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EXTRACTION AND ANALYSIS OF DISPERSE DYES ON POLYESTER TEXTILES

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SUMMARY

The analysis and extraction of disperse dyes from polyester textile materials is described. Extraction with boiling chlorobenzene was found to be the best routine procedure for sample preparation. A new high-performance liquid chromatographic method of analysis is described and whilst this supplements a number of recommended thin-layer chromatographic methods it has significantly better resolution and sensitivity. The procedure is designed for forensic comparison of polyester textiles but would be suitable for control of dye matching and blending during manufacture.

INTRODUCTION

Disperse dyes are used extensively to colour polyester and cellulose acetate fabrics. Many disperse dyes, like most other dyes, are blends of several components. The blends may differ because of the production process, in which side reactions occur, and as a result of blending, which is often used to obtain a particular shade. A knowledge of the composition of dye blends is needed for the proper control of dye manufacture as well as for characterizing commercial products. Furthermore the analysis of dyes, extracted from textile fibres, can be very valuable in forensic investigations involving textile evidence.

Thin-layer chromatography (TLC) of disperse dye mixtures has been carried out on silica gel by a number of workers and some very successful systems have been recommended[1,2].The two systems that have been most useful in our laboratory were recommended by Dousheva *et al.*[1]. These are *n*-hexane–ethyl acetate–acetone (5:4:1) and light petroleum (b.p. 60–80°C)–tetrahydrofuran–acetone (6:2:1).

The main purpose of this work was to evaluate existing methods for the extraction and analysis of disperse dyes on polyester fabrics and, if necessary to modify these into a routine procedure for examining samples of a forensic nature. It was my intention to select those TLC systems that provided the most discrimination between the commercial disperse dyes that were available to us. During preliminary studies I found that the solvent used to extract the dye from the fabric interfered in subsequent TLC and so high-performance liquid chromatography (HPLC) was considered as an alternative approach. An efficient HPLC method which gives better qualitative dis-

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crimination than the corresponding TLC system was developed and this new method has the advantage of providing quantitative results. This HPLC method is a valuable complement to the TLC methods for forensic work and may be useful to manufacturers for quality control and blend characterisation.

EXTRACTION OF DYES

In order to analyse the dyes from small quantities of fibres it is essential that the dyestuff be efficiently extracted from the fibres and that all components of the dye remain unchanged in the extract. Disperse dyes are readily extracted from polyester fibres by boiling in dimethyl formamide (DMF). During initial investigations I noted that boiling DMF, although completely extracting most of the dyes studied, caused slight changes in the colour of some dyes. Unfortunately DMF also interfered in TLC analyses causing the dyes to move as crescent shaped spots which differed significantly in R_F value from the corresponding DMF free samples. DMF could be removed from the TLC plate by heating but some fading of the dyes occurred.

A number of solvents have been used to extract disperse dyes from polyester. Those most frequently used include DMF, acetic acid and chlorobenzene[3]. A study was undertaken to find solvents that extracted the dyes but did not interfere in subsequent TLC. The following systems were examined:

(A) extraction with boiling dimethyl formamide
(B) extraction with boiling amyl acetate
(C) extraction with boiling cellosolve
(D) extraction with methylene chloride on a water bath
(E) multiple extraction with methylene chloride on a water bath
(F) extraction with chloroform on a water bath
(G) extraction with boiling acetic acid
(H) extraction with boiling chlorobenzene.

DMF and chlorobenzene extracted most of the dye from the samples. Chlorobenzene was not only an efficient extractant but did not interfere in subsequent TLC. It could be spotted onto TLC plates to give compact spots and is therefore ideal for extracting disperse dyes from polyester fibres.

Methylene chloride was found to be an efficient extractant at relatively low temperatures and therefore did not cause significant thermal decomposition. It is easy to carry out multiple extractions with methylene chloride and to concentrate the extract by evaporation. Chloroform was an effective extractant for many dyes but was relatively inefficient for some.

Acetic acid was an effective extractant but it did change the R_F values of some dyes appreciably. Since some disperse dyes are weak bases this effect is probably due to the acid nature of the extractant. Acetic acid is corrosive and I prefer to use the chlorinated hydrocarbons but in some applications acetic acid may be useful.

The extractants listed, with the exception of DMF, did not interfere in subsequent TLC provided the plate was not developed for 15 min after spotting. The interference caused by DMF can be eliminated if the extract is evaporated to dryness on a water bath and the dye dissolved in ethyl acetate or acetone.

Acetone, ethyl acetate and methanol were also tested and were found to be unsuitable as extractants.

It is recommended that extraction of the sample with chlorobenzene on a hot plate or methylene chloride on a water bath be tried first. Repeated extractions may be necessary to increase yields and the extracts should be concentrated to give a solution that is distinctly coloured. If this procedure is unsatisfactory it is recommended that the sample be extracted in boiling dimethyl formamide followed by evaporation of the solvent.

Some polyester fibres are soluble in boiling DMF and chlorobenzene but the dyes are readily extracted from these fibres with methylene chloride.

ANALYSIS OF DYES

Thin-layer chromatography

TLC was performed on 20 × 20 cm Merck aluminium sheets pre-coated with silica gel 60 F_{254}. The extracted dyes were applied to the plate in chlorobenzene, acetone, ethyl acetate, methylene chloride or chloroform solution and the plate developed in acetone for about 1 cm beyond the point of application to produce a sharp, narrow band. The plate was dried and then developed in the solvents listed in Table II. This predevelopment is not necessary if the dyes are spotted in chlorobenzene solution.

The dyes investigated were extracted from an ICI sample chart of Dispersol dyes. These dyes are listed in Table I. Several samples of fabric which had been dyed with mixtures of dyes were obtained from ICI (Sydney, Australia) and these were examined in a similar manner.

The TLC systems studied are listed in Table II. Systems 1 and 2 were recommended by Dousheva *et al.*[1] and are very good for general separations. I found that the three systems, ethyl acetate–hexane; tetrahydrofuran–hexane, and chloroform were the most uncorrelated. The system acetone–hexane was strongly correlated with the ethyl acetate–hexane system but had lower resolution. In general when these three system (*i.e.*, systems 3, 5 and 7) were used on the sample better discrimination was obtained than when system 1 or 2 was used. System 7 gave the best resolution of the yellow dyes tested but required two developments to obtain adequate mobility. Poor mobility was obtained with some non-yellow dyes in system 7. Better mobility of these dyes was obtained with system 6 but resolution of the yellow dyes was reduced considerably. Furthermore, system 6 was quite sensitive to ethyl acetate concentration, and since small changes caused significant change in relative R_F values, it is not recommended. R_F values for the major components in some typical dyes are shown in Table I. Many of the dyes contained trace components and in cases where the major dyes were not separated the trace components were often different. For example, Dispersol red C-3B had a trace component at R_F value 0.21 but Dispersol rubine C-B did not. Since the eluents are relatively non-polar, significant changes in R_F will occur with variation in activity of the plates. We find that it is convenient to use prefab plates that have not been stored under any special conditions and therefore new boxes of plates which are normally more active should be left stand a few days after opening.

Although some disperse dyes not considered in this study may have higher or lower R_F values, the recommended solvents are easily adapted to these situations. If the dyes do not migrate sufficiently, increase the proportion of polar constituent until

TABLE I
TLC AND HPLC OF DISPERSE DYES
The colours and R_F values for the major components are tabulated but most dyes also contained trace components. TLC: Solvents 3, 4, 5 and 7 according to Table II. HPLC: conditions as described in text.

Dye	*Colour of spots*	*TLC: R_F value in solvent*				*HPLC: Retention time (min)*
		3	*4*	*5*	*7*	
Scarlet CG	Red	0.29	0.53	0.35	0.30	3.44
Navy D-2G-133	Violet	0.15	0.46	0.31	0.11	5.44
Black BT	Orange	0.58	0.62	0.53	0.51	1.09
	Yellow	0.42	0.52	0.46	0.06	–
	Blue	0.39	0.52	0.38	0.20	2.06
Orange CB	Orange	0.49	0.59	0.47	0.25	1.28
Black D-2B	Violet	0.15	0.46	0.31	0.11	5.38
	Yellow	0.42	0.54	0.42	0.06	1.66
	Orange-brown	0.05	0.30	0.14	0.01	7.78
Yellow D-3R	Yellow	0.42	0.54	0.41	0.06	1.69
Yellow C-4R	Yellow	0.41	0.54	0.40	0.04	1.69
Scarlet BR	Red	0.36	0.56	0.46	0.43	2.84
Rubine C-B	Maroon	0.29	0.50	0.41	0.30	3.44
Red D-2G	Red	0.12	0.46	0.28	0.04	5.91
Red C-3B	Maroon	0.29	0.49	0.39	0.26	3.56
Navy C-4R	Violet	0.40	0.54	0.44	0.63	2.44
	Blue	0.48	0.58	0.51	0.67	1.91
Yellow D-7G	Yellow	0.45	0.55	0.49	0.51	
Yellow C-5G	Yellow	0.46	0.54	0.49	0.50	
Yellow CT	Yellow	0.50	0.54	0.54	0.34	
Yellow BA	Yellow	0.46	0.48	0.48	0.12	
Yellow D-3R	Yellow	0.47			0.03	
Yellow C-4R	Yellow	0.46			0.02	

TABLE II
ELUENTS FOR TLC

System	*Composition*	*Proportions*
1	hexane–ethyl acetate–acetone	50:40:10
2	light petroleum (b.p. 60–80°C)–tetrahydrofuran–acetone	60:20:10
3	hexane–ethyl acetate	40:60
4	hexane–acetone	50:50
5	hexane–tetrahydrofuran	40:60
6	chloroform–ethyl acetate	90:10
7	chloroform (developed twice)	

a suitable eluent is obtained. Alternatively, if the dyes move too rapidly a lower proportion of polar solvent is required.

It is recommended that systems 3, 5 and 7 be used for routine tests and if the dye mixture contains a yellow dye, system 7 may be best. If these systems do not give adequate separation try two-dimensional TLC or systems 1 and 2. Adjust the eluent composition to increase or decrease mobility when necessary.

High-performance liquid chromatography

Liquid chromatography wass carried out on a silica column with a mobile phase consisting of programmed mixtures of ethyl acetate and hexane.

The liquid chromatograph employed in this study was an Altex Model 312 (including the Model 400 solvent programmer) and equipped with an Altex/Hitachi Model 155-10 variable-wavelength UV–VIS detector. The column was 250 × 3.2 mm stainless steel packed with LiChrosorb Si-60 having a particle size of 10 μm. The analytical column was protected by a small pre-column, 40 mm long packed with silica 60 (Merck, Darmstadt, G.F.R.) having a particle size of about 400 μm.

The mobile phase was a mixture of hexane and ethyl acetate varied automatically by the solvent programmer. The solvent composition was linearly programmed from 25 to 100% ethyl acetate in 20 min, held at 100% for 4 min and then automatically reset to 25% ethyl acetate. A flow-rate of 1 ml/min was used. Aliquots (10 μl) of the dye extracts were injected and the solvent program started.

The wavelength setting of the detector should be selected for the colour of the dye examined and for routine forensic analysis it is recommended that the sample be monitored at 600, 500 and 420 nm. These wavelengths will detect blue, red and yellow dyes respectively and therefore cover the visible range but in particular cases other wavelengths may be more appropriate.

The chromatogram of a mixture of disperse dyestuffs is shown in Fig. 1. The peaks are well formed and the resolution of the system is illustrated. When examined by TLC the following partial separations were obtained. Dyes 8 and 12 were just resolved, dyes 9 and 11 appeared as a single spot, dyes 6 and 12 partly overlapped as did dyes 2 and 10. By contrast dyes 9 and 11 were partly resolved and the other pairs

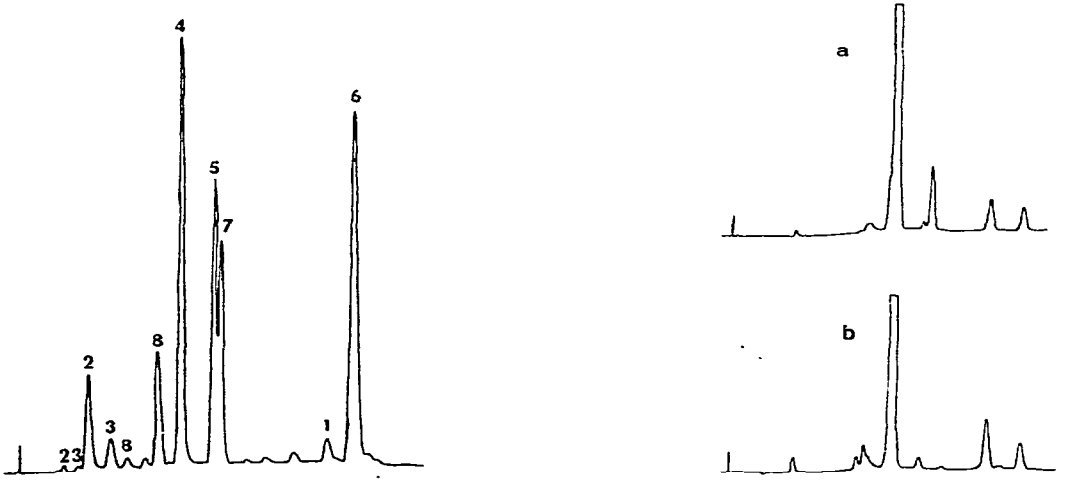

Fig. 1. Chromatogram of a mixture of Dispersol dyes with detector set at 500 nm. 1 = Navy D-2G-133; 2 = orange CB; 3 = yellow D-3R; 4 = scarlet B-R; 5 = rubine CB; 6 = red D-2G; 7 = red C-3B; 8 = navy C-4R. Dyes were obtained from ICI Australia.

Fig. 2. Chromatograms of (a) red C-3B and (b) same dyestuff but extracted from material on the ICI Dispersol dyes sample chart. The detector was set at 500 nm.

were well resolved by HPLC. These results clearly demonstrate the better resolution of HPLC over TLC.

The chromatograms shown in Fig. 2 illustrate the sensitivity of HPLC. When the same quantity of dye was applied to a TLC plate the smaller peaks were not all visible thus indicating the limit of detection for TLC. It is possible to increase the detector sensitivity so that about one tenth of the amount of dye could be detected above baseline noise. The HPLC method is therefore about ten times more sensitive than TLC for the red dye used here and for other colours such as yellow the differential is even greater.

The chromatograms in Fig. 3 are of extracts from two dark blue fabrics that were indistinguishable by eye. The dyes were found to be quite different by HPLC and TLC, although sample a produced a very streaky TLC.

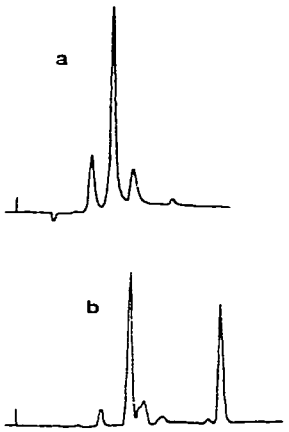

Fig. 3. Chromatograms of blue dyes extracted from pieces of material. The detector was set at 600 nm. (a) Cloth dyed with Dispersol navy B-T; (b) cloth dyed with a mixture of Dispersol navy C-4R and Dispersol green C-6B.

The wavelength of the detector can be set so that dyes of a particular colour are detected or the sample may be monitored at preselected wavelengths, such as 600, 500 and 420 nm so that all dyes are detected. A multi-channel detector, capable of monitoring these three wavelengths simultaneously would be most useful. Fig. 4 illustrates the results obtained when a black dye was monitored at the three wavelengths.

The retention times for a number of dyes are listed in Table I.

Selection of either TLC or HPLC for a particular application would depend on availability of equipment and the needs of the laboratory. For forensic work I believe the two techniques to be supplementary and would recommend that the HPLC method be used in combination with TLC systems 5 and 7.

I prefer the HPLC method to the corresponding TLC system (*i.e.*, system 3) because it has the following features.

(a) Slightly better resolution is obtained and this is particularly important when there are large differences in the amounts of dyes present.

(b) Better sensitivity and consequently smaller amounts of dye can be examined. Some dyes fade on TLC plates thus reducing the sensitivity.

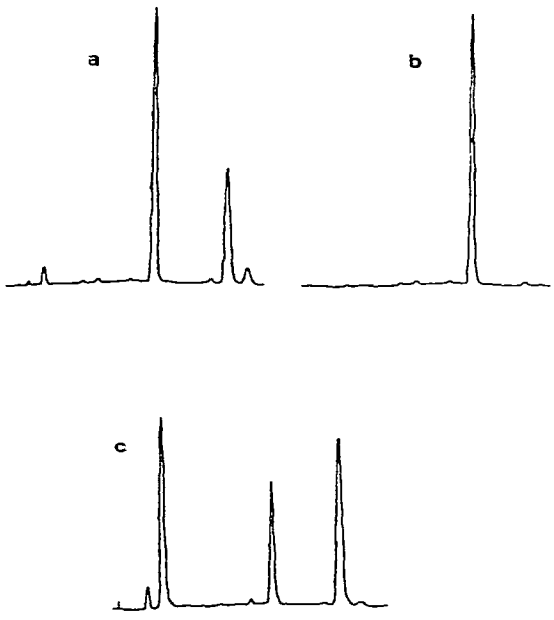

Fig. 4. Chromatograms of Dispersol black D-2B with detector set at (a) 500 nm, (b) 600 nm and (c) 420 nm.

(c) The results are quantitative.

(d) Trace components are easily observed.

(e) Certain colours, particularly the yellow, are poorly visible on TLC plates. This natural bias of the human eye is not observed with photometric detectors and all dyes may be detected provided an appropriate wavelength is chosen.

(f) A more permanent record of results is obtained.

(g) If two dyes have the same R_F value they are difficult to analyse by TLC. In contrast, dyes of different colours which have the same retention time may be quantitated with HPLC provided their spectra do not interfere. For example, many green dyes are mixtures of blue and yellow dyes and both dyes may be quantitated by HPLC even when they have the same retention time.

A number of alternative HPLC systems (incorporating acetone, tetrahydrofuran and/or chloroform in the mobile phase) and a reversed-phase system were evaluated but the system reported gave the best shaped peaks and the best overall resolution.

It is important to ensure that all the sample will migrate through the HPLC column in a reasonable time and that the sample does not contaminate the column. We protect our analytical column with a small pre-column packed with chromatographic grade silica gel. If the samples are particularly dirty it may be necessary to carry out some sort of preliminary clean-up procedure. The dye, in ethyl acetate solution, may be passed through a Waters Assoc. (Milford, MA, U.S.A.) Sep-Pak silica cartridge or a pasteur pipette packed with TLC-grade silica 60. The samples should be washed with sufficient ethyl acetate to elute all the components of interest.

SUMMARY OF RECOMMENDED PROCEDURES

Extraction of dyes

Extraction is conveniently carried out in small beakers (5 ml) or test tubes (50 × 6 mm). Cover the sample (fibres or small pieces of fabric) with a small quantity (0.5–3 ml) of chlorobenzene and bring to the boil on a hot plate or in an oil bath. Boil for 5 min or until most of the dye has been extracted. A beaker of paraffin oil is a convenient oil bath for small test tubes. Single fibres may be extracted with a drop of chlorobenzene in sealed capillary tubes. Alternatively, extract the sample with a little methylene chloride or chloroform on a heated water bath for 5–10 min and decant the coloured solution. Repeat the extraction with fresh solvent if necessary. Combine the extracts and evaporate to give a strongly coloured solution. Examine the extract by TLC and HPLC if available.

Thin-layer chromatography

Use Merck aluminium sheets pre-coated with silica gel 60 F_{254} and the developing solvents shown in Table II. Apply the extracted dyes to the plate directly. Pre-develop the plate in acetone for about 1 cm beyond the point of application to produce a sharp, narrow band. Dry the plate and develop in solvents 3, 5 and 7. This pre-development step is not necessary when chlorobenzene solutions are spotted onto the plate. If the dye is yellow system 7 will give the best resolution. If insufficient separation is obtained try two-dimensional TLC with systems 3, 5 and 7 or try systems 1 and 2. Adjust the eluent composition to increase or decrease mobility if required.

High-performance liquid chromatography

Use a 25-cm column packed with 10-μm LiChrosorb Si-60 and a 4-cm pre-column packed with 400-μm chromatography-grade silica gel. Set up the chromatograph to linearly program the ethyl acetate–hexane solvent mixture from 25 to 100% ethyl acetate in 20 min, hold at 100% for 4 min and then automatically reset to 25% ethyl acetate. Set the flow-rate to 1 ml/min. Select the appropriate detector wavelength for the colour examined or monitor at 600, 500 and 420 nm. Inject 10 μl of dye solution. The attenuation is normally set at 0.1 a.u.f.s. and the sample may need to be diluted.

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