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A Semi-Micro Technique for the Extraction and Comparison of Dyes in Textile Fibers

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ABSTRACT: Solid dye samples and extracted dyes from semi-micro samples of textile fibers are separated by using thin-layer chromatography. The extraction process is nondestructive, leaving the fibers intact for further analysis or court presentation. Acid, basic, disperse, vat, direct, and reactive dyes are used in this study. No single solvent system was found that would successfully separate all of these usage classes of dyes, necessitating the introduction of a screening solvent system. The behavior of the dyes in the screening solvent system gives the criminalist an indication of the usage class of dye being examined. Subsequent separation of the dyes is then carried out in appropriate solvent systems. The procedure is a general one that has been used successfully on a variety of natural and synthetic fibers.

KEY WORDS: criminalistics, fibers, dyes

Textile fibers are one of the most commonly occurring types of evidence encountered by the forensic microscopist, and while the continuing development and use of man-made fibers and dyes have made textile fiber analysis increasingly complex, the diversity of dyes and fabrics has increased the forensic science value of such evidence. When comparing textile fibers the criminalist must consider generic origin and subclassification, physical characteristics, and dye content because fibers containing dyes of different composition may appear to be the same color in transmitted and reflected light. There are numerous publications dealing with chemical and instrumental methods for the generic identification of textile fibers, but the subject of fiber dye content has not been completely investigated. The dye content of a fiber represents a very small percentage of the total sample weight and the overwhelming fiber bulk is likely to prevent resolution of lesser dye components in most instrumental methods. In addition, it is doubtful that most instrumental methods will discriminate between structurally similar dyes, or mixtures of dyes, in fibers that are generically alike. Macrae et al [1] have recently reported a high degree of discriminating power in microspectrophotometry of whole fiber samples, and in solution spectrophotometry and thin-layer chromatography of extracted dyes from wool fibers. Thin-layer chromatography (TLC) has the added advantage of disclosing the presence of small amounts of shading colors and intermediates that are often found in the extracted dye mixtures.

There are hundreds of textile dyes in use today and their identification is possible only in laboratories with considerable experience in dye analysis and an extensive collection of

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dyes and dyeings for comparison purposes.² There is little uniformity in the naming of textile dyes, and in most cases dyes are listed by commercial or brand name. The Society of Dyers and Colorists has, for the purpose of reference, classified textile dyes according to their usage class, color, and chemical index (CI) number [2]. Commercial textile dyes are not homogeneous compounds, and rigid standards of purity are not commonly specified; for example, TLC of Orange 1 (CI Acid Orange 20) yielded six colored bands in addition to the main dye component [3]. Most textile fibers contain multiple dyes to obtain a desired shade or color and TLC of a few fibers from a crime scene may produce a very complex dye pattern, thus adding weight to determinations of similarity.

A screening solvent system was developed in which the acid and basic dyes were mobile and could be assigned R_f values. The disperse dyes ran with the solvent front, and the direct, vat, and reactive dyes remained at the origin. The use of this screening solvent system provides a means of eliminating a large percentage of the general population of textile dyes when dye extracts from questioned and known fiber samples are compared. The vat and reactive dyes that remained at the origin in the screening solvent system were generally used on natural fibers and could not be readily extracted because they combined directly with the fiber [4]. Additional solvent systems were developed for the separation of the acid, basic, and disperse dyes. These produced a relatively random distribution of coordinates when R_f versus R_f values of individual dye components were plotted. The extraction process is nondestructive, leaving the fiber intact for further analysis or court presentation [4]. A general approach was developed, with readily available reagents and equipment, affording the criminalist an additional method for textile fiber comparisons.

Experimental Procedure

Materials

Silica gel 60 F-254 plates (Merck), 10 by 20 cm, were used. The extraction solvent system was pyridine/water (53:47 v/v). Two TLC development solvents were used for acid/basic dyes: (1) chloroform/methanol/glacial acetic acid (70:20:10 v/v) and (2) benzene/*n*-butanol/methanol/6*M* ammonium hydroxide (60:10:30:2 v/v). Two systems were also used for disperse dyes: (1) hexanes/benzene/diethylamine/methanol (56:40:5:3 v/v) and (2) cyclohexane/toluene/ethyl acetate/95% ethanol (80:10:10:10 v/v).

The glassware consisted of a Knott 216- by 102- by 229-mm (8½- by 4- by 9-in.) developing tank, 1.6- to 1.8- by 100-mm capillary tubes (Kimble Products), and 10-lambda Drummond microcaps.

The procedure involved 58 dyeings and solid dye samples from four manufacturers (Table 1).

Dye Extraction

Fiber samples were placed in the center of capillary tubes and the pyridine/water extraction solvent was then drawn into the capillary tubes by capillary action to a height of approximately 40 mm. The average fiber sample was approximately 5 mm long and 1 mm in diameter. Both ends of the capillary tubes were sealed by using an alcohol lamp, and the tubes were placed in an oven at 100°C for ½ h. (The amount of solvent was determined by the sample size and the color density of the fiber.) The capillary tubes were then removed from the oven and examined under a low-power microscope to confirm the extraction of the dye from the fiber. Most of the dye had been extracted from the fiber at this point, although the fiber may not have been completely colorless.

The solid dye samples were dissolved in the pyridine/water solvent for spotting.

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TABLE 1—Dyed textile fibers and solid dye samples used in extraction and separation procedure.

Number	Sample	Commercial Name	Chemical Index Name	
1	solid dye	Intracid Pure Blue L ^a	Acid Blue	9
2	nylon fiber	Merpacyl Blue SW ^b	Acid Blue	25
3	solid dye	Amacid Milling Blue 5R ^c	Acid Blue	113
4	nylon fiber	Merpacyl Blue SK ^b	Acid Blue	78
5	solid dye	Amasol Blue 2G ^c	Acid Blue	158
6	solid dye	Amalan Orange RL ^c	Acid Orange	60
7	wool fiber	Merpacyl Orange R ^b	Acid Orange	128
8	solid dye	Merpacyl Yellow 9G ^b	Acid Yellow	49
9	solid dye	Amalan Yellow NLWS ^c	Acid Yellow	151
10	solid dye	Anthraquinone Green GNN ^b	Acid Green	25
11	wool fiber	Merpacyl Red L ^b	Acid Red	151
12	solid dye	Nylanthrene Red B2BSA ^c	Acid Red	266
13	nylon fiber	Merpacyl Red G ^b	Acid Red	337
14	solid dye	Sevron Blue 5GNF ^b	Basic Blue	3
15	Orlon [®] fiber ^d	Sevron Blue BGL ^b	Basic Blue	21
16	Dacron [®] fiber ^e	Sevron Blue ER ^b	Basic Blue	77
17	Orlon fiber ^d	Sevron Brilliant Red B ^b	Basic Red	15
18	solid dye	Sevron Brilliant Red BN ^b	Basic Red	49
19	solid dye	Sevron Red YCN ^b	Basic Red	73
20	Acrilan [®] fiber ^d	Sevron Brilliant Red 2B ^b	Basic Violet	16
21	solid dye	Sevron Yellow R ^b	Basic Yellow	11
22	solid dye	Sevron Yellow 6DL ^b	Basic Yellow	29
23	Dacron fiber ^e	Latyl Yellow 3G ^b	Disperse Yellow	54
24	solid dye	Latyl Yellow 3GB ^b	Disperse Yellow	64
25	solid dye	Latyl Yellow GFSW ^b	Disperse Yellow	67
26	nylon fiber	Latyl Bright Yellow 6GFS ^b	Disperse Yellow	131
27	Dacron fiber ^e	Latyl Orange NST ^b	Disperse Orange	25
28	solid dye	Amacron Orange 1403 ^c	Disperse Orange	37
29	solid dye	Latyl Yellow 5R ^b	Disperse Orange	41
30	Arnel [®] fiber ^f	Latyl Orange 2GFS ^b	Disperse Orange	44
31	Vycron fiber ^e	Latyl Brown Y-FS ^b	Disperse Orange	62
32	solid dye	Mayester Orange R2 ^g	Disperse Orange	80
33	nylon fiber	Latyl Orange 4-RFS ^b	Disperse Orange	98
34	solid dye	Amacron Red BM ^c	Disperse Red	60
35	wool fiber	Latyl Cerise NSN ^b	Disperse Red	60
36	wool fiber	Latyl Brick Red EV ^b	Disperse Red	128
37	nylon fiber	Latyl Scarlet BFSW ^b	Disperse Red	135
38	Verel fiber ^h	Latyl Ruby Red BR-FS ^b	Disperse Red	140
39	solid dye	Intrasil Red FTS ^a	Disperse Red	177
40	solid dye	Intraspase Blue BNG ^a	Disperse Blue	3
41	solid dye	Latyl Blue BCN ^b	Disperse Blue	56
42	Dacron fiber ^e	Latyl Brilliant Blue BG ^b	Disperse Blue	60
43	solid dye	Intrasil Navy Blue ^a	Disperse Blue	79
44	Arnel fiber ^f	Latyl Blue 4-GFS ^b	Disperse Blue	109
45	acetate fiber	Latyl Blue GFE ^b	Disperse Blue	165
46	solid dye	Latyl Blue GFE ^b	Disperse Blue	165
47	solid dye	Intracron Yellow FRA ^a	Reactive Yellow	3
48	solid dye	Intracron Brilliant Red ^a	Reactive Red	4
49	solid dye	Intracron Blue RL-E ^a	Reactive Blue	52
50	solid dye	Intralite Yellow 5GL ^a	Direct Yellow	44
51	solid dye	Intralite Red 5B ^a	Direct Red	81
52	solid dye	Diazo Black BHX ^a	Direct Blue	2
53	solid dye	Amafast 8GLL ^c	Direct Blue	86
54	solid dye	Intralite Blue L ^a	Direct Blue	98
55	solid dye	Amantherne Green BMF ^c	Vat Green	3
56	solid dye	Amantherne Olive TMF ^c	Vat Black	25
57	solid dye	Mayvat Blue BN-MN ^g	Vat Blue	18
58	solid dye	Mayvat Blue D-NM/Y ^g	Vat Blue	...

^aCrompton & Knowles Co.^cAmerican Color and Chemical Corp.^fAcetate fiber.^bE. I. du Pont de Nemours & Co.^dAcrylic fiber.^gOtto B. May Co.^ePolyester fiber.^hModacrylic fiber.

Separation

They pyridine/water solutions containing the extracted and dissolved solid dye samples were spotted with 10-lambda microcapillary pipets on silica gel plates that had been previously dried in an oven for ½ h at 100°C. A total volume of approximately 5 lambda was applied to each spot for the darker colors, while approximately 10 lambda was spotted for the lighter colors. Drying was facilitated by using a hand-held hair dryer. After spotting, the plates were returned to the oven for 15 min, allowed to cool in a desiccator, and developed in the screening solvent system until the solvent front had reached a 5-cm mark. Development took approximately 15 min. The screening solvent system employed was solvent System 1, acid/basic dyes.

Multiple Solvent Systems

Samples of those extracted and dissolved dyes that were separated with the screening solvent system were then spotted on a second plate and developed in solvent System 2, acid/basic dyes.

Samples of those extracted and dissolved dyes that ran with the solvent front in the screening solvent system were spotted on two plates, each of which was developed in a separate solvent system. The solvents were Systems 1 and 2, disperse dyes.

Results and Discussion

The behavior of the extracted and dissolved dye samples in the screening solvent system gives an indication of the usage class of the dye being examined (Table 2).

The solvent systems developed to separate the acid/basic and disperse dyes produce a random distribution of coordinates when R_f versus R_f values of individual dye components are plotted (Figs. 1 and 2).

In many cases there are actually reversals of the R_f values of dye components in the two systems, and as a result when a pair of dye mixtures gives identical patterns in both systems one can make a strong presumption that it is the same dye mixture.

Samples 34 and 35, and 45 and 46, represent the same dyes in solid form and as extracted from fiber samples. The solid dye samples were dissolved in the pyridine/water solvent without heating. The resulting R_f values of the chromatographed dyes were identical, indicating no chemical change in the dye structure resulting from the extraction process. Sample 19 (Basic Red 73) was the only acid/basic dye that did not separate in the screening solvent system.

In actual case work the extracted dyes from questioned and known fiber samples are spotted on the same plate so that a side-by-side comparison of the chromatographed dye components may then be made. Spotting questioned and known dyes on the same plate

TABLE 2—Behavior of dyes developed in the screening solvent system (SSS).

Identification Number	Usage Class	Development in SSS
1-13	acid	separated
14-18	basic	separated
19	basic	remained at origin
20-22	basic	separated
23-46	disperse	ran with solvent front
47-49	reactive	remained at origin (some bleeding)
50-54	direct	remained at origin
55-58	vat	remained at origin

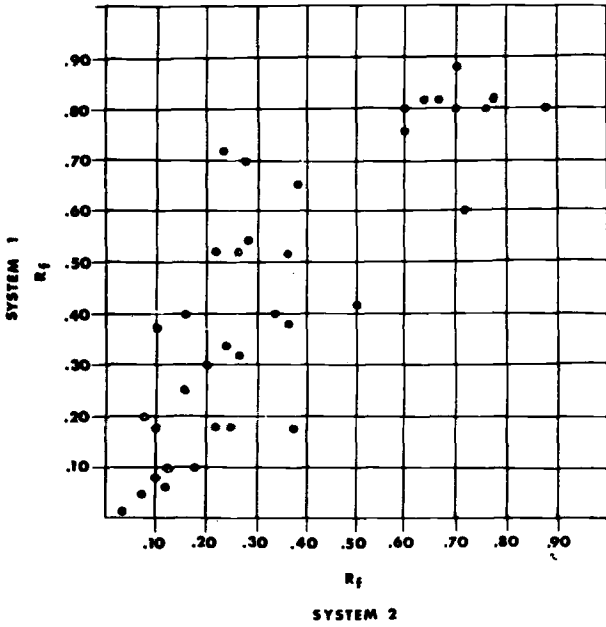


FIG. 1—Coordinates (R_f) of disperse dyes chromatographed in two solvent systems.

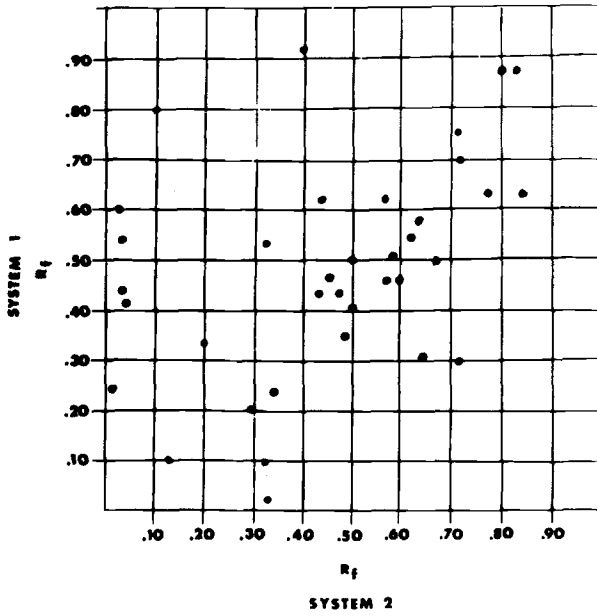


FIG. 2—Coordinates (R_f) of acid and basic dyes chromatographed in two solvent systems.

will also negate the effects of the many variables inherent in TLC as both samples are chromatographed under identical conditions.

Internal standards, or standard dyes, are not used when dye extracts from questioned and known fiber samples are compared, and R_x values³ are of use only when actual dye identification is attempted, which is beyond the scope of most forensic science laboratories. In addition, the method deals with usage classes of dyes, each of which contains structurally dissimilar compounds [5].

The method has been used successfully in cases involving a variety of natural and synthetic fibers.

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³Where R_x is the R_f of the compound divided by the R_f of the internal standard.