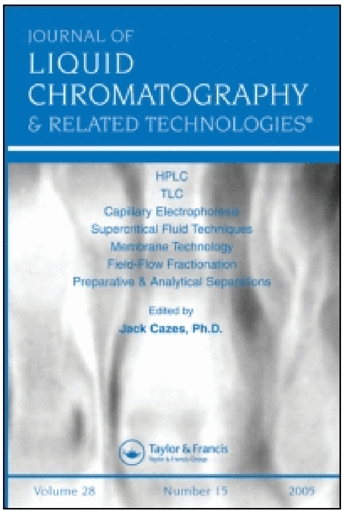

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Sequential Thin Layer Chromatography of Carbaryl and Related Compounds

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SEQUENTIAL THIN LAYER CHROMATOGRAPHY OF CARBARYL AND RELATED COMPOUNDS

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SUMMARY

Sequential thin layer chromatography is performed on silica gel G plates (0.5 mm thick layer) for the separation of carbaryl and related compounds. Common solvents such as benzene, carbon tetrachloride, chloroform, distilled water, 1,4-dioxane, and ethyl acetate are used for sequential development of the plates. Some important separations are: carbaryl from phenol, o-nitrophenol, α-naphthol and carbofuran; in carbon tetrachloride followed by distilled water; carbofuran from phenol, o-nitrophenol, α-naphthol, carbaryl and β-naphthoxyacetic acid in distilled water followed by chloroform etc.

INTRODUCTION

TLC is used for quantitative and qualitative analysis of wide variety of pesticides. It is particularly useful to herbicides containing carboxylic group because of their non-volatile and polar nature. In our previous publication[1], the behaviour of some herbicides on admixtures of silica gel G and calcium sulphate is described. It is shown that admixture, silica gel G; calcium sulphate (1:4 w/w), is an excellent TLC material for the separation of these compounds. Pandilkar et al.[2] developed a TLC procedure for the detection of carbaryl at trace level in biological fluids. Srivastava et al.[3] detected and separated several carbamates on layers of silica gel containing 1% zinc acetate.

Sequential thin-layer chromatography (S-TLC) has more advantages than normal-phase thin-layer chromatography (NP-TLC). When a mixture contains compounds that differ considerably in polarity, a single development with one mobile phase may not provide the desired separation. If the plate is developed successively with different mobile phases that have different polarity or strength, separation will be possible. Rathore and Saxena[4] performed S-TLC of 2,4-D and related compounds on calcium sulphate layers in different solvents and used bromophenol blue as a detector. Abou-donia and Komeil[5] have claimed that S-TLC is a rapid and fast method for the analysis of complex mixtures.

Therefore, in continuation to our previous work, now the sequential chromatographic behaviour of carbaryl and related compounds is studied. The separations achieved on silica gel G plates in common solvent are described in this paper.

EXPERIMENTAL

Apparatus

A Stahl apparatus with universal applicator (thickness of applied layers adjustable from 0.25-2.00 mm) glass plates (20 x 4 cm), glass jars (25 x 5 cm), hot air drier, temperature controlled electric oven (Tempo,India), spectrophotometer (Spectronic-20), centrifuge machine (Instrument Manufacturing Company,India), electric hot plate with magnetic stirrer (Sunvic,U.K.), variable volume micropipette (Gilson,France) were used.

Chemicals

Silica gel G (Merck,India), carbaryl 50% WP (Paushak Ltd., India), carbofuran 3% GR (Pesticides,India), propoxur 1% w/w (Bayer India Ltd.), bavistin 50% WP (BASF India Ltd.), phenol LR, p-chlorophenol LR (BDH India), β-naphthoxyacetic acid PR (Sigma, U.S.A.), p-nitrobenzenediazoniumtetrafluoroborate (Merck,India), potassium hydroxide LR (s.d. Fine CHEM,Pvt.Ltd.), sulphanilic acid, sodium nitrite (CDH,India) and sodium hydroxide (Qualigens,India) were used. All other reagents used were of analytical grade.

The following solutions were used: Solutions (2%) of carbaryl, carbofuran, phenol and α-naphthol in ethyl acetate; propoxur, bavistin, β-naphthoxyacetic acid, o-nitrophenol and p-chlorophenol in ethanol; p-nitrobenzenediazoniumtetrafluoroborate (0.1 g) in 100 ml of acetone; aqueous sodium nitrite (0.3%) and sodium hydroxide (16%), sulphanilic acid (0.2%) in 1:10 HCl and methanolic potassium hydroxide (1%). When 2% solution of pesticide was not possible to prepare, the saturated solution was used.

Preparation of plates

A slurry containing silica gel G (25 g) and distilled water (65 ml) was applied to the glass plates with the help of an applicator to give the film thickness 0.5 mm. The plates were first allowed to dry at room temperature and then at 110° for 1 hr for activation.

Spotting of test solutions

Test solutions were applied on TLC plates with the help of a fine capillary or a variable volume micropipette. The solvent was removed by hot air drying, the plate was developed upto the length of 5 cm in first solvent, the plate was taken out from the jar, the solvent was removed and then the plate was again developed upto the length of 10 cm in second solvent using ascending mode of development.

Detection of pesticides

The carbamates, phenols and β-naphthoxyacetic acid were detected on TLC plates by the following procedure; potassium hydroxide solution was sprayed on TLC plates, the plates were dried, cooled and then p-nitrobenzenediazoriumtetrafluoroborate solution was sprayed. Orangish-brown spots were appeared on white background for all the compounds while carbofuran appeared as purple spot.

Calculation of R_f values

For tailing spots, the front limit (RI) and rear limit (RT) were measured while for compact spots R_f values were calculated by the following relation

$$R_f = \frac{\text{distance travelled by the solute (cm)}}{\text{distance travelled by the solvent front (cm)}}$$

Quantitative separations

For quantitative separation of carbaryl the following method was applied: A known volume of standard pesticide solution was spotted on the plate with the help of a graduated micro-pipette, the solvent was removed, plates were developed and spots were located as above. The demarcated area of the plate was scratched out, carbaryl was extracted with methanol (5 ml) and the solid was removed by centrifugation. Carbaryl in the centrifugate was determined.

In 5 ml of centrifugate, 10 ml of distilled water, 2 ml of sodium nitrite and 2 ml sulphanilic acid were added, then after 10 minutes 5 ml of 16% sodium hydroxide and 50 ml of distilled water were added. Pink colour appeared. Finally the absorbance was measured at 520 nm against a blank. The blank contains all the above components except carbaryl.

RESULTS

Plots of R_f values vs. dielectric constants of various solvents on silica gel G plates are depicted in figure 1. R_f values by TLC

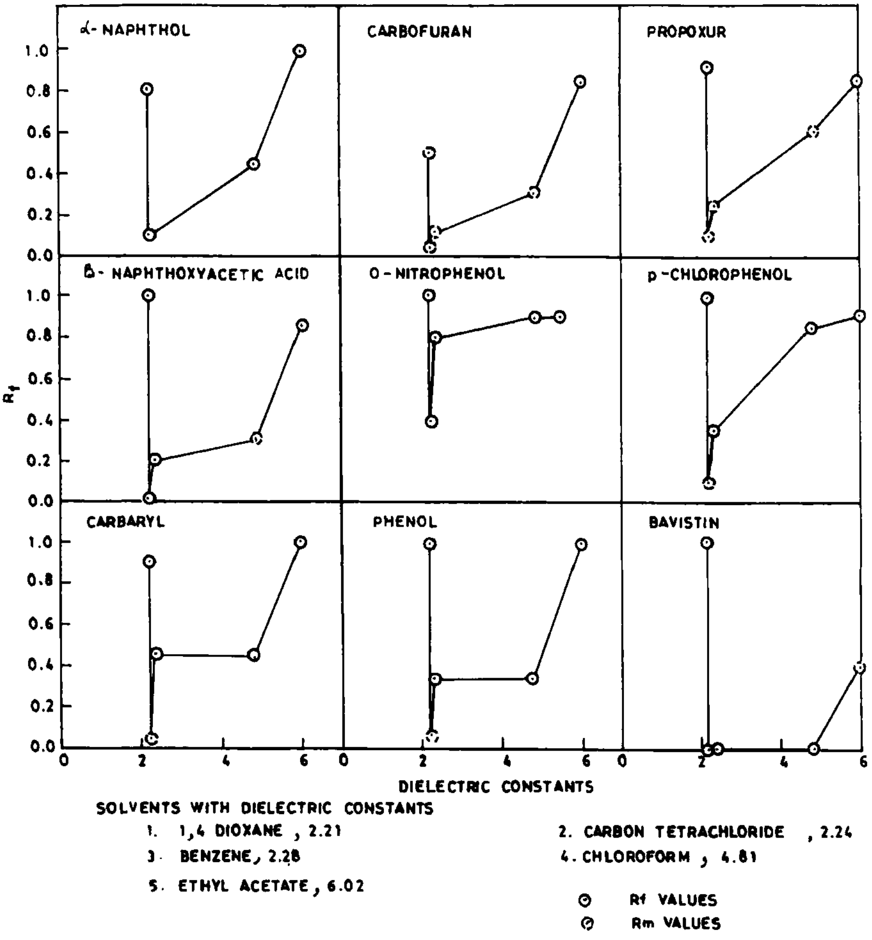

FIG.1- PLOT OF R_f Vs DIELECTRIC CONSTANTS OF VARIOUS SOLVENTS ON SILICA GEL G PLATES OF THICKNESS 0.5mm.

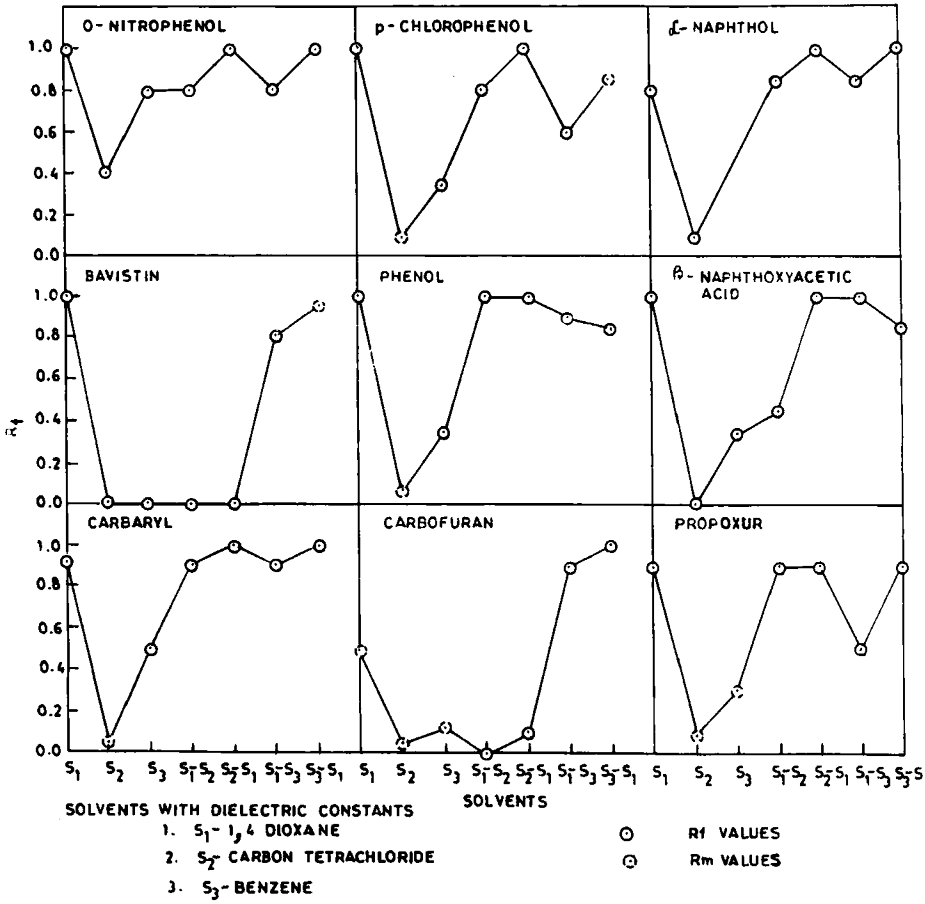

FIG.2- PLOT OF R_f Vs SINGLE AND MIXED SOLVENTS ON SILICA GEL G PLATES OF THICKNESS 0.5mm.

and S-TLC in different solvent systems are given in figures 2, 3, 4, 5 and 6. Separations achieved are recorded in Table 1. Table 2 summarizes S-TLC separations of carbaryl from other pesticides. In S-TLC, the first solvent that was allowed to ascend from 0-5 cm is listed first and the second solvent which was allowed to ascend from 0-10 cm is listed second.

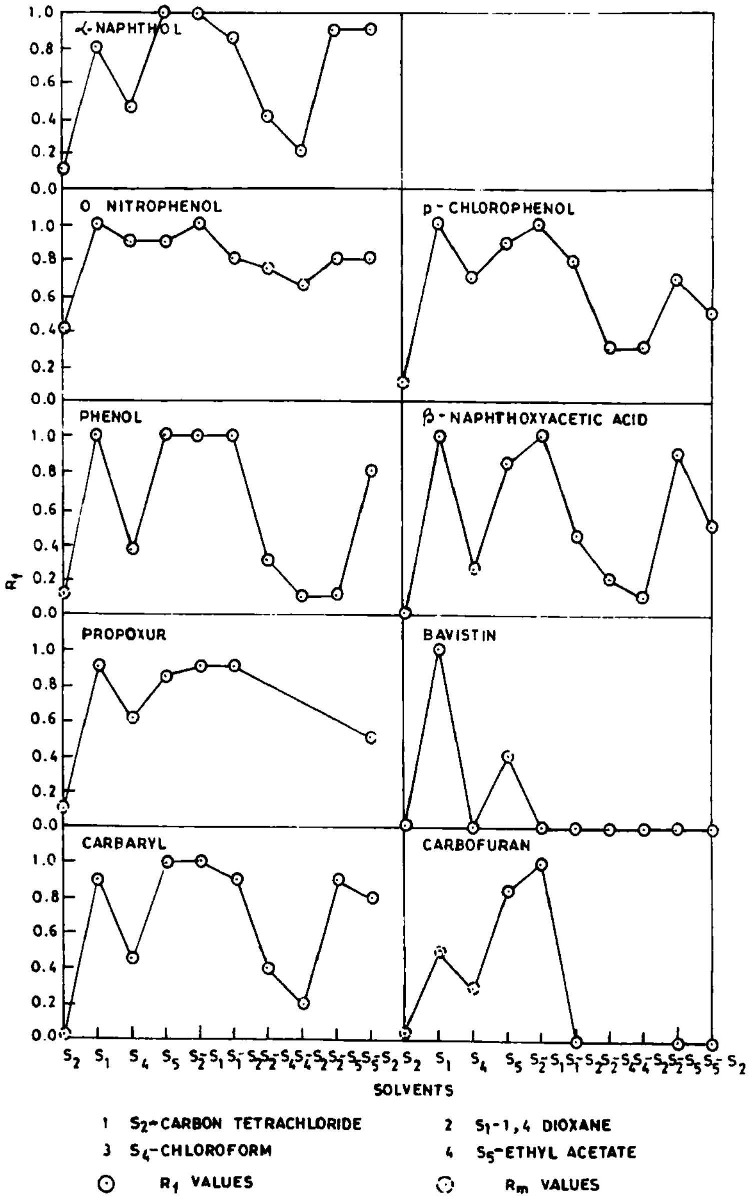

FIG.3 - PLOT OF Rf Vs VARIOUS SINGLE AND MIXED SOLVENT ON SILICA GEL G PLATES OF THICKNESS 0.5mm.

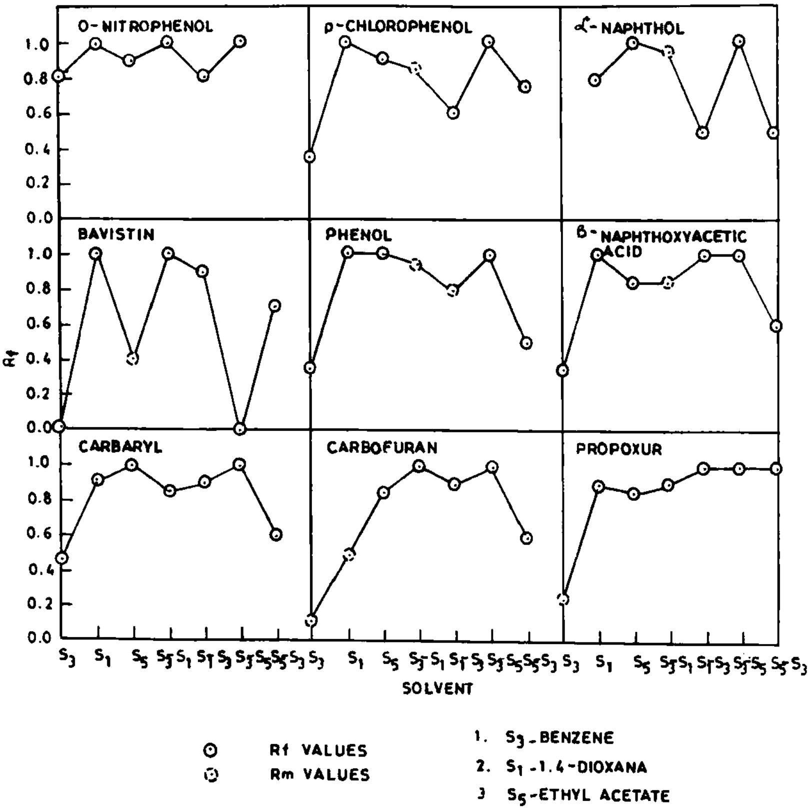

FIG.4- PLOT OF Rf Vs VARIOUS SINGLE AND MIXED SOLVENTS ON SILICA GEL G PLATES OF THICNESS 0.5mm.

DISCUSSION

Figure 1 shows that there is no definite correlation between R_f values and dielectric constants of the developers. However R_f values are higher in 1,4-dioxane than those in carbon tetrachloride. The R_f values increase with dielectric constant in benzene, chloroform and ethyl acetate. It shows that bavistin can be separated from carbaryl, carbofuran, phenols etc. in chloroform and benzene.

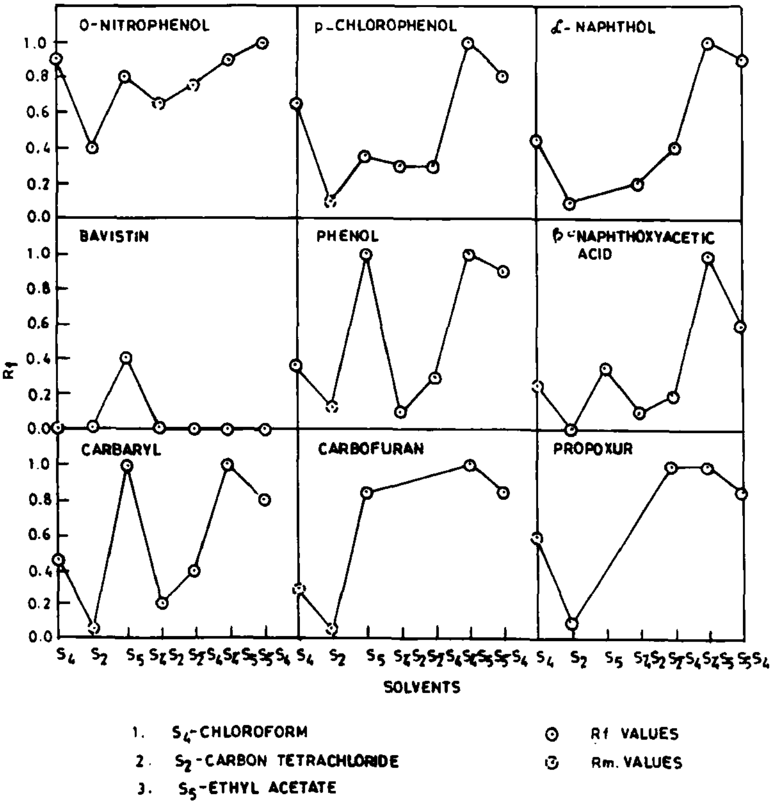

FIG.5- PLOT OF R_f Vs VARIOUS SINGLE AND MIXED SOLVENTS ON SILICA GEL G PLATES OF THICKNESS 0.5mm.

Figures 2, 3, 4, 5 and 6 show that there is a appreciable difference in R_f values on NP-TLC and S-TLC. For example, R_f values of β-naphthoxyacetic acid are 1 and 0 in 1,4-dioxane and carbon tetrachloride respectively; 0.45 and 1 in 1,4-dioxane followed by carbon tetrachloride and in carbon tetrachloride followed by 1,4-dioxane respectively. Thus S-TLC can be used for the separation which are not possible by NP-TLC. The results given in Tables 1 and 2 support the above conclusion i.e. various separations are possible by S-TLC.

Table 1 - Sequential thin layer chromatographic separation achieved on silica gel G coating with different solvent systems

Compounds	From	Solvent systems
Bavistin (0)	Carbaryl (0.9), carbofuran (1), p-chlorophenol (1), B-naphthoxyacetic acid (1), o-nitrophenol (1) and phenol (1).	Benzene-ethyl acetate
Bavistin (0)	Carbofuran (0.45), p-chlorophenol (1), α-naphthol (0-7 cm) and B-naphthoxyacetic acid (1).	Carbontetrachloride-distilled water
Bavistin (0)	Carbaryl (1), α-naphthol (9-10) and β-naphthoxyacetic acid (9-10 cm), o-nitrophenol (1), phenol (9-10 cm) and propoxur (0.8).	Carbon tetrachloride-1,4-dioxane
Bavistin (0)	Carbaryl (1), p-chlorophenol (0.75), α-naphthol (1), β-naphthoxyacetic acid (1), o-nitrophenol (1) and phenol (1).	Carbon tetrachloride-ethyl acetate
Bavistin (0)	Carbaryl (0.25), α-naphthol (0.25) and phenol (0.25).	Chloroform-carbon tetrachloride
Bavistin (0)	Carbaryl (9-10 cm).	Chloroform-distilled water
Bavistin (0)	Carbaryl (0.8) and β-naphthoxyacetic acid (0.8).	Distilled water-chloroform
Bavistin (0)	Carbaryl (0.6), α-naphthol (0.6) and phenol (1).	1,4-dioxane-carbon tetrachloride
Bavistin (0)	Carbaryl (0.75), α-naphthol (0.75) and phenol (0.6).	Ethyl acetate-benzene
Bavistin (0)	Carbaryl (0.5), p-chlorophenol (0.5), α-naphthol (0.5), β-naphthoxyacetic acid (0.5), o-nitrophenol (0.7) and phenol (0.6).	Ethyl acetate-carbon tetrachloride

(Table 1 continued)

Compounds	From	Solvent systems
Bavistin (0)	Carbaryl (0.8), carbofuran (1), p-chlorophenol (0.85), α-naphthol (0.9), β-naphthoxyacetic acid (0.9), o-nitrophenol (0.9) and phenol (0.75).	Ethyl acetate-chloroform
Carbaryl (0)	Carbofuran (0.6), α-naphthol (0.3), o-nitrophenol (0.6) and phenol (0.8).	Carbon tetrachloride-distilled water
Carbofuran (0)	Carbaryl (0.9) and α-naphthol (5-8 cm).	Chloroform-distilled water
Carbofuran (0)	Carbaryl (0.85), α-naphthol (0.7), β-naphthoxyacetic acid (0.7), o-nitrophenol (1) and phenol (0.5).	Distilled water-chloroform
Carbofuran (0)	Carbaryl (0.8), p-chlorophenol (0.8), α-naphthol (0.9), β-naphthoxyacetic acid (0.9) and phenol (1).	1,4-Dioxane-carbon tetrachloride
Carbofuran (0)	Carbaryl (0.5), p-chlorophenol (0.5), α-naphthol (0.5), β-naphthoxyacetic acid (0.5), o-nitrophenol (0.75), phenol (0.5) and propoxur (0.5).	Ethyl acetate-carbon tetrachloride
o-nitrophenol (0.8)	Bavistin (0), carbaryl (0.4), p-chlorophenol (0.3), α-naphthol (0.4) and phenol (0.2).	Carbon tetrachloride-chloroform
o-nitrophenol (0.7)	Bavistin (0), p-chlorophenol (0.25) and β-naphthoxyacetic acid (0.25).	Chloroform-carbon tetrachloride

Table 2 - Quantitative sequential-thin-layer chromatographic separation of carbaryl from other pesticides using different solvents

Amount of pesticides separated on TLC (ug)		Solvent system	Absorbance at 520 nm			% error
Carbaryl	Other pesticides		x_1	x_2	Average value (u)	
	Bavistin					
20	5	Dioxane-carbon tetrachloride	0.07	0.07	0.07	0
10	5	"	0.04	0.05	0.045	±0.5
5	5	"	0.02	0.01	0.015	±0.5
20	5	Carbon tetrachloride-dioxane	0.05	0.05	0.05	0
10	5	"	0.02	0.02	0.02	0
5	5	"	0.01	0.02	0.015	±0.5
30	5	Carbon tetrachloride-ethyl acetate	0.92	0.94	0.93	±1
25	5	"	0.7	0.72	0.71	±1
20	5	"	0.54	0.53	0.535	±0.5
15	5	"	0.34	0.35	0.345	±0.5
10	5	"	0.25	0.25	0.25	0
5	5	"	0.1	0.2	0.015	±0.5

(Table 2 continued)

Amount of pesticides separated on TLC (ug)		Solvent system	Absorbance at 520 nm			% error
Carbaryl	Other pesticides		x_1	x_2	Average value (u)	
	Carbofuran					
20	5	Carbon-tetrachloride distilled water	0.02	0.03	0.025	±0.5
10	5	"	0.01	0.02	0.015	±0.5
5	5	"	0.01	0.01	0.01	0
	Bavistin					
20	5	Chloroform-carbon tetrachloride	0.05	0.05	0.05	0
10	5	"	0.02	0.03	0.025	±0.5
5	5	"	0.01	0.02	0.015	±0.5
	o-Nitrophenol					
20	5	Carbon tetrachloride-distilled water	0.025	0.03	0.0275	±0.25
10	5	"	0.02	0.02	0.02	0
5	5	"	0.01	0.01	0.01	0
	p-Chlorophenol					
20	5	"	0.03	0.04	0.035	±0.5
10	5	"	0.02	0.02	0.02	0
5	5	"	0.01	0.01	0.01	0

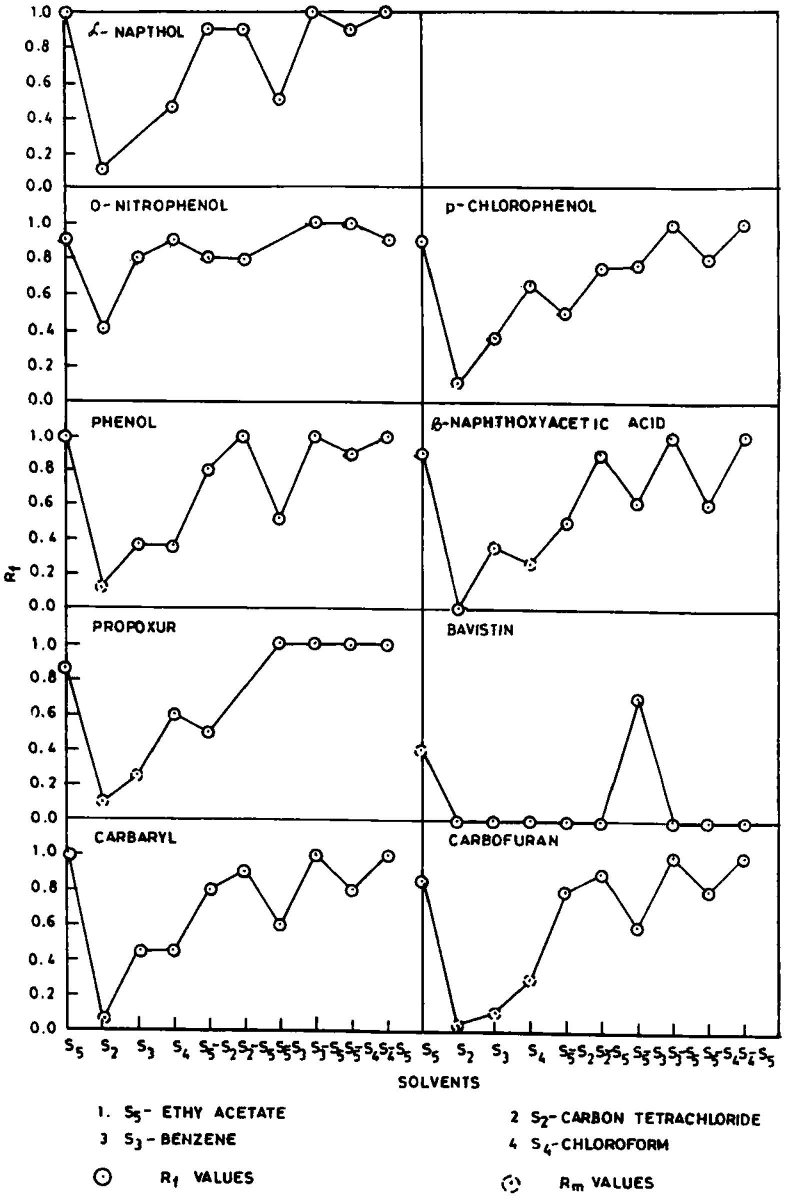

FIG.6- PLOT OF R_f Vs VARIOUS SOLVENTS OF SILICA GEL G PLATES WITH THICKNESS 0.5mm.

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