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Note

Thin-layer chromatography of acid and of 1:1 and 1:2 metal-complex dyes on silica gel

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Acid and metal-complex dyes belong to different groups of chemical substances and are produced on a large scale under different trade names. Often, dyes known by different names are chemically identical, but on the other hand, the trade products are often mixtures of components belonging to different groups of substances; these components can differ in their colouring properties, although this is not desirable. Control of the composition of the trade product and of the crude dye assists in maintaining and improving the quality of the dye and is desirable from the point of view of the consumer (the textile industry) and of the producer.

It is well known that thin-layer chromatography (TLC) is a rapid, sensitive and routine method having high separating power. The technique has been used for studying acid and metal-complex dyes on silica gel¹⁻¹⁰; aluminium oxide-silica gel (1:1) and aluminium oxide alone¹¹⁻¹⁸ have also been used, as have polyamide and cellulose powder^{1,3,19,20}. The separation of acid dyes is discussed in refs. 1-3, 6-12 and 20, and that of the 1:1 and 1:2 metal-complex dyes in refs. 4, 5 and 13-20. Schlegelmilch and Fuchs¹³ reported the group separation of 1:1 and 1:2 metal-complex dyes on ion-exchange paper, but several other papers on paper chromatographic separation will not be considered here. The purpose of this paper is to report on the use of TLC in textile-dye control and to investigate the behaviour of acid and metal-complex dyes in several solvent-silica gel TLC systems. We have studied 38 commercial dyes.

EXPERIMENTAL

Materials

The solvents were treated as follows. Ethyl acetate (puriss) was washed (until neutral) with 10% NaHCO₃ solution and then washed with 20% of its volume of 50% CaCl₂ solution, dried over Na₂SO₄ and distilled; the fraction distilling from 74-76° was used. Methyl acetate (puriss) was treated in the same way as ethyl acetate, the fraction distilling from 54-56° being used. Chloroform (p.a.) was washed with 10% NaHCO₃ solution and with water, dried over CaCl₂ and distilled through a column; the fraction distilling from 57-58° was used. Pyridine (puriss) was boiled for 24 h with CaO, then distilled through a short column; the fraction distilling from 113.5-114.5° was used.

Glacial acetic acid (p.a.) was heated under reflux for 4 h with 3% of CrO_3 and distilled through a short column; the fraction distilling from 115–116° was used. Other solvents were used purified by distillation of the commercial p.a. product.

Chromatography

TLC was carried out as described by Stahl²¹ on glass plates (10 × 20 cm) coated with Kieselgel G für DC (Merck, Darmstadt, G.F.R.). The dyes were applied on the start line as 2–3- μl portions of 0.1% aqueous solutions. The chromatograms were developed until the solvent front had migrated 10–12 cm, and the separation was recorded photographically (colour slides).

RESULTS AND DISCUSSION

We first tested the dyes in solvent systems recommended in the literature^{1–10} for use with silica gel, then we studied their behaviour in a large number of our own solvent systems; only those solvent systems that yielded the best separation and were better than those described in the literature are mentioned in this paper. The best results for the separation of acid dyes (expressed as R_F values of the colour components) are shown in Table I.

The system S4, without NaCl, separates into two layers during chromatography; this causes the appearance of a second solvent front and so produces deterioration of the separation pattern. This undesirable effect can be avoided by adding NaCl (5% of the water content of the system) and then separating the resulting aqueous phase. The phenomenon of forming "double fronts" occurs in many other systems containing, *e.g.*, ethyl methyl ketone and methyl acetate (in certain proportions) and in systems containing pyridine with formic acid (in all the proportions tested). The same is true for the following systems: *n*-butanol–ethyl methyl ketone–pyridine–glacial acetic acid–water (15:15:2:4:25); methyl acetate–glacial acetic acid–water–pyridine (30:3:20:1); chloroform–isopropanol–pyridine–formic acid (8:6:2:1). In all systems except those containing both pyridine and formic acid, this undesirable effect could be removed by salting out with 2–10% (w/v) of NaCl (or $\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$) with respect to the water content of the system. Systems so treated often form an organic phase suitable as developing solvent for TLC; when salting out produces a one-phase system, the whole mixture is used directly for TLC.

Fig. 1 shows the separation pattern of the acid dyes. Of all the systems tested, the most successful were S1 and S2.

The 1:1 metal-complex dyes, all of the Palatine series (produced by BASF, Ludwigshafen, G.F.R.) showed the worst behaviour in TLC. For their separation, solvent systems S1, S2, S3, S4 (see Table I) and S5 (see Table II) are recommended. The R_F values of the spots obtained are listed in Table II, and the separation patterns with systems S2 and S4 are shown in Fig. 2; these two systems produce the best separation. Many of these dyes leave insoluble material at the origin, but this does not prevent formation of relatively well-defined spots (although some tailing occurs). The addition to the solvent of 4% of sodium dodecyl sulphate helps to produce more compact spots. This can be seen by comparing the chromatograms in Fig. 3.

The optimum TLC separation of the 1:2 metal-complex dyes was attained

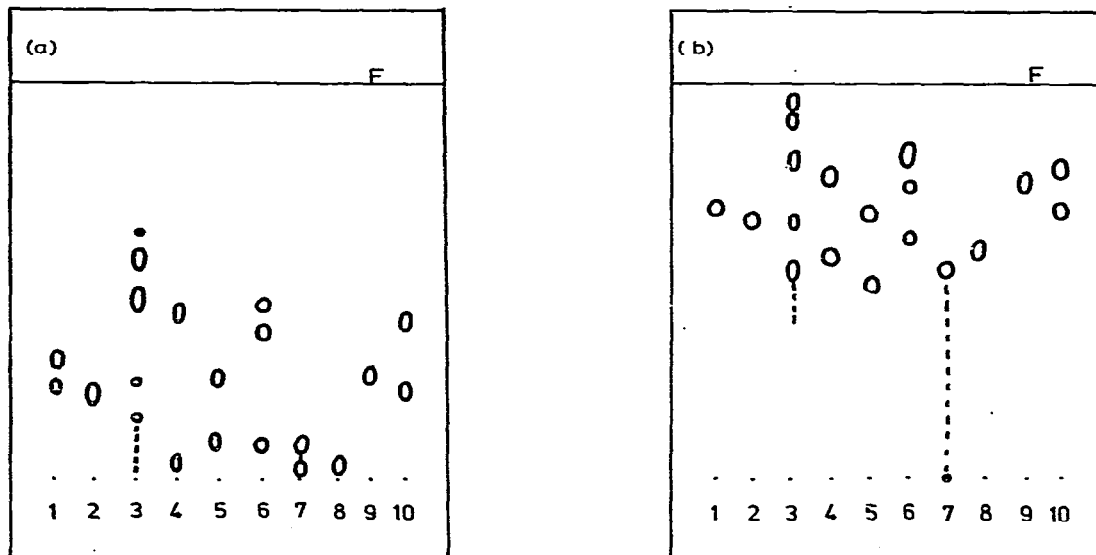


Fig. 1. TLC separation of acid dyes in solvent systems S1 (a) and S2 (b). The numbers of the dyes are as in Table I.

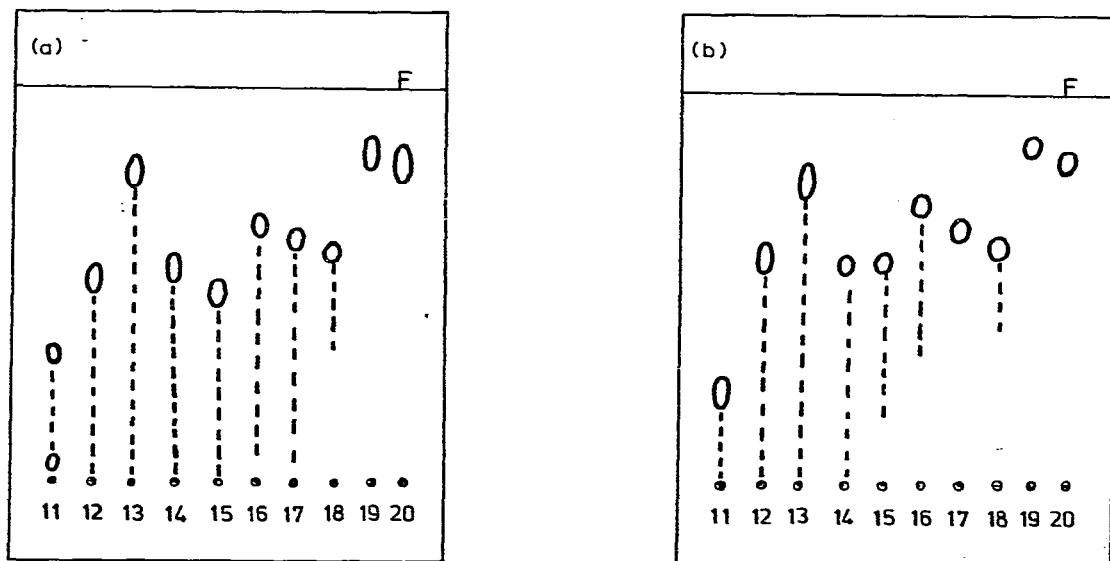


Fig. 2. TLC separation of 1:1 metal-complex dyes in solvent systems S2 (a) and S4 (b). The number of the dyes are as in Table II.

in systems S1, S3, S7 (see Table I) and S6 [chloroform–isoamyl alcohol–ethyl methyl ketone–methanol–pyridine (6:5:3:2:2)]. The separations achieved in systems S1 and S3 are shown in Fig. 4, and the R_F values for these separations are given in Table III.

It can be seen that the systems proposed give good separation of 1:2 metal-complex dyes from different producers, forming well-shaped spots without tailing. In studying the TLC of dyes from the same producer, we tested 10 dyes of the

TABLE I

R_F VALUES OF COLOUR COMPONENTS OF ACID DYES DURING TLC ON KIESELGEL G

The solvent systems used were: S1: ethyl acetate-glacial acetic acid-water (3:1:2); S2: *n*-butanol-ethyl methyl ketone-glacial acetic acid-pyridine-water (15:15:4:2:10); S3: methyl acetate-glacial acetic acid-water (30:3:20) + 5% of NaCl (with respect to H₂O); S4: methyl acetate-glacial acetic acid-water (30:5:20) + 5% of NaCl (with respect to H₂O); S7: *n*-butanol-glacial acetic acid-water (15:4:5).

Dye No.	Dye name	Producer	Colour of component	Solvent system ^a						
				S1	S2	S3	S4	S7		
1	Polar brillantrot GEN	Ciba-Geigy (Basel, Switzerland)	Pink	0.23	—	0.35	0.52	0.57d		
2	Polar brillantblau RAW	Ciba-Geigy	Scarlet	0.31	0.69	0.51	0.58	0.82d		
3	Xylenechtgrau P	Sandoz (Basel, Switzerland)	Blue	0.21	0.65	0.32	0.53	0.52d		
			Pink	0.55	0.90	0.77	0.76	0.89		
			Light blue	0.62	0.96	0.86	0.85	0.95		
			Violet	0.45	0.80	0.67	0.71	—		
			Marine blue	0.24	0.65	0.40	0.55	0.45		
4	Ponceau 2RL	Ciech (Warsaw, Poland)	Blue	0.15t	0.51	0.27l	0.59	—		
			Orange	0.41	0.77	0.65	0.70	0.87		
5	Acid black 10BS	Ciech	Red	0.04	0.56	0.07	0.37	0.15		
			Light blue	0.25	0.67	0.03	0.53	0.50		
			Blue	0.09	0.48 ^b	—	0.19	0.00		
6	Acid brown GOL	Ciech	Yellow	0.44	0.82	0.73	0.75	0.87		
			Orange	0.37	0.75	0.65	0.68	0.80		
			Violet	0.07	0.60	0.15	0.42	0.25		
7	Acid pink M**	Sojuzchimexport (Moscow, U.S.S.R.)	Pink	0.09	0.52l	0.05t	0.50	0.28dt		
8	Acid fast red 100%	Sojuzchimexport	Orange	0.03t	—	—	0.36t	0.10dt		
			Red	0.03	0.58	0.07l	0.40	0.15d		
9	Acid blue RN	Sojuzchimexport	Blue	0.26	0.75	0.50	0.64	0.70d		
10	Acid black ATT	Sojuzchimexport	Orange	0.40	0.77	0.70	0.63	0.83		
			Blue	0.22	0.68	0.38	0.50	0.50		
				80	80	30	40	110		

Time (min) for 12-cm migration of solvent front

^a d = diffuse spot; t = tailing spot.

** Insoluble residue at the origin.

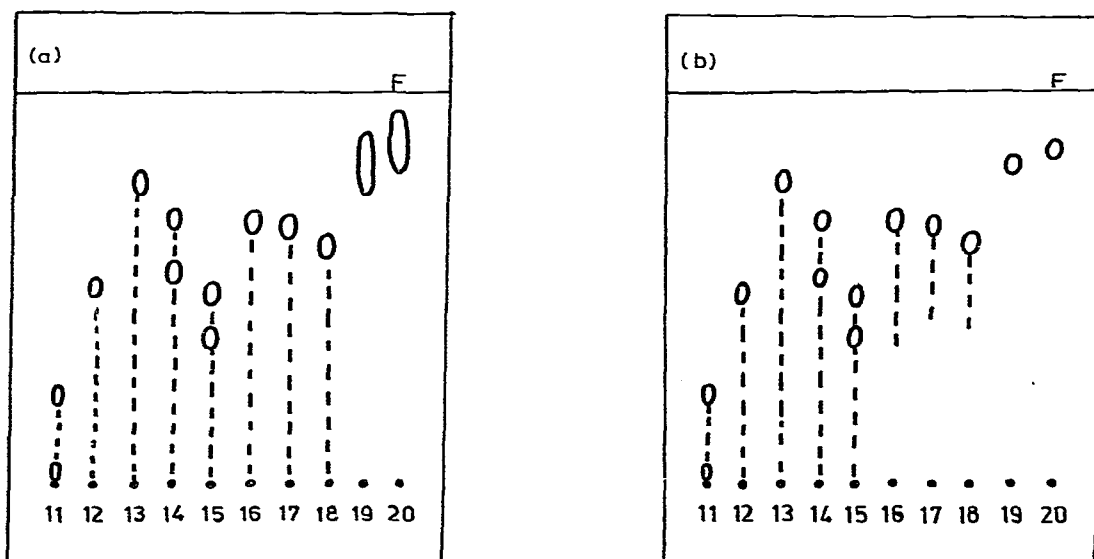


Fig. 3. Effect of adding 4% of sodium dodecyl sulphate to the solvent system on TLC of 1:1 metal-complex dyes. a: System S7; b: System S5. The numbers of the dyes are as in Table II.

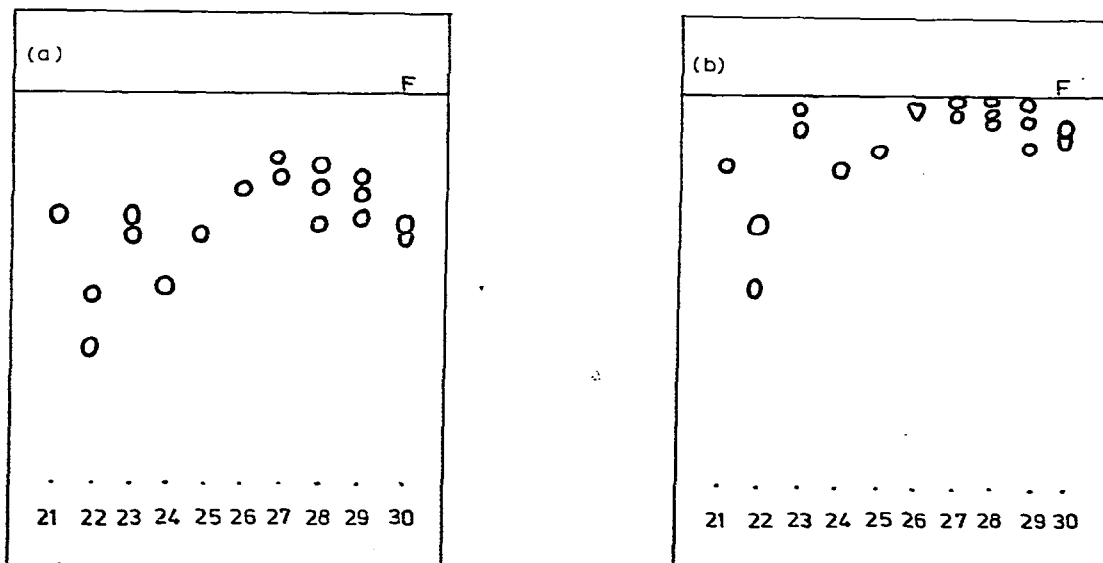


Fig. 4. TLC separation of 1:2 metal-complex dyes in solvent systems S1 (a) and S3 (b). The numbers of the dyes are as in Table III.

Irgalan series. The results in solvent systems S1, S3 and S6 were very good, the dyes giving clear spots with R_F values sufficiently different to permit identification. The results are shown in Table IV and Fig. 5.

An important problem from the practical point of view is the possible analytical differentiation and preparative separation of 1:1 and 1:2 metal-complex dyes. This was achieved by use of system S8 [isoamyl alcohol-pyridine-25% ammonia solution

TABLE II

R_f VALUES OF COLOUR COMPONENTS OF 1:1 METAL-COMPLEX DYES DURING TLC ON Kieselgel G

The solvent systems used were: S1, S2, S3, S4 and S7 as in Table I; S5; *n*-butanol-glacial acetic acid-water (15:4:5) + 4% (w/v) sodium dodecyl sulphate (with respect to water).

Dye No.	Dye name	Colour Index No.	Colour of component	Solvent system*						
				S1	S2	S3	S4	S5	S7	
11	Palatinechtgelb EIN**	19010	Lemon yellow	—	0.31t	—	—	—	0.23	0.13t
12	Palatinechtgelb 3GN**	14006	Yellow	0.00	0.05	0.14	0.25dt	—	0.03	0.25dt
			Light yellow	0.38	—	—	0.57dt	—	—	—
13	Palatinechtorange RN**	18740	Yellow	0.08t	0.51dt	0.36dt	—	—	0.50dt	0.37t
			Orange	0.42t	0.78dt	0.86t	0.76dt	0.77t	0.75dt	—
14	Palatinechtröt GREN**	18800	Pink-orange	0.12dt	—	0.38dt	—	—	—	0.25dt
			Orange-yellow	—	0.54dt	—	—	0.67dt	0.57dt	—
15	Palatinechtrösa BN**	18810	Orange	0.25t	—	0.74t	0.55t	—	0.53t	0.41t
			Pink-red	0.13d	—	—	—	0.48dt	0.46dt	—
16	Palatinechtviolett 3RN**	16055	Pink	0.05t	0.48dt	0.31t	0.55t	—	0.37t	0.23t
			Violet	0.33	0.65t	0.77t	0.70t	0.67t	0.58t	—
17	Palatinechtgrün BLN**	13425	Green	0.39	0.62t	0.82	0.64	0.65t	—	—
18	Palatinechtblau GGN**	—	Blue	0.21	0.58	0.66	0.60t	0.60t	—	—
19	Palatinechtbraun RN	14251	Brown	0.60d	0.83d	—	0.86	0.80	—	—
20	Palatinechtbordeaux RN**	19351	Red	0.57dt	0.80d	—	0.82	0.85	—	—
Time (min) for 12-cm migration of solvent front				80	80	30	40	100	110	110

* d = diffuse spot; t = tailing spot.

** Insoluble residue at origin.

TABLE III

 R_f VALUES OF COLOUR COMPONENTS OF 1:2 METAL-COMPLEX DYES DURING TLC ON KIESELGEL G

The solvent systems used were: S1, S3 and S7 as in Table I; S6: chloroform-isoamyl alcohol-ethyl methyl ketone-methanol-pyridine (6:5:3:2:2).

Dye No.	Dye name	Producer	Colour of component	Solvent systems*			
				S1	S3	S6	S7
21	Ortolangelb G	BASF (Ludwigshafen, G.F.R.)	Lemon yellow	0.68	0.81	0.69	0.88
22	Irgalanbrillantrot BL	Ciba-Geigy	Red	0.34	0.50	0.24 ^t	0.83
23	Irgalanbraun 3BL	Ciba-Geigy	Orange-red	0.48	0.67	0.53	—
			Orange	0.68	0.96	0.78	0.91
			Grey-blue	0.63	0.91	0.71	0.88
24	Irgalangrau BRL	Ciba-Geigy	Grey-blue	0.50	0.80	0.68	0.81
25	Isolanorange GGL	Bayer (Leverkusen, G.F.R.)	Orange	0.63	0.86	0.67	0.89
26	Wofalanrubin RL	Wolfen (Bitterfeld, G.D.R.)	Ruby	0.74	0.97	0.78	0.93
27	Wofalanoliv BL	Wolfen	Blue-green	0.83	0.99	0.82	0.95
			Yellow-green	0.77	0.95	0.75	0.90
			Pink	0.75	0.94	0.86	0.95
28	Grigio stenolana RL	ACNA (Milan, Italy)	Pink	0.80	1.00	—	—
			Marine blue	0.65	0.90	0.71	0.87
			Pink	0.68	0.87	—	—
29	Bordo stenolana 2BL	ACNA	Bordeaux	0.74	0.94	—	—
			Bordeaux	0.78	0.99	—	—
			Grey	0.61	0.88	—	—
30	Bruno stenolana 2 GL	ACNA	Orange	0.66	0.92	—	—
Time (min) for 12-cm migration of solvent front				80	30	65	110

* t = tailing spot.

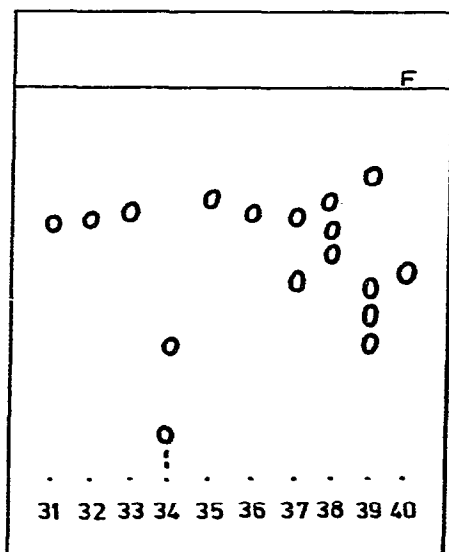


Fig. 5. TLC separation of 1:2 metal-complex Irgalan and acid Irganol dyes in the solvent system S1. The numbers of the dyes are as in Table IV.

TABLE IV

R_F VALUES OF COLOUR COMPONENTS OF 1:2 METAL-COMPLEX (IRGALAN) AND ACID (IRGANOL) DYES ON KIESELGEL G

The solvent systems used were S1, S3 (as in Table I) and S6 (as in Table III).

Dye No.	Dye name (Ciba-beigy)	Colour of component	Solvent system*		
			S1	S3	S6
31	Irganolbrillantgelb 3GL	Lemon yellow	0.65	0.61	0.66
32	Irgalangelb 2BRL	Orange-yellow	0.66	0.86	0.82
33	Irgalanorange RL	Orange	0.68	0.90	0.82
34	Irganolbrillantscarlet RL	Red	0.34	0.50	0.21t
		Red-orange	0.11t	0.31dt	0.03dt
35	Irgalanbordeaux GRL	Violet	0.71	0.93	0.92
36	Irgalanscarlet GL	Orange-red	0.68	—	—
37	Irganolbrillantrot BL	Orange-red	0.67	0.57	0.59
		Red	0.50	0.50	0.33t
38	Irgalangrau 2GL	Grey	0.57	—	—
		Grey-blue	0.63	0.80	0.74
		Grey-green	0.71	0.93	—
39	Irgalanschwarz 2BL	Blue-grey	0.77	1.00	0.93
		Dark-grey	0.48	0.54	0.18t
		Dark grey	0.41	—	—
		Dark grey	0.34	—	—
40	Irgalangrau BRL	Grey	0.52	0.74	0.75
Time (min) for 10-cm migration of solvent front			55	20	50

* t = tailing spot; d = diffuse spot.

TABLE V

R_F VALUES OF COMPONENTS OF 1:1 AND 1:2 METAL-COMPLEX DYES DURING TLC ON KIESELGEL G

The solvent system (S8) was isoamyl alcohol-pyridine-25% ammonia solution (8:4:1).

Dye No.	Dye name	Colour of components	R_F
22	Irganolbrillantrot BL	Orange-red	0.75
		Red	0.53
		Orange	0.30t
		Orange	0.95
25	Isolanorange GGL	Orange	1.00
23	Irgalanbraun 3BL	Grey	0.92
		Grey-green	1.00
		Yellow-green	0.97
27	Wofalanoliv BL	Pink	1.00
28	Grigio stenolana RL	Marine blue	0.92
		Pink	0.60
13	Palatinechtorange RN	Orange	0.00
		Pink-red	0.00
		Violet	0.00
		Green	0.00
		Blue	0.00
15	Palatinechtrosa BN	Orange	0.00
16	Palatinechtviolet 3RN	Pink	0.00
17	Palatinechtgrün BLN	Green	0.00
18	Palatinechtblau GGN	Blue	0.00

* t = tailing spot.

(8:4:1)]. In this system, 1:1 metal-complex dyes remained at the origin, while the 1:2 dyes exhibited fairly high R_F values; the results are shown in Table V and Fig. 6.

This solvent system can thus be used for analysing a mixture of these two groups of dyes by two-dimensional TLC, with system S8 in the first direction, and system S2 or S4 in the second. In the last two systems, the 1:1 metal-complex dyes are better separated than in other systems, and separation of the 1:2 metal-complex dyes is satisfactory.

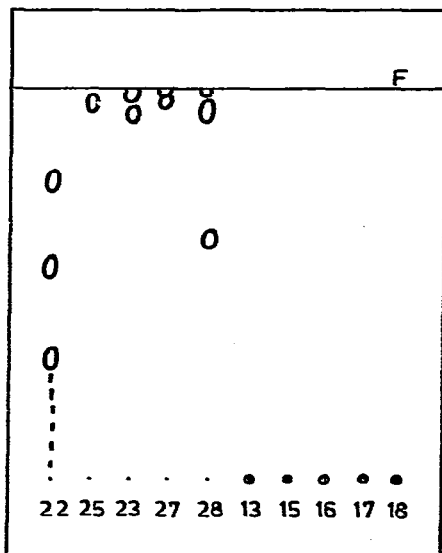


Fig. 6. TLC separation of 1:1 and 1:2 metal-complex dyes in solvent system S8. The numbers of the dyes are as in Table V.

CONCLUSIONS

Comparison of the behaviour of the three groups of dyes studied leads us to the conclusion that the solvent systems proposed give good separation of acid and of 1:2 metal-complex dyes; separation of the 1:1 metal-complex dyes is clear, but the spots are diffuse and exhibit tailing. For the acid dyes, the best solvent systems were S1 and S2; for the 1:1 metal-complex dyes, S2 and S4; and for the 1:2 metal-complex dyes, S1 and S3. We also found that addition of sodium dodecyl sulphate to the solvent system sometimes led to formation of more compact spots of the 1:1 metal-complex dyes.

The good separation of the components of the dyes studied suggests that the proposed solvent systems for TLC on silica gel could be used successfully for the preparative isolation of different dye components in order to study their chemical structures. TLC of these groups of dyes in our chromatographic systems offers a useful method to the consumer (the textile industry) for homogeneity control, standardization and testing commercial products from different firms. This method could also be used by the producer to control the synthesis of different batches of dye.

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