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Capillary Zone Electrophoresis Analysis of Chlorotriazinyl Reactive Dyes in Dyebath Effluent

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ABSTRACT

In order to determine the feasibility of reusing/recycling monochlorotriazinyl reactive dyes in the dyeing of cellulosic fibres, methodologies were established for the identification and quantification of residual organic species derived from monochlorotriazinyl dyes using capillary zone electrophoresis. This enabled information to be secured concerning the level of hydrolysis occurring in the dyebath as well as the relative amounts of coloured species present at the end of both dyeing and subsequent rinsing. © *1997 Elsevier Science Ltd*

Keywords: reactive dyes, cotton, effluent, analysis, capillary electrophoresis.

INTRODUCTION

Reactive dyes are currently one of the most widely used classes of colorant on cellulosic fibres, combining high wet fastness with relative ease of application [1,2] and allowing the generation of a wide range of hues of high purity. In recent times, such has been the expansion of reactive dye production, that the dyes are now one of the largest selling classes, both by volume and value of sales [3].

The introduction of environmental legislation over recent years has lead to an increase in the costs of dyeing through the imposition of consent limits pertaining to the discharge of process effluent [4–6]. Typically, the costs incurred in the treatment of effluent produced in the batchwise reactive dyeing of cotton are similar to the total cost of the water consumed in the

process [7]. The ability to recycle and/or reconstitute exhausted dyebaths offers potential to reduce processing costs by reducing the amounts of dye, water, auxiliaries and energy used whilst simultaneously reducing effluent costs. Such potential economic benefits combined with the increased awareness of the consumer towards environmental issues has promoted consideration of the feasibility of the re-use and recycling of process water and reclamation of dyes from such effluent [8–14].

In order to reuse or reconstitute exhausted dyebaths two approaches can be made. One such approach is to remove colour from the exhausted dyebath and so allow the dyebath to be reused for subsequent dyeing. In order to decolourise a residual dyebath, the dye must either be destroyed or removed; various techniques for decolourising dyebaths have been described including reverse osmosis, [15] ozonolysis [16,17] and charged ultrafiltration [18].

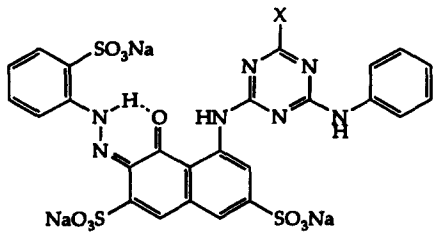
An alternative approach is to reuse the dye in subsequent dyeing, this being possible by spectrophotometric determination of the concentration of dye in the residual dyebath followed by reconstitution to the desired level using fresh dye. Acid dye–polyamide [19,20], disperse dye–polyamide and disperse dye–polyester [21] systems are examples where reconstitution has been shown to be possible. In order to reuse the dye, the dyeing behaviour of the residual dye should be identical to that of the original dye; [22] consequently, this particular approach requires the establishment of a suitable methodology for the identification and quantification of species present in the residual dyebath liquor.

In this context, whilst analyses of dyes to determine impurities during dye synthesis have been carried out using thin layer chromatography (TLC), high performance liquid chromatography (HPLC), gas chromatography (GC) [23] and, more recently, capillary electrophoresis (CE), [24] little work has been carried out to identify components present within a dyebath effluent possibly due to separation difficulties. Capillary electrophoresis is a powerful analytical technique and the purpose of the work presented in this paper was to determine whether the technique could be used to separate and quantify residual species present within a residual monochlorotriazinyl reactive dyebath so that information about the extent of dye hydrolysis and, thus, the possibility of reusing/recycling the dyebath could be secured.

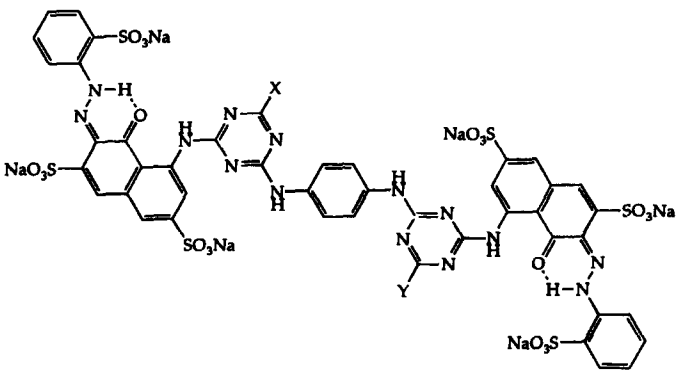
EXPERIMENTAL

Materials

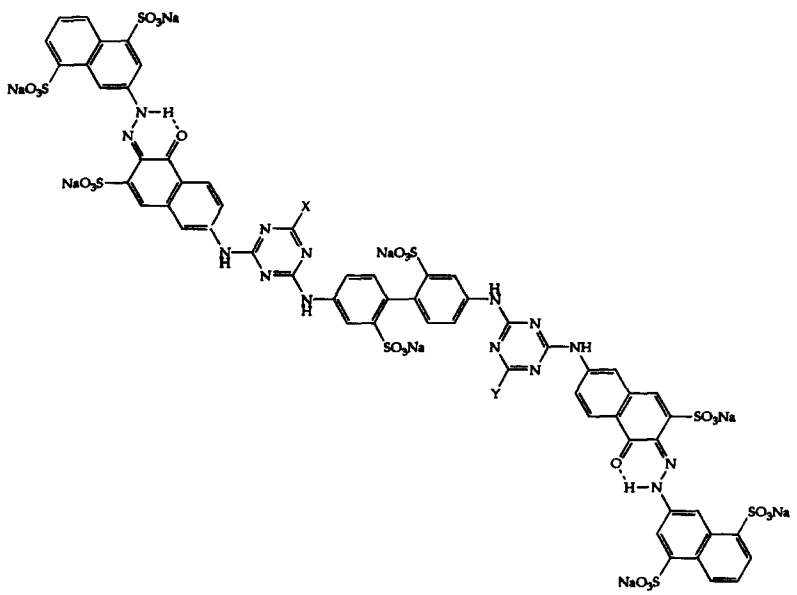
A sample of bleached, unmercerised woven cotton (124 g m^{-2}) was used. Commercial samples of Procion Red H3B (C.I. Reactive Red 3; I [25]),



Procion Red HE-3B (C.I. Reactive Red 120; II [26])



and Procion Orange HER (C.I. Reactive Orange 84; III [27]),



were used, each generously supplied by Zeneca Colours.

Procedures

Preparation of hydroxy analogues of monochloro- and bis-(monochlorotriazinyl) dyes

The hydroxytriazinyl analogues (I: X = OH; II and III: X,Y = OH), which represented the hydrolysis products of the monochlorotriazinyl and bis-(monochlorotriazinyl) dyes used, were required as internal standards in electrophoretic analysis. The hydroxytriazinyl analogues were prepared using a method developed from that suggested by Taylor *et al.* [28], employing treatment with diazabicyclooctane (DABCO) under aqueous alkaline conditions as follows.

The unpurified commercial product (5.0 g) was dissolved in distilled water (50 cm^3) and the solution adjusted to pH 12 by means of aqueous 1 M sodium hydroxide solution. DABCO (0.5 g) was added and the mixture stirred magnetically at ambient temperature, the pH of the mixture being maintained at 12 by means of an automated pH controller linked to a peristaltic pump that enabled the addition of aqueous 1 M sodium hydroxide solution as required. The extent of dye hydrolysis was monitored using TLC (eluent: 0.880 ammonia: 1-propanol: 2-butanone 1:1:1 (vol.); stationary phase: silica gel on an aluminium support, particle size 2–25 μm, layer thickness 200 μm). In all cases, reaction appeared to have reached completion after a period of about 18 h, after which time, the pH of the solution was adjusted to pH 7 by the addition of a solid mixed phosphate buffer [1:2 Na_2HPO_4:KH_2PO_4] and the solution then dialysed against distilled/deionised water for 12 h prior to freeze drying. The complete hydrolysis of each of the dyes to the required products was subsequently verified via CZE and Fast atom Bombardment Mass Spectrometry (FAB-MS).

Dyeing

All dyeings (6% omf) were carried out in sealed stainless steel dyeing tubes of 250 cm^3 capacity housed in a Roaches fluidised bed laboratory dyeing machine, using the method shown in Fig. 1. At the end of dyeing the dyed fabric was removed from the dyebath and excess liquor squeezed from the sample and retained. The combined residual dyebath liquor was allowed to cool to ambient temperature and neutralised by the addition of mixed phosphate buffer (2:1 Na_2HPO_4:KH_2PO_4), so as to preclude further hydrolysis of the residual dye. The neutralised residual liquor was then dialysed against distilled water for 12 h.

The dyed sample was dried in a circulating hot-air oven at 40°C and then rinsed, either once, twice or three times, as follows. The dry dyeing was treated in 200 cm^3 of distilled water at 80°C for 15 min in a sealed stainless steel dyeing tube of 250 cm^3 capacity housed in a Roaches fluidised bed

laboratory dyeing machine. At the end of rinsing, the fabric was removed from the water and excess liquor squeezed from the sample and retained. The combined residual rinse liquor was allowed to cool to ambient temperature and neutralised by the addition of mixed phosphate buffer (2:1 Na_2HPO_4:KH_2PO_4) and the neutralised residual liquor then dialysed against distilled water for 12 h. In the case of the dyeings which were rinsed twice and three times using the above method, the rinsed sample was dried, as described above, prior to further rinsing.

Capillary zone electrophoresis

CZE analyses were performed using a Dionex CES-1 System fitted with a variable wavelength visible absorbance detector. Data manipulation was carried out employing Waters Baseline Chromatography Software (Version 8.10) running on a personal computer. The following methodology was employed in the analysis of residual liquors via CZE.

Capillary	polyimide-coated unmodified fused silica of length 60 cm and internal diameter 75 μm;
Mobile Phase	10mM dipotassium hydrogen phosphate, pH 9.2 (liquid chromatography grade obtained from Aldrich);
Detection	visible absorbance;
Current	30 A;
Polarity	positive;
Injection	gravity: 100 mm 10 s^{-1}.

Prior to installation, the column was activated using aqueous 0.5 M NaOH solution. Following activation, the column was rinsed sequentially with deionised/distilled water and mobile phase. Residues remaining on-column following each analysis were conveniently removed from the system by rinsing the column, sample destination vial and source vial with mobile phase introduced by the application of pneumatic pressure.

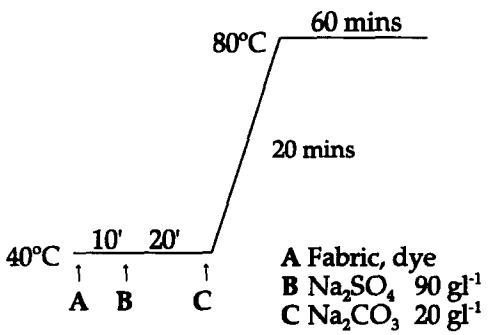
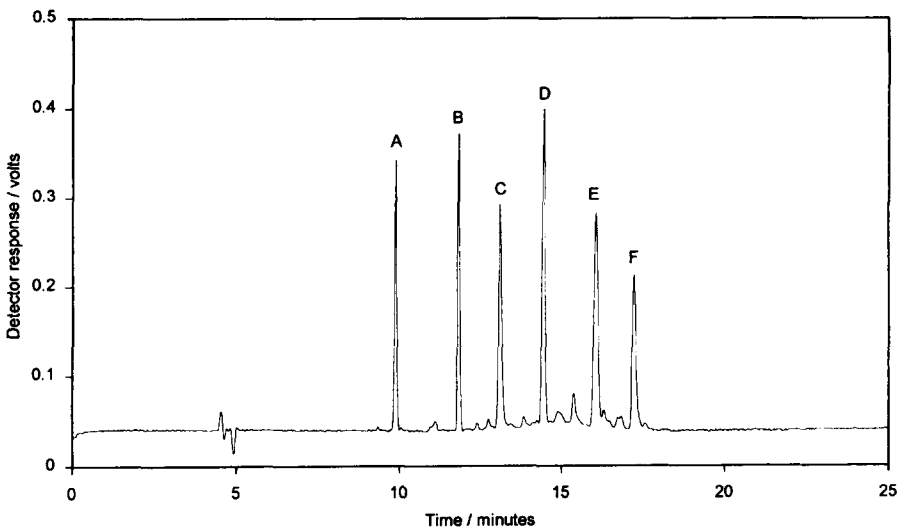


Fig. 1.

Whilst operating under the above conditions, the dialysis of liquor samples prior to analysis was found to be advantageous in promoting column selectivity and enhanced resolution of the species present. The liquors were dialysed against a large excess of distilled water (*ca.* 3 litres) for at least 12 h, replacing the dialysate at least twice. This procedure was found to be sufficient to reduce the ionic strength of the samples to a level where zone broadening and excessive joule heating were prevented. During the dialysis procedure, the loss of dye through the membrane was found to be minimal; changes in the state of hydrolysis of the sample were also considered negligible during dialysis. This was verified separately via observation of freshly prepared solutions of the unhydrolysed dye, dialysed under identical conditions. Loss of the monochlorotriazinyl dyes was found to be $<4\%$ and loss of the bis-(monochlorotriazinyl) dyes to be typically $<2\%$.



A = CI Reactive Red 3, (X=Cl)

B = CI Reactive Red 3, (X=OH)

C = CI Reactive Red 120, (X=Cl, Y=Cl)

D = CI Reactive Red 120, (X=OH, Y=OH)

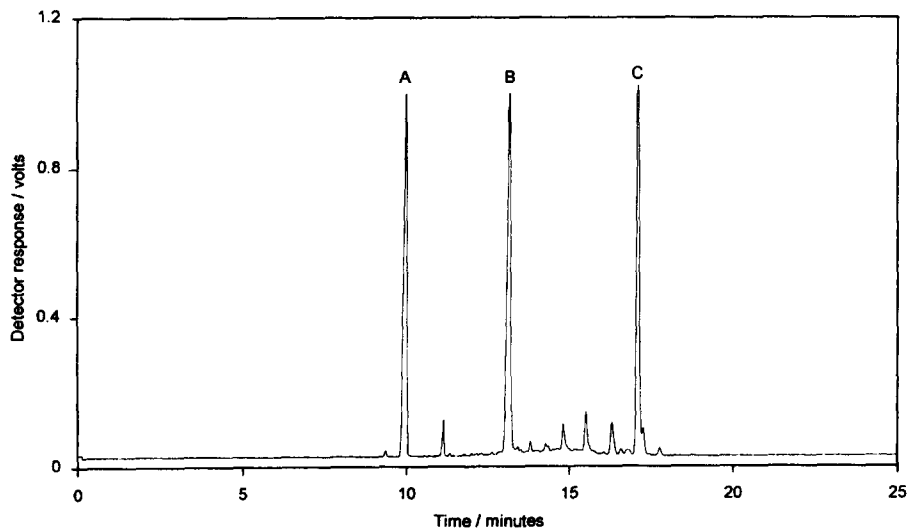
E = CI Reactive Orange 84, (X=Cl, Y=Cl)

F = CI Reactive Orange 84, (X=OH, Y=OH)

Fig. 2. Electropherogram of reactive and hydrolysed dyes.

RESULTS AND DISCUSSION

Figure 2 indicates that efficient separation of both the original and the fully hydrolysed chlorotriazinyl dyes was achieved using CZE. An electropherogram of the dyebaths before dyeing (Fig. 3) reveals that each of the three dyes was present in its parent chlorotriazinyl form and that hydrolysates were not present, as expected at this stage in the dyeing process. At the end of the dyeing process, this situation was reversed as demonstrated by Fig. 4 which shows the relative amounts of the parent monochlorotriazinyl (MCT) and the monohydroxytriazinyl (MHT) analogues of C.I. Reactive Red 3, as well as the parent, MCT-MHT and bis-MHT analogues of both C.I. Reactive Red 120 and C.I. Reactive Orange 84 present in the residual dyebaths obtained for the three parent dyes. From Fig. 4 it is evident that original, partially and fully hydrolysed dye was present in the dyebaths at the end of dyeing, indicating that incomplete dye hydrolysis had occurred during application of the dyes to cotton.



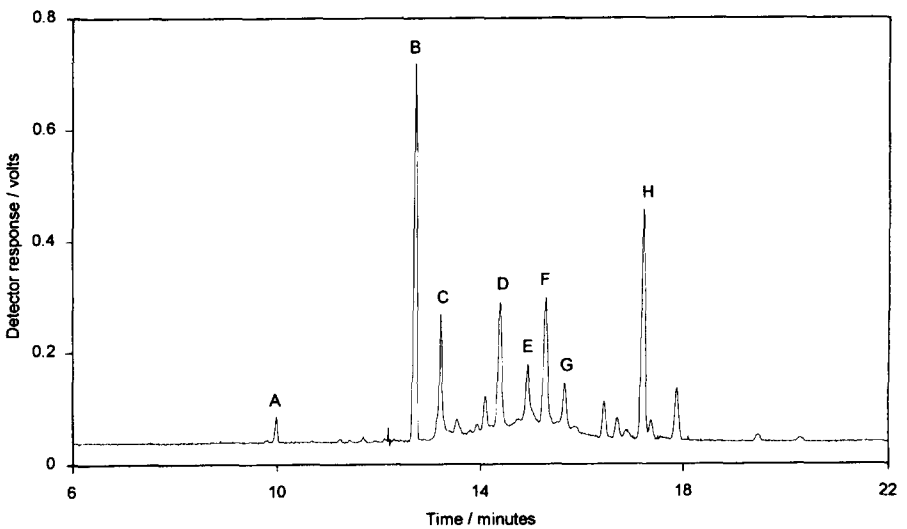
A = CI Reactive Red 3, (X=Cl)

B = CI Reactive Red 120, (X=Cl, Y=Cl)

C = CI Reactive Orange 84, (X=Cl, Y=Cl)

Fig. 3. Electropherogram of dyebaths before dyeing.

Figure 5 represents an electropherogram of the liquor obtained at the end of the first rinse procedure that followed dye application. It is evident that dye hydrolysis was incomplete and that the relative concentration of MCT and bis-(MCT) analogues was apparently greater than that of the MHT, MCT-MHT and bis-(MHT) derivatives, suggesting the possibility of preferential dye hydrolysis having occurred within the dyebath. Figures 6 and 7 represent electropherograms of the liquors secured at the end of the second and third rinse procedures following dye application, which again clearly show that



A = CI Reactive Red 3, (X=Cl)

B = CI Reactive Red 3, (X=OH)

C = CI Reactive Red 120, (X=Cl, Y=Cl)

D = CI Reactive Red 120, (X=Cl, Y=OH)

E = CI Reactive Red 120, (X=OH, Y=OH)

F = CI Reactive Orange 84, (X=Cl, Y=Cl)

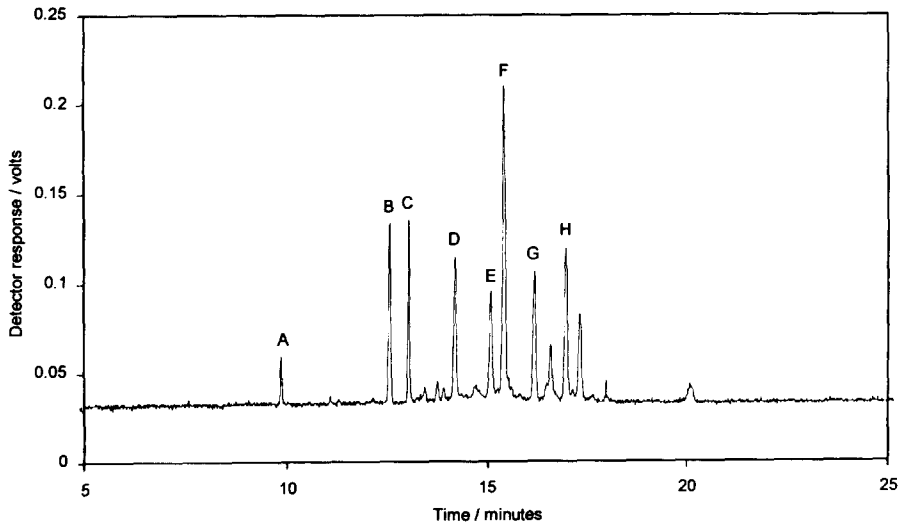
G = CI Reactive Orange 84, (X=Cl, Y=OH)

H = CI Reactive Orange 84, (X=OH, Y=OH)

Fig. 4. Electropherogram of dyebath at the end of dyeing.

incomplete hydrolysis of the dyes occurred within the rinse liquor and, also, the possibility of preferential hydrolysis having occurred during dyeing.

The electropherograms displayed indicate that separation of reactive dyebath effluents and subsequent rinse liquors can be carried out with great efficiency using CZE. The results are of interest when dealing with multiple dye mixtures in a dyebath, as information concerning relative dye uptake can be studied in detail. Assessment of the level of dye hydrolysis occurring in the bulk dyebath and also the relative amounts of hydrolysed/unhydrolysed dye



A = CI Reactive Red 3, (X=Cl)

B = CI Reactive Red 3, (X=OH)

C = CI Reactive Red 120, (X=Cl, Y=Cl)

D = CI Reactive Red 120, (X=Cl, Y=OH)

E = CI Reactive Red 120, (X=OH, Y=OH)

F = CI Reactive Orange 84, (X=Cl, Y=Cl)

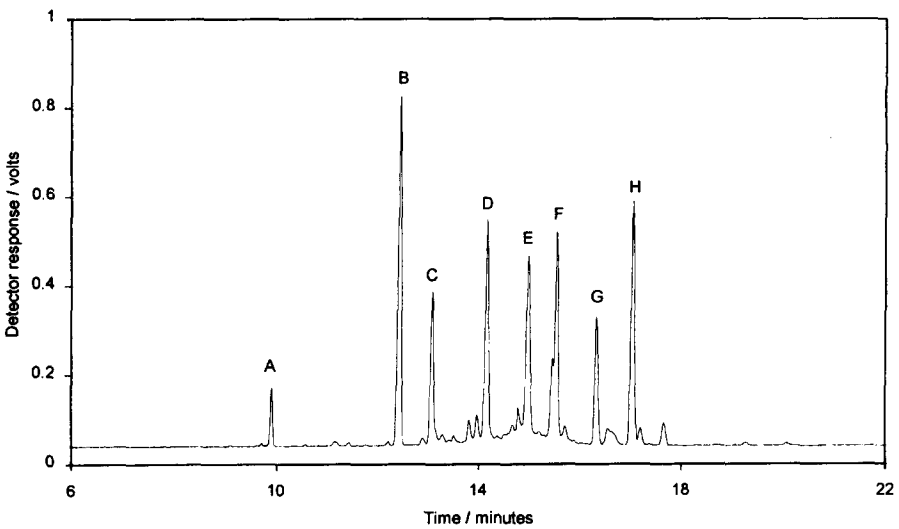
G = CI Reactive Orange 84, (X=Cl, Y=OH)

H = CI Reactive Orange 84, (X=OH, Y=OH)

Fig. 5. Electropherogram of first wash liquid.

present upon subsequent rinsing are of interest, especially with the present concern over the levels of adsorbable organo halogens (AOXs) present within disposable effluent [29].

The information presented in Figs 2–7 can be used to determine whether dyeing is complete, the ability to reuse or recycle dyes and also to indicate areas for possible improvement. If more information can be obtained as to the efficiency of a dyeing, effluent loads produced during reactive dyeing could be further reduced.



A = CI Reactive Red 3, (X=Cl)

B = CI Reactive Red 3, (X=OH)

C = CI Reactive Red 120, (X=Cl, Y=Cl)

D = CI Reactive Red 120, (X=Cl, Y=OH)

E = CI Reactive Red 120, (X=OH, Y=OH)

F = CI Reactive Orange 84, (X=Cl, Y=Cl)

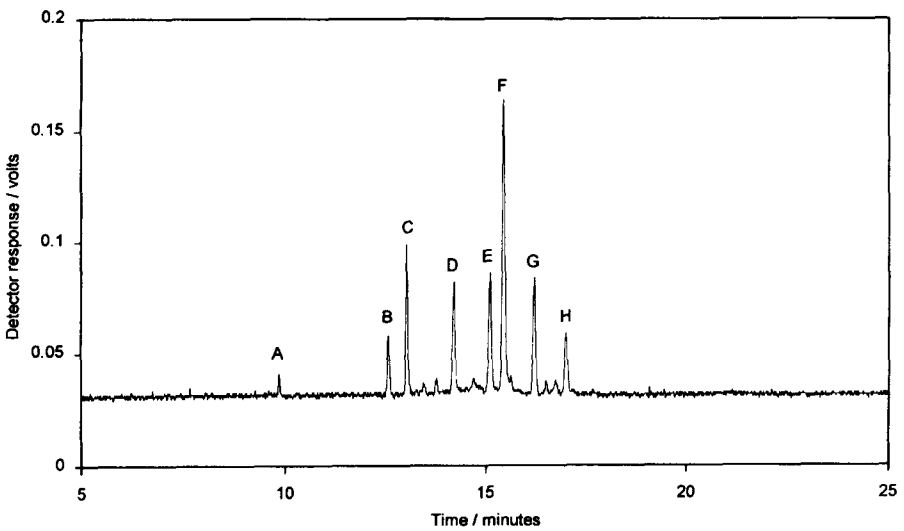
G = CI Reactive Orange 84, (X=Cl, Y=OH)

H = CI Reactive Orange 84, (X=OH, Y=OH)

Fig. 6. Electropherogram of second wash liquid.

CONCLUSIONS

CZE provided a suitable methodology for analysing both the residual dye-baths obtained from the application of chlorotriazinyl reactive dyes to cotton and the residual rinse liquors. The technique afforded excellent separation and reproducibility with respect to relative peak areas. One disadvantage that became apparent early in the study was the need to dialyse all residual dye solutions so as to remove electrolyte which, otherwise, impaired the efficiency of separation. Further develoments in the methodology, namely an



A = CI Reactive Red 3, (X=Cl)

B = CI Reactive Red 3, (X=OH)

C = CI Reactive Red 120, (X=Cl, Y=Cl)

D = CI Reactive Red 120, (X=Cl, Y=OH)

E = CI Reactive Red 120, (X=OH, Y=OH)

F = CI Reactive Orange 84, (X=Cl, Y=Cl)

G = CI Reactive Orange 84, (X=Cl, Y=OH)

H = CI Reactive Orange 84, (X=OH, Y=OH)

Fig. 7. Electropherogram of third wash liquid.

increase in concentration of components in the mobile phase, coupled with efficient capillary cooling, may overcome this problem. Clearly, CZE has proven to be a useful tool for the analysis of reactive dye liquors providing essential information on the hydrolysis behaviour of the dye during its application to cotton and the subsequent rinsing of the dyeing.[28]

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