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Note

Thin-layer chromatographic identification of leather dyes

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Thin-layer chromatographic (TLC) identification of dyes on silica gel G layers is much used in the analysis of foods, textiles, etc.[1,2]. This technique has several advantages over paper chromatography. For example, it is suitable for direct dyes which cannot be chromatographed on paper without using solvents that break hydrogen bonds[3]. However, the available literature on the use of TLC on silica gel G for leather dyes is scanty. Dyes used in the leather industry are generally selected from those used in other industries like textiles, wool, etc., as they are meant for use on a material having a three-dimensional structure, namely collagen, which is subjected to various physical and chemical treatments including tanning.

Wada *et al.*[4] studied the TLC of acid and direct dyes for leather and suggested that *n*-butanol–ethanol–water (9:2:3) gave the most satisfactory results. Sagala and Studniarski[5] used TLC on silica gel G to determine the dye purity and optimum concentration of the dyeing bath for leather and observed that *n*-butanol–ethanol–ammonia–pyridine–water (8:3:4:4:3) gave good results. Biedermann and Golz[6] carried out the TLC of various commercial leather dyes and concluded that this technique is very useful, having high sensitivity, speed and good separation power. Tzicas[7] studied the TLC separation and identification of water-soluble dyes and suggested that good results were obtained using the solvents chloroform–isopropanol–water (1:3:1), butanol–ethanol–water (8:1:3), *n*-butanol–acetic acid–water (4:1:5) and isopropanol–ammonia–water (7:1:1). Clearly, not much information is available on solvents useful for the TLC separation and identification of acid, direct, premetallized and basic dyes used in the leather industry.

Studies were therefore undertaken of the TLC of leather dyes on silica gel G layers. 86 Solvent systems used in the TLC of dyes for food, textiles, pharmaceuticals, etc., including those reported for leather dyes were studied for their suitability for the separation and identification of 34 leather dyes: 10 acid dyes, 4 direct dyes, 16 premetallized dyes and 4 basic dyes.

EXPERIMENTAL

Chromatographic plates (20 cm × 20 cm) were coated with 0.25-mm layers of silica gel G (BDH-Glaxo, India) and activated for 1 h at 110°C as described by Stahl[8]. Analytical grade solvents and doubly distilled water were used for the preparation of solvent systems. Multicomponent solvent systems were thoroughly shaken in a

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TABLE I

R_F VALUES OF ACID DYES ON SILICA GEL G PLATES

Solvent systems: 1 = *n*-butanol–acetic acid–water (4:1:5, upper layer)[7]; 2 = *n*-butanol–ethanol (95%)–ammonia (1:9) (9:2:3)[4]; 3 = isopropanol–ammonia (0.91)–water (7:1:1)[7]; 4 = isopropanol–ammonia (0.91)–water (10:1:1)[10]; 5 = ethyl acetate–acetic acid–water (3:1:2)[11]; 6 = isopropanol–ammonia (0.91) (4:1)[12]; 7 = isopropanol–chloroform–water–diethylamine (50:25:20:15)[12]; 8 = *n*-butanol–ethanol–water (9:1:1)[13]; 9 = *n*-butanol–ethanol–water–acetic acid (6:1:2:0.05)[14]; 10 = *n*-propanol–ammonia (0.91) (6:3)[15]; 11 = methanol–ethyl acetate–dilute ammonia (3 parts diluted in 7 parts water) (3:15:3)[16]; 12 = *n*-amyl alcohol–ethanol–ammonia (0.91) (10:10:1)[13]; 13 = *n*-amyl alcohol–ethanol–ammonia (0.91) (50:45:5)[13].

Dye	*Solvent system*												
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*
1 Acid Leather Orange	0.70	0.61	0.84	0.61 0.75	0.64	0.93	0.72	0.56	0.64	0.82	0.43	0.80	0.78
2 Naphthalene Leather Orange G 132	0.68	0.58	0.82	0.72	0.57	0.89	0.84	0.54	0.60	0.82	0.43	0.78	0.76
3 Polar Brilliant Blue GAW	0.40 0.50 0.65 0.82	0.34 0.37 0.45 0.57 0.78	0.59 0.76 0.85	0.46 0.66 0.79	0.14 0.29 0.51 0.40	0.64 0.84 0.92	0.54 0.89 0.94	0.06 0.23 0.42 Streak	0.15 0.32 0.48	0.82 0.89	0.24 0.34 0.42	0.77 0.93	0.79 0.93
4 Solar Turquoise Blue FBL	0.00 0.50	0.00 0.30 0.43 0.54 0.95	0.00 0.55 0.71 Streak	0.00 0.03 0.44	0.00 0.06	0.62 0.86 0.93	0.11 0.54	0.00	0.00 Streak up to 0.14	0.57 0.63 Streak	Streak up to 0.15	0.00	0.00

5 Derma Brown G	0.00 0.83	0.00 0.15 0.31 0.50	0.00 0.53 Streak	0.00 0.40 0.50	0.00 0.07	0.00 0.65 0.84	0.09 0.44 0.54 0.59	0.00 0.05	0.00 0.03 0.11 0.15	0.00 0.57 0.60 0.72 0.78	0.00 0.01 0.04 0.15	0.00 0.79	0.00 0.83
6 Xyline Fast Green B	0.40	0.40 0.27	0.67	0.43 0.48 0.70	0.12	0.81	0.58	0.13	0.29	0.72	0.18 0.24 0.28	0.57	0.64
7 Polar Red 3 B	0.50	0.31 0.42 0.73	0.58 0.77 0.92	0.40 0.55	0.06 0.14 0.21 0.31	0.63 0.71 0.83 0.96	0.52 0.60 0.66 0.75 0.98	0.16 0.28	0.15 0.35 0.41	0.72 0.79	0.32 0.36	0.78	0.80
8 Ranomil Brilliant Red 3 BN	0.39	0.37	0.67	0.41	0.17	0.73	0.60	0.19	0.28	0.73	0.27	0.58	0.60
9 Sandopal Blue	0.48 0.67	0.30 0.44 0.48 0.59	0.59 0.73 0.85 0.92	0.41 0.51 0.68	0.25 0.53	0.61 0.81 0.92	0.67 0.92	0.30 0.56	0.40 0.64	0.78 0.84	0.31 0.35 0.42	0.73 0.84	0.77 0.86
10 Derma Brilliant Red 3 B	0.40	0.40	0.69	0.44	0.18	0.73	0.60	0.20	0.33	0.77	0.27	0.62	0.61

TABLE II

R_F VALUES OF DIRECT DYES ON SILICA GEL G PLATES

Solvent systems: 14 = *n*-butanol–acetone–water–ammonia (0.91) (5:5:1:2)[3]; others as in Table I.

Dye	*Solvent system*					
	2	*4*	*6*	*8*	*11*	*14*
1 Eriochrome Blue Black	0.18 0.33 0.39 Streak	0.59	0.52 0.81 0.89 0.95	0.09 0.23 Streak up to 0.70	0.00 0.18 0.35	0.42 0.65 0.68
2 Chlorozol Orange Brown XS	0.29 0.45 0.56	0.00 0.59 0.79 0.90	0.58 0.69 0.91	0.07 0.25 0.35 0.51	0.00 0.08 0.23 0.29 0.40	0.44 0.63 0.66 0.74
3 Chlorozol Orange Brown	0.29 0.45 0.54	0.00 0.58 0.65 0.79 0.90	0.55 0.78	0.07 0.23 0.35 0.50	0.00 0.09 0.24 0.28 0.42	0.46 0.64 0.73
4 Chlorozol Green BNS	0.24 0.40 0.64 0.98	0.00 0.53 0.56 0.90	0.00 0.49 0.67 0.79 0.91	0.00 0.08 0.22	0.00 0.22 0.26 0.31	0.41 0.57 0.69

TABLE III

R_F VALUES OF PREMETALLIZED DYES ON SILICA GEL G PLATES

Solvent systems: 8 as in Table I; 15 = *n*-butanol–ethanol (95%)–water (8:1:3)[7]; 16 = chloroform–isopropanol–water (1:3:1)[7]; 17 = isoamyl alcohol–pyridine–ammonia (0.91) (8:4:1)[11]; 18 = chloroform–methanol (8:2)[13]; 19 = *n*-butanol–acetic acid–water (2:1:5)[17]; 20 = benzene–isopropanol–acetic acid (6:4:0.1)[13]; 21 = chloroform–ethanol–morpholine (8:1:1)[9]; 22 = chloroform–methyl ethyl ketone–acetic acid–formic acid (8:6:1:1)[18]; 23 = chloroform–methyl ethyl ketone–formic acid (6:8:1)[18].

Dye	*Solvent system*									
	8	*15*	*16*	*17*	*18*	*19*	*20*	*21*	*22*	*23*
1 Metalan Dark Blue	0.00 0.06 0.26	0.40	0.60	0.03	0.00 0.20	0.54	0.00	0.00 0.02	0.00	0.00
2 Neolan Violet Brown BY	0.07 0.45 0.66	0.24 0.59	0.61 0.69 0.75 Streak	0.00 0.04 0.21	0.00 0.05 0.13 0.17	0.45 0.71	0.00 0.14 Streak up to 0.31	0.00 0.02	0.00 0.03	0.00 0.03

TABLE III *(continued)*

Dye	*Solvent system*									
	8	*15*	*16*	*17*	*18*	*19*	*20*	*21*	*22*	*23*
3 Metalan Red S-BR	0.76	0.72	0.79	0.30	0.22	0.88	0.00 0.26	0.03	0.00 0.07	0.00 0.06
4 Dermalight yellow	0.80	0.24 0.33 0.74	0.62 0.83	0.88	0.33	0.93	0.33	0.16	0.42	0.63
5 Metalan Bordeaux S-B	0.00 0.10 0.22	0.23	0.57	0.02	0.00	0.51	0.00	0.00	0.00	0.00
6 Metalan Brown S-GL	0.10 0.17 0.28 0.32 0.67	0.22 0.28 0.58	0.43 0.52 0.59 0.79	0.03 0.07 0.16	0.00 0.07	0.44 0.49 0.55 0.73	0.00	0.00	0.00	0.00
7 Irgalan Red 4 GL	0.81	0.70	0.83	0.84	0.47	0.89	0.51	0.56	0.39	0.57
8 Cibalan Olive 3 BL	0.00 0.74	0.21 0.60	0.10 0.17 0.29 0.60 0.64 0.75	0.00 0.87	0.00 0.29 0.36	0.87	0.00 0.39 Streak	0.00 0.12 0.15	0.00 0.41	0.00 0.56
9 Metalan Brown S-RL	0.81	0.65	0.78	0.80	0.15 0.38	0.87	0.23 Streak	0.23	0.37 0.42	0.54 0.57
10 Metalan Yellow 5 RL	0.72	0.67	0.69	0.17	0.20	0.55 0.72	0.00 0.03 0.16	0.02	0.00 0.04	0.00 0.03
11 Dermalight Brown GRL	0.82 0.88	0.69	0.57 0.73 0.79	0.78 0.85	0.26 0.29 0.33	0.84 0.90	0.30 0.33 0.38	0.20 0.33	0.26 0.38	0.00 0.39 0.52 0.55
12 Ranolan Orange RL	0.87	0.68	0.63 0.75	0.85	0.37	0.89	0.44	0.24	0.41	0.55
13 Dermalight Yellow 2 RL	0.88	0.68	0.74	0.82	0.26	0.87	0.38	0.27	0.25	0.38
14 Dermalight Orange RLN	0.94	0.33 0.79	0.56 0.72	0.19 0.87	0.00 0.26	0.65 0.91	0.00 0.23	0.00 0.11	0.00 0.38	0.00 0.52
15 Dermalight Green 5 GL	0.50 0.96	0.34 0.77	0.56 0.77	0.15 0.83	0.00 0.27	0.64 0.90	0.00 0.25	0.00 0.11	0.00 0.39	0.00 0.52
16 Sandopal Grey WSI	0.98	0.69	0.57 0.64 0.77	0.80	0.00 0.32	0.88	0.00 0.22	0.00 0.23	0.00 0.37	0.00 0.50

TABLE IV

R_F VALUES OF BASIC DYES ON SILICA GEL G PLATES

Solvent systems: 24 = *n*-propanol–acetone–water–acetic acid (4:3:1:0.1)[19]; 25 = pyridine–water (1:2)[20]; others as in Tables I, II.

Dye	*Solvent systems*											
	1	*2*	*3*	*4*	*5*	*6*	*7*	*11*	*14*	*23*	*24*	*25*
1 Malachite Green	0.86	0.95	0.96	0.94	0.84	0.94	0.95	0.93	0.98	0.69	0.91	0.23
2 Methylene Blue G	0.54	0.34 0.39 0.45	0.00 Streak up to 0.36	Streak up to 0.47 0.61	0.26	Streak up to 0.76	0.80	0.15 0.40	0.65 0.70	0.43	0.20 0.32	0.15
3 Fast Rubine 4BN	0.48	0.36	0.69	0.48	0.19	0.61	0.52	0.17	0.62	0.00	0.83 0.89	0.85
4 Auromine O	0.93	0.77	0.87	0.83	0.63 0.74 0.90	0.91	0.90	0.63 0.70 0.76	0.95	0.64	0.76 0.90	0.32

separating funnel before use and wherever two layers were obtained the organic layer was taken. The dye samples were dissolved in methanol (0.1%) and spotted 2 cm above the edge of the TLC plates and developed for 10 cm at 30°C.

RESULTS AND DISCUSSION

From the literature on TLC on silica gel G of dyes used in textiles, food, cosmetics, pharmaceuticals, leather, etc., 86 solvent systems, both single and multi-component, were studied for their usefulness and those solvents giving better resolution as indicated by the R_F values recorded on our TLC plates are given in Tables I–IV.

Acid dyes

Thirteen solvent systems gave encouraging results with regard to their resolution of the individual dyes. In systems 2, 5, 8, 9 and 11, though the resolution was good, the majority of the compounds had R_F values less than 0.5. Systems 7, 12 and 13 gave encouraging results, but the resolution was not good. Systems 1, 3, 4, 6 and 10 gave good results with good resolution (Table I).

Direct dyes

For direct dyes, solvent systems 2, 4 and 6 gave good resolution with different R_F values. System 14 gave encouraging results, but there was litle difference in R_F values. Systems 8 and 11 gave poor resolution with R_F values less than 0.5. Systems 2, 4 and 6 gave good separations (Table II).

Premetallized dyes

In most of the solvent systems, the majority of the dyes moved along with the solvent front. About ten solvent systems were chosen. In the case of systems 18, 20 and 21, the R_F values were less than 0.5. Even though Brown[9] stated that solvent system 21 is good for premetallized dyes, for the dyes studied by us this solvent system did not give good resolution and the R_F values were less than 0.5. Systems 15, 16 and 19 gave good results (Table III).

Basic dyes

Twelve solvent systems gave encouraging results for the basic dyes. Systems 1, 5 and 14 gave the best resolution as indicated by the R_F values (Table IV).

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