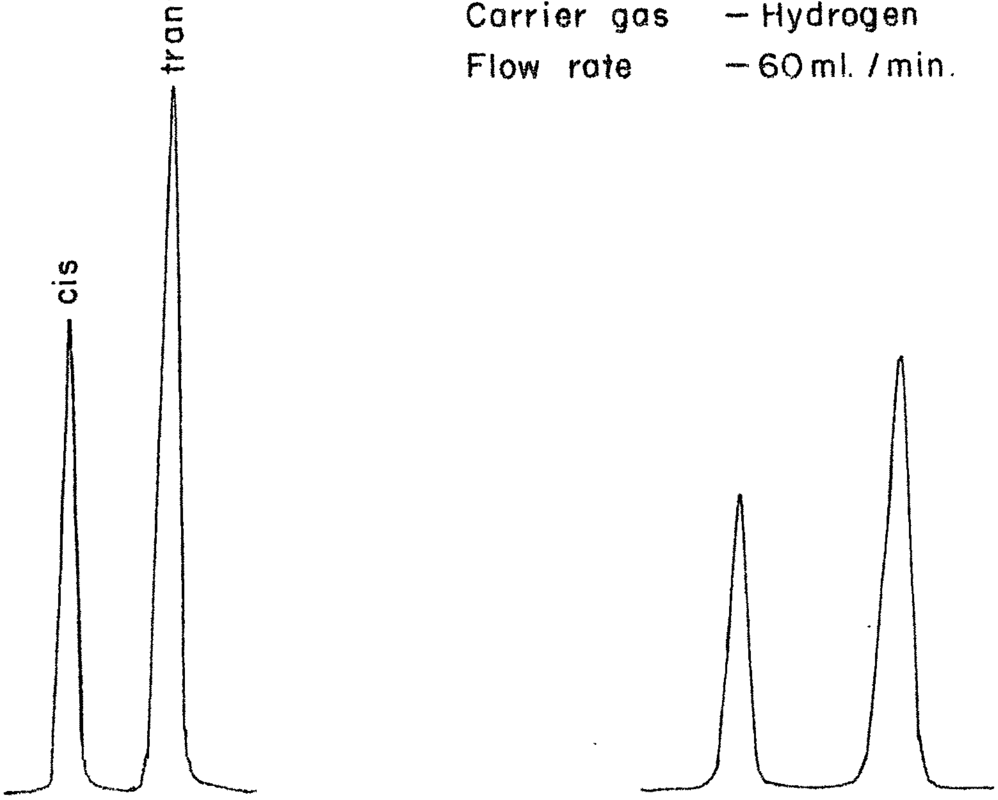


GLC CONDITIONS:

Column length – 12'
Temperature – 80°
Carrier gas – Hydrogen
Flow rate – 60 ml./min

a) 10% DEGS Column　　b) 10 % DEGS – CuCl Column

FIG.1.
RESOLUTION OF A MIXTURE OF p–CYMENE & TERPINOLENE



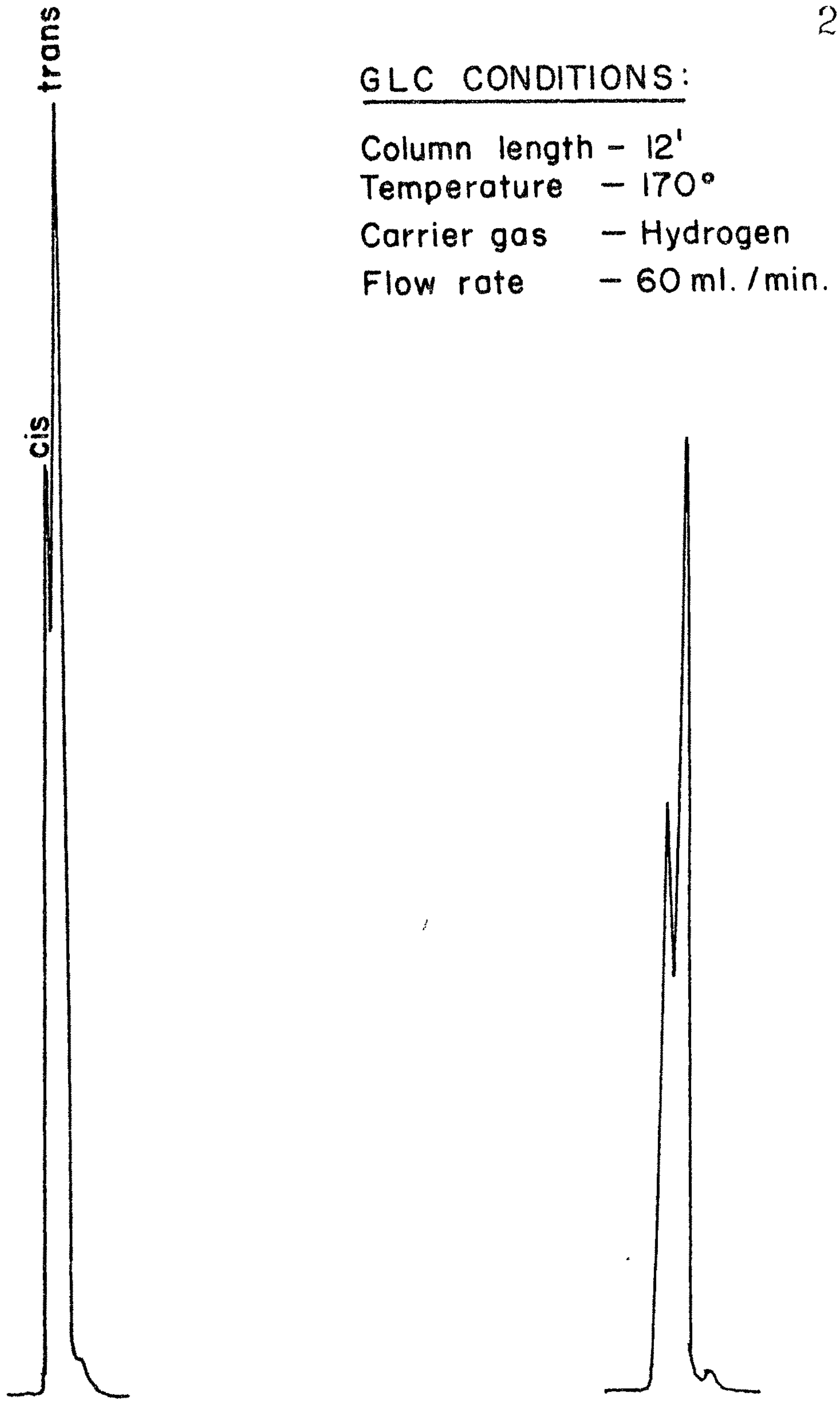
GLC CONDITIONS :

Column length – 12'
Temperature – 170°
Carrier gas – Hydrogen
Flow rate – 60 ml. / min.

a) 10% DEGS Column

b) 10% DEGS–CuCl Column

FIG. 2.
RESOLUTION OF cis AND trans ψ – IONONE



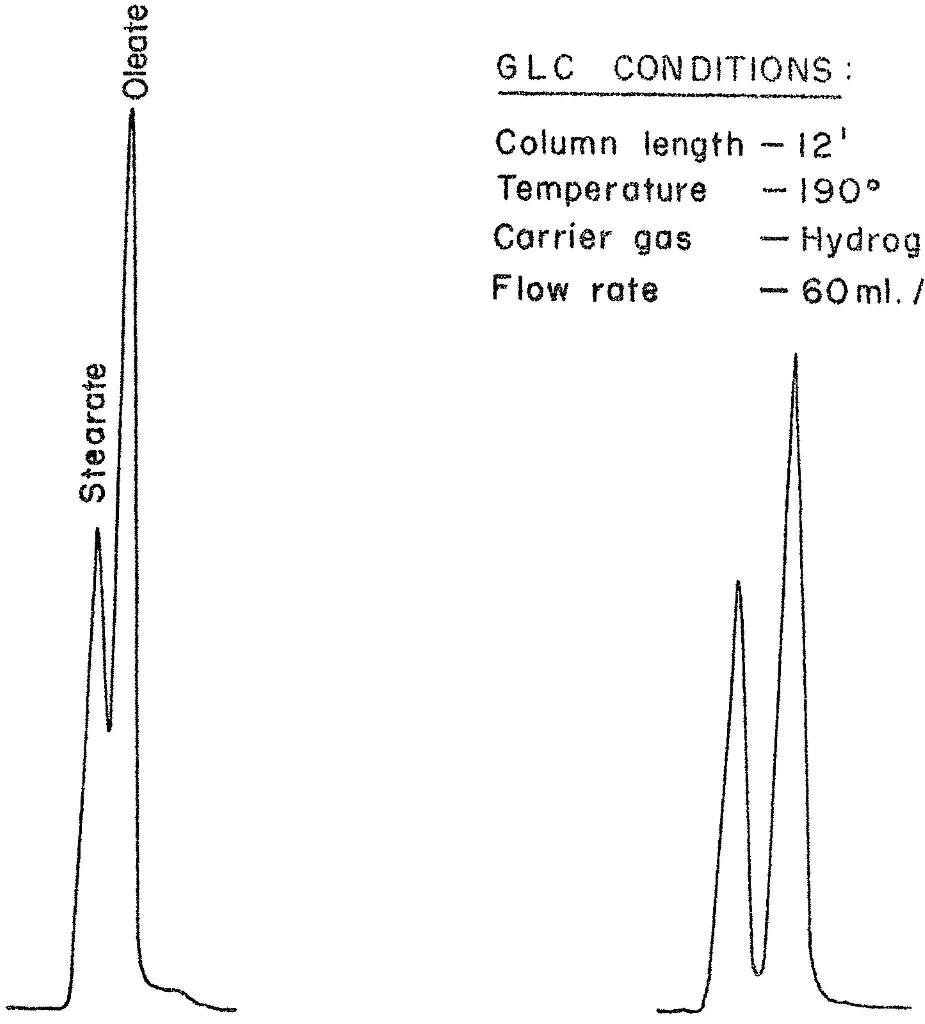
GLC CONDITIONS:

Column length - 12'
Temperature - 170°
Carrier gas - Hydrogen
Flow rate - 60 ml./min.

a) 10 % DEGS Column

b) 10 % DEGS-CuCl Column

FIG. 3.
RESOLUTION OF *cis* AND *trans* GERANYL ACETONE



GLC CONDITIONS:

Column length — 12'
Temperature — 190°
Carrier gas — Hydrogen
Flow rate — 60 ml./min.

a) 10% DEGS Column b) 10% DEGS-CuCl Column

FIG.4.
RESOLUTION OF A MIXTURE OF METHYL STEARATE & METHYL OLEATE

(i) Effect of counter ion

As a sequel to the above investigations a comparative study with other cuprous halides viz: CuBr and CuI was undertaken. For the purpose of these studies 10' columns were employed. Separate columns were prepared by the incorporation of 0.01 mole % (w.r.t. the solid support) on DEGS (10 percent) and the resolution of some olefin mixtures was studied. Of the three cuprous halides, CuBr gave the best results in terms of resolution of the olefin mixtures (Table-3, Fig. 5 to 8). This is particularly emphasized in the case of the methyl stearate, methyl oleate mixture (Fig-8). Table-4 gives a comparison of the retention times (RT) for the individual components of the mixtures. It can be seen that the retention time for most olefins is longest on the DEGS-CuBr column suggesting that the olefin-CuX interaction is maximum with CuBr.

TABLE—3.

Relative performance of 10' DEGS and DEGS – CuX Columns in the GLC resolution of some two component mixtures (a)

No	COMPONENTS		Col. Temp °C°	Rs (resolution) in 10' columns of 10 % DEGS contg 0·01 mole % CuX			
	A	B		DEGS	DEGS-CuCl	DEGS-CuBr	DEGS-CuI
1	β – Pinene	Δ^3 – Carene	80	0·6110	1·015	1·030	0·9706
2	cis-Geranyl acetone	trans-Geranyl acetone	140	slight shoulder	0·5516	0·6372	0·5714
3	Longifolene	Isolongifolene	140	0·500	1·000	1·0135	1·000
4	Methyl stearate	Methyl oleate	170	0·0	0·6896	1·0660	0·6489

a) GLC CONDITIONS: Al columns, 300 cm. X 0·6 cm., Support 60–80 mesh Chromosorb W, Stationary phase 10% DEGS / 10% DEGS + 0·01 mole % CuX, Carrier gas 60 ml. / min.

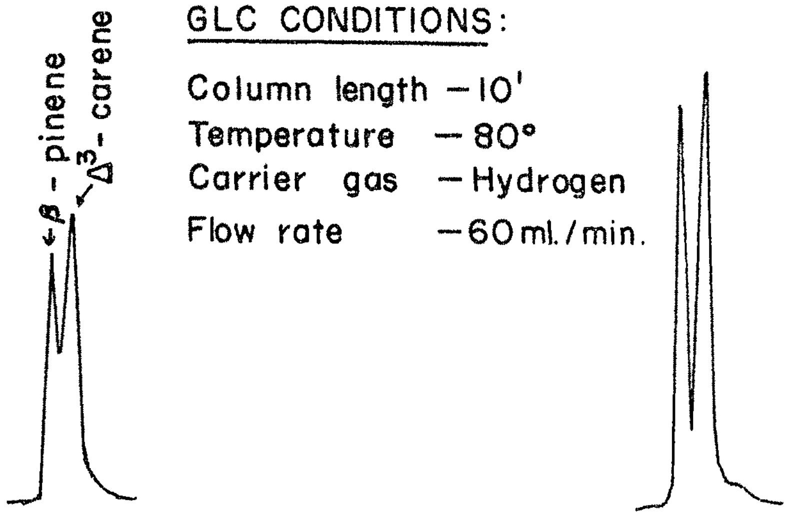
TABLE–4.

GLC[a)] Retention times (RT) of the individual components of the different columns of 10' length

No.	Compound	Col. Temp. °C	Retention time (RT) in minutes b)			
			DEGS	DEGS-CuCl	DEGS-CuBr	DEGS-CuI
1	β - Pinene	80	1·60	2·02	2·66	2·36
2	Δ^3 - Carene	80	2·04	2·56	3·40	2·94
3	Isolongifolene	140	1·34	1·80	2·72	2·48
4	Longifolene	140	1·60	2·20	3·30	2·98
5	cis - Geranylacetone	140	5·7 to 6·0	7·68	12·16	10·40
6	trans - Geranylacetone	140	6 00	8·40	13·20	11·40
7	Methyl stearate	170	10·40	14·24	18·40	19·02
8	Methyl oleate	170	10·40	15·60	20·80	21·04

a) GLC CONDITIONS: Al columns, 300cm. X 0·6cm., Support 60-80 mesh Chromosorb W, Stationary phase 10% DEGS / 10% DEGS + 0·01 mole % CuX, Carrier gas 60 ml. / min.

b) Relative to air peak, measured in min. from peak maxima.

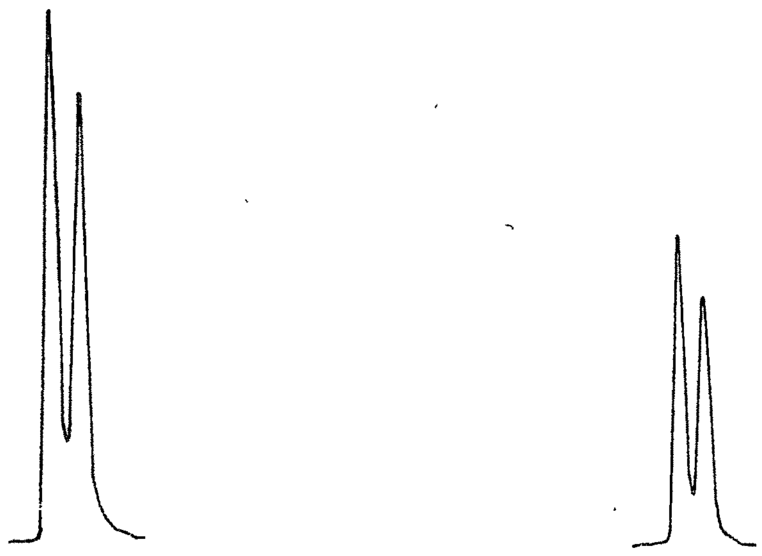


GLC CONDITIONS:

Column length – 10'
Temperature – 80°
Carrier gas – Hydrogen
Flow rate – 60 ml./min.

a) 10% DEGS Column

b) 10% DEGS-0·01 mole % CuCl Column



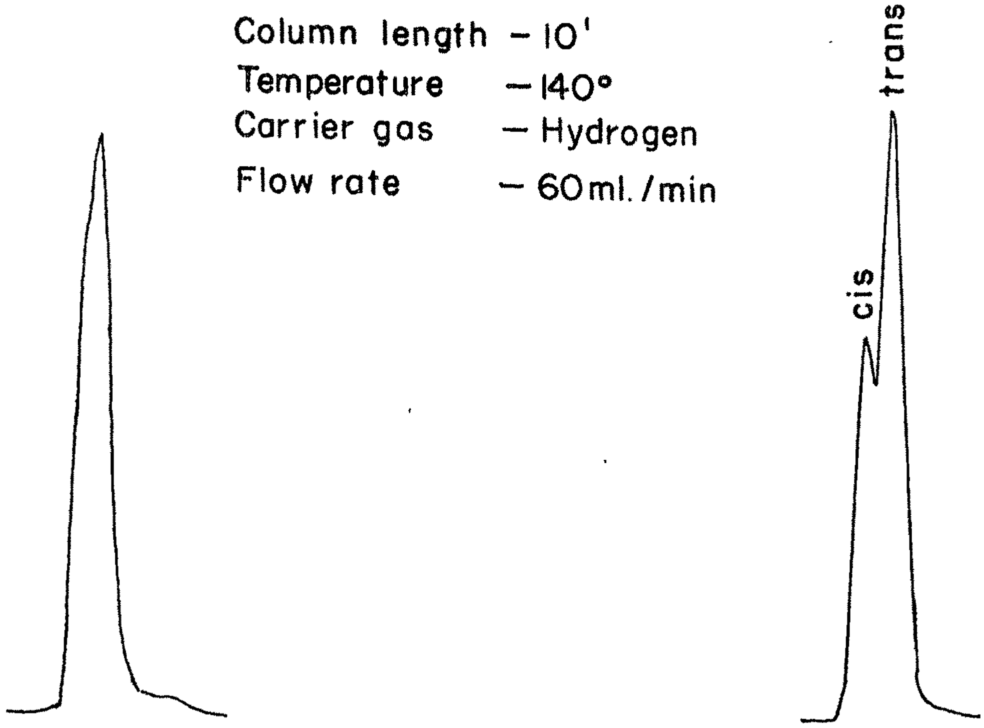
c) 10% DEGS-0·01 mole % CuBr Column

d) 10% DEGS-0·01 mole % CuI Column

FIG.5.
RESOLUTION OF β-PINENE AND Δ^3 - CARENE

GLC CONDITIONS:

Column length - 10'
Temperature - 140°
Carrier gas - Hydrogen
Flow rate - 60 ml./min



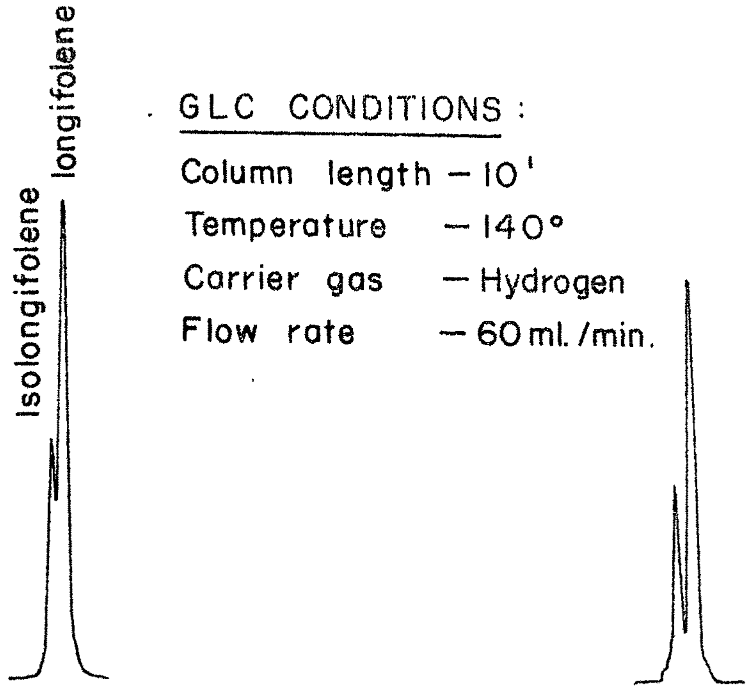
a) 10% DEGS Column

b) 10% DEGS-0·01 mole % CuCl Column

c) 10% DEGS-0·01 mole % CuBr Column

d) 10% DEGS-0·01 mole % CuI Column

FIG.6.
RESOLUTION OF cis AND trans GERANYL ACETONE



GLC CONDITIONS :

Column length – 10'
Temperature – 140°
Carrier gas – Hydrogen
Flow rate – 60 ml./min.

a) 10% DEGS Column

b) 10% DEGS-0·01 mole % CuCl Column

c) 10% DEGS-0·01 mole % CuBr Column

d) 10% DEGS-0·01 mole % CuI Column

FIG.7.
RESOLUTION OF LONGIFOLENE + ISOLONGIFOLENE

GLC CONDITIONS:

Column length - 10'
Temperature - 170°
Carrier gas - Hydrogen
Flow rate - 60 ml./min.

a) 10 % DEGS Column

b) 10 % DEGS - 0·01 mole % CuCl Column

c) 10 % DEGS - 0·01 mole % CuBr

d) 10 % DEGS - 0·01 mole % CuI

FIG.8.
RESOLUTION OF METHYL STEARATE & METHYL OLEATE

(ii) Influence of solvent

For the preparation of the above columns acetone was employed as solvent for the impregnation. It was later felt that cuprous halides being insoluble in acetone, a desirable dispersion of the salt on the stationary phase/solid support may not have been achieved. A solvent known to dissolve cuprous salts would perhaps be a better choice. As a result allyl alcohol which dissolves cuprous halides via π-complexation[26] was chosen. Two columns containing 0.01 mole percent and 0.02 mole percent of CuBr respectively were prepared(see experimental). These columns were then compared to the DEGS-CuBr column prepared using acetone as solvent, in terms of resolution of the olefinic mixtures. Surprisingly it was found that the latter column was superior to either of the former ones(Table-5). In addition it was also observed that the retention times of individual components were less on the columns prepared using allyl alcohol(Table-6). It appears that allyl alcohol in some way deactivates the cuprous bromide.

Table-5 A comparison between acetone and allyl alcohol loading

No.	Component		Col. temp (°C)	Resolution (Rs)		
				0.01 mole % CuBr		0.02 mole % CuBr
	A	B		acetone loading	allyl alcohol loading	allyl alcohol loading
1	β-Pinene	Δ^3- Carene	80	1.030	1.0435	1.000
2	Cis-geranyl acetone	Trans-geranyl acetone	140	0.6372	0.5217	0.4615
3	Longifolene	Isolongifolene	140	1.0135	0.9750	0.7600
4	Methylstearate	Methyloleak	140	1.0660	0.0	0.0

a) for other GLC parameters see footnote Table-3

Table.6: GLC Retention times (RT) of the individual components

No.	Compound	Col. temp. (°C)	Retention time (RT) in min. 0.01 mole % CuBr		0.02 mole % CuBr
			acetone loading	allyl alcohol loading	allyl alcohol loading
1	β-Pinene	80	2.66	1.84	2.00
2	Δ^3-Carene	80	3.40	2.34	2.44
3	Isolongifolene	140	2.72	1.56	1.60
4	Longifolene	140	3.30	1.80	1.90
5	Cis-geranyl acetone	140	12.16	6.24	6.40
6	Trans-geranyl acetone	140	13.20	6.80	6.80
7	Methyl stearate	170	18.40	14.28	17.20
8	Methyl oleak	170	20.80	14.28	17.20

Thus of the three cuprous halides studied, CuBr gives the best separation of a given mixture of olefins on the DEGS(10 percent) column. In addition acetone seems to be the solvent of choice in comparison with allyl alcohol for the preparation of these columns.

(iii) Effect of stationary phase

It has thus so far been shown that incorporation of some cuprous halides in the stationary phase(DEGS) results in an increase in the olefin-stationary phase interaction thereby bringing about (i) an increase in retention times and (ii) an increased resolution of a mixture of olefinic components.

The effect of cuprous halides on the performance of 10 percent SE-30 and 10 percent carbowax columns was next investigated. Columns containing 10 percent SE-30 and carbowax respectively and 0.01 mole % CuBr on Chromosorb W were prepared and their efficacy tested. The results were however unsatisfactory. Of the four olefin mixtures tried(see eg. Table-5), the hydrocarbons were eluted only after very long retention times(>4 to 5 times that on CuBr-DEGS column in the case of CuBr-SE-30) with little or no resolution. On the other hand the oxygenated compounds did not elute out even at higher temperatures suggesting a much stronger stationary phase(CuBr)-olefin interaction in these columns which perhaps results in the decrease in selectivity for the hydrocarbons. In order to see the effect of a lowered concentration of CuBr a 5 percent SE-30 Column(10) impregnated with 0.005 mole percent CuBr(w.r.t.Chromosorb) was prepared and tested. Similar results were obtained.

(iv) In conclusion

It has been shown that the incorporation of cuprous salts on DEGS enhances the resolution of a mixture of olefins the best results being obtained with cuprous bromide. Though the enhanced separation may be rationalized in terms of different stabilities of the olefin-CuX complexes the increase in retention times cannot be fully explained in this way. It has been observed that even fully saturated hydrocarbons such as p-menthane and β-pinane have longer retention times on these columns[27].

At the moment the applicability of this mode appears to be restricted to the polyester-type stationary phase. Inspite of this, these columns ought to be particularly useful in the GLC analysis of complex mixtures of high boiling olefinic components like the essential oils.

EXPERIMENTAL

1) CHEMICALS:-

The cuprous halides used were freshly prepared[28]. Acetone was refluxed over $KMnO_4$ for 3 hrs and distilled prior to use. Distilled toluene and allyl alcohol were used.

The solid support was Chromosorb W(mesh 60-80).

2) APPARATUS

A commercial chromatographic unit, 7624A, Research Chromatograph, Hewlett-Packard model was used. The columns consisted of aluminium tubing 12 ft. or 10 ft. long with an outer diameter of 1/4 inches wound into a coil of 7 inches in diameter. A thermal conductivity detector was employed. Hydrogen was the only carrier gas used.

3) Preparation of the 10 ft. Columns

The amount of cuprous halide taken was 0.01 mole percent with respect to Chromosorb. Columns of 10 percent stationary phase(again w.r.t chromosorb) were prepared. Thus for 15 g Chromosorb W, 1.5 g stationary phase and 0.15 g CuCl or 0.215 g CuBr or 0.285 g CuI were taken respectively.

(a) The carbowax and DEGS columns:-

The cuprous halide was dispersed in 15 ml acetone in a 250 ml two-necked flask fitted with a mechanical stirrer. To this was added a solution of 1.5 g stationary phase in 50 ml acetone under continued stirring. After about 5 min., 50 ml more of the acetone was added followed by addition of 15 g Chromosorb. After a further 5 min. period of stirring the flask was transferred to a rotary evaporator and the acetone removed under a slightly reduced pressure at 30° and finally at 70°. The impregnated chromosorb becomes free-flowing. This material was then filled in portions into the tubing with tapping and under a slight vacuum($\sim$500 mm). The column was conditioned for 72 hrs upto a temperature of 190°.

(b) The SE-30 column:-

The procedure employed here was the same except that toluene was used instead of acetone as solvent. The SE-30(1.5 g) was dissolved in toluene under reflux(4 hrs.).

(c) Using allyl alcohol as solvent:-

Two columns of CuBr on DEGS(10 percent on chromosorb) were prepared containing 0.01 mole percent and 0.02 mole of CuBr(w.r.t.chromosorb) respectively.

The freshly prepared CuBr was dissolved with stirring in 50 ml distilled allyl alcohol during 10 min. To this was added a solution of 1.5 g DEGS in 20 ml allyl alcohol after further stirring for 5 min., 50 ml more of allyl alcohol was added followed by 15 g chromosorb. The resulting slurry was stirred vigorously for 15 min. The solvent was then removed in a rotary evaporator at 50° under reduced pressure(50 mm) and finally at 70°/10 mm. The free flowing solid was then packed into the tubing as described earlier.

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