Determination of black dyes from cotton and wool fibres by capillary zone electrophoresis with UV detection: application of marker technique

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Abstract

The development of capillary zone electrophoresis (CZE) for routine screening of black reactive dyes and black acid dyes, isolated from cotton and wool materials, is described. Detection was based on UV absorption. The electrolyte solution used was 3-(cyclohexylamino)-1-propanesulphonic acid buffer (pH 10.8), which was chosen to maintain the current at a low level under high voltages. Pretreatment of the cotton and wool samples involved extraction with NaOH or NH_3, respectively. With the CZE technique the dyes were detected at very low concentration levels. The dye components were identified by using a newly developed marker technique. The marker components for the calculations were UV-absorbing phenylacetic acid, benzoic acid and meso-2,3-diphenylsuccinic acid. The marker technique proved effective in determining the electrophoretic mobilities of the analytes, since the relative standard deviations of the migration indices and the electrophoretic mobilities for the analytes were below 0.6%.

1. Introduction

Recently, there have been numerous publications on the determination analysis of dyes and other components in the dye-manufacturing and dye-using industries [1–3]. The methods described have mainly been applied to pure standard dye components.

The excellent separation efficiency of capillary zone electrophoresis (CZE) has created possibilities for the separation and determination of many dyes and other components employed in the dye industry [4–7]. The dyes must be isolated from the matrix and be detectable by ultraviolet

(UV) or fluorescence (FL) detection with routinely available instrumentation.

Acid (anionic) dyes contain hydrophilic groups. These dyes are mostly used for colouring polyamide and wool fibres and are usually substituted by sulphonic acid groups. The dyes are attached to the fibres with ionic interactions, Van der Waals forces and in special cases with coordination bonds. Reactive dyes, which are also anionic, form only covalent bonds with cotton fibres. The most important groups of reactive dyes are those which can form bonds with cellulose fibres containing hydroxyl groups or with protein fibres containing amines, sulphates and thiols or with polyamide fibres [8].

Anionic dyes are rapidly separated by capillary

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zone electrophoresis (CZE) [1]. This means that in these systems electrolyte solutions which have a high ionic strength and high pH must be used, but the high ionic strength increases the current and thus the Joule heating inside the capillary increases. However, when organic buffers are present the current remains low even when electrolytes with high ionic strengths are used.

In this study, CZE was used for the separation of black reactive dyes and black acid dyes isolated from cotton and wool, respectively. Dyeing industry laboratories often do not want to give information about the dyes they used in manufacturing processes and it is therefore sometimes difficult to identify the colour mixtures used. However, in our work the marker techniques developed in our laboratory [9,10] improved the reliability of the migration values of the dye components.

2. Experimental

2.1. Apparatus

In this study, two different capillary electrophoresis instruments were applied for separation of the dye components. One consisted of a ChemStation 3D Capillary Electrophoresis Model G 1600 AX (Hewlett-Packard, Avondale, PA, USA), an HP Ergo Ultra VGA monitor, an HP Vectra 486/66 XM workstation and an HP DeskJet 510 printer. The system was controlled by Windows Soft, which was modified to the HP system. Detection was performed by diode-array detection (DAD), with collection of the spectra of peaks in the electropherograms from 190 to 600 nm. The detection wavelengths were 195, 214, 225, 217 and 254 nm. Injection was performed hydrostatically by pressure at 50 bar for 30 s. The voltage was 25 kV. The capillary cassette was temperature controlled by air pressure. The separation temperature was 22°C.

The other apparatus was a Model 2050 P/ACE capillary electrophoresis system with UV–Vis detection and a liquid cooling system for the capillary (Beckman Instruments, Fullerton, CA, USA). The detection wavelength was at 254 nm.

Injection was performed hydrodynamically by pressure (0.500 p.s.i.) for 9 s. The voltage was 18 kV. The separation temperature was 22°C.

CZE runs were carried out in fused-silica capillaries (50 μm I.D. and 360 μm O.D.) (Composite Metal Services, Worcester, UK, or Hewlett-Packard). The lengths of the uncoated capillaries were 58 or 68 cm (50 or 60 cm to the detector).

All calculations were carried out with MAT-LAB (Mathworks, Sherborn, MA, USA). The algorithms were described earlier [10].

2.2. Materials

3-(Cyclohexylamino)-1-propanesulphonic acid (CAPS) was obtained from Sigma (Poole, UK), NaOH, ammonia solution (25%), methanol and benzoic acid from Merck (Darmstadt, Germany) and phenylacetic acid (99%) from Aldrich (Steinheim, Germany). meso-2,3-Diphenylsuccinic acid (TCI, Trade Mark, Japan) was a gift from Toyohashi University (Toyohashi, Japan).

Distilled water was purified with a Water-I apparatus (Gelman Sciences, Ann Arbor, MI, USA) and was further purified by filtering through 0.45-μm membranes (Millipore, Molsheim, France). All chemicals and solvents were used as received.

Black cotton and wool materials and yarns were obtained from the Crime Laboratory (Vantaa, Finland) or were purchased from drapery shops in Helsinki.

2.3. pH adjustment

The pH of the electrolyte used was adjusted with a Model 3030 pH meter connected to an electrode (Jenway, Felsted, UK) containing 4 M KCl and saturated calomel. The pH meter was calibrated with standard buffer solutions (pH 7.0 and 10.0) purchased from Radiometer (Copenhagen, Denmark).

2.4. Electrolyte solutions

A 0.14 M electrolyte solution for CZE separations was prepared from CAPS. The solution

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┌─────────────────┐
│  Cotton Fibres  │
└─────────────────┘
         │
1.5% NaOH (25 min, 100°C)
         │
         │
┌─────────────────┐
│  Reactive dyes  │
└─────────────────┘
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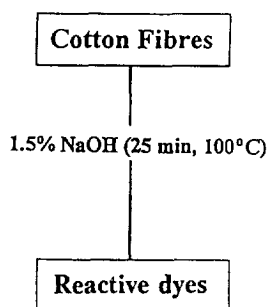
Fig. 1. Extraction of black dyes from cotton materials.

was prepared by adding 3.0982 g of CAPS reagent to about 70 ml of Water-I purified water, adjusting the pH to 10.8 by adding about 5 ml of 0.1 M NaOH and diluting to 100 ml. The solution was filtered through 0.45-μm filters (Millipore) and degassed before use.

2.5. Pretreatment of the samples

The samples were 0.25–5.5 cm² of black cloth (cotton or wool) and 2.5 mm–1 cm thread (wool). The samples were pretreated according to Figs. 1 and 2. A 10% (v/v) concentration of methanol was added to the samples to obtain a better stacking effect by decreasing the ionic strength in the sample for narrower component zones. Most of the solvent was evaporated and the precipitate was dissolved into 300 μl of water–methanol (1:1, v/v).

Since the dyes were extracted into a very small

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┌─────────────────┐
│  Wool Fibres    │
└─────────────────┘
         │
  NH₃/ water (4:3)
  (50 min, 100 °C)
         │
         │
┌─────────────────┐
│  Acidic dyes    │
└─────────────────┘
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Fig. 2. Extraction of black dyes from wool materials.

volume of solvent, the ionic strengths were too high for direct injection of the sample into the capillary electrophoretic system. Therefore, the samples were always diluted with water (1:10) to improve the zone shapes and electropherograms. Before injection, each sample was filtered through 0.45-μm PTFE filters (Gelman Sciences, Ann Arbor, MI, USA).

3. Results

Usually, pyridine is used as a solvent to extract dyes. However, this study showed that it can be changed to ammonia solution, which is a more convenient solvent for routine work. For surface-treated materials, pyridine can extract those dyes which form salts when extracted with ammonia. It is suggested that pyridine has a catalytic effect, which ammonia does not have, because it only forms ammine complexes with the coloured components.

Figs. 3–5 show the electropherograms of dye components extracted from black cotton and wool fibres. Satisfactory separations were achieved after base extraction from the materials. When the sample sizes were large, the electropherograms were easily screened. However, when the material was surface-treated, the concentrations of the dye components were low, which made the screening of the electropherograms difficult.

The determination of dyes is usually very simple, but black dyes at low concentration levels are difficult to extract and screen with chromatographic separation techniques, since they have different solubilities in water. A high ionic strength was used to help the extraction. However, the extraction had a negative effect on the analysis using CZE. Therefore, the absolute migration times of the components changed from run to run, although the temperature was controlled (Figs. 3–5). Further, even the relative retention times calculated by dividing the absolute migration time of the unknown component by that of the reference component (benzoic acid) changed. The main reason was the high
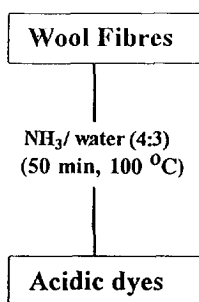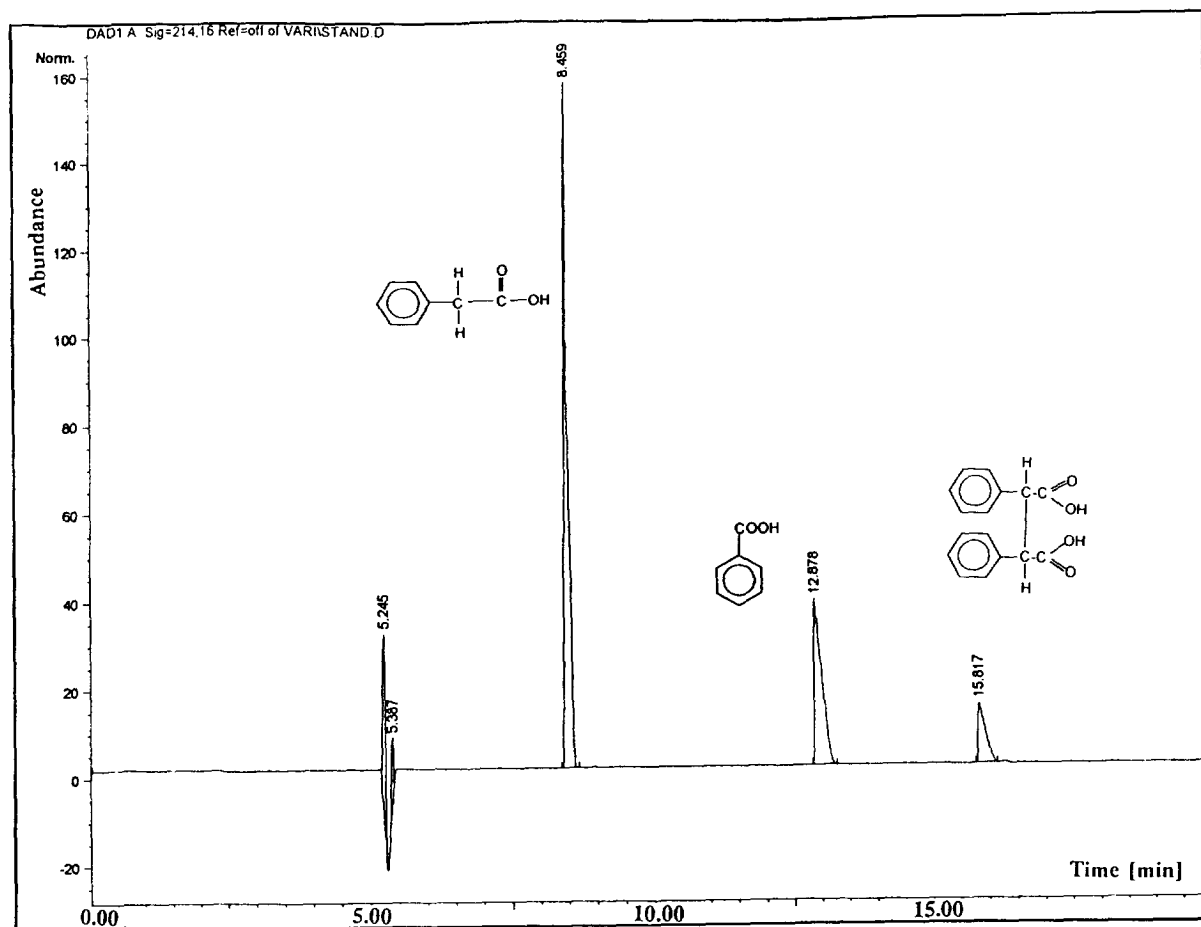
Fig. 3. Electropherogram of the marker compounds obtained with the HP ChemStation 3D capillary electrophoresis Model G 1600 AX instrument. Conditions as described under Experimental.

ionic strength in the sample and therefore the times of the separated component zones changed during the separation processes. This made the screening of the electropherograms very difficult, especially when the components were present at very low concentrations. For these reasons, two different marker techniques were introduced. The results showed that more reliable screening for the dye components could then be achieved. The technique was superior especially when two component zones were overlapped.

The repeatability of the CZE technique was tested by injecting the samples six times. Table 1 shows that the relative standard deviations of the migration indices [10] for two components are

below 0.6% and for five components below 0.3%. Also, repeatabilities of electrophoretic mobilities [9] for the analytes (K.S.D. mostly below 0.3%) were superior to absolute migration times (Table 2). These values show that by using the two marker techniques the analyses are more repeatable than when using only absolute migration times (average relative standard deviations 1–2%). In this study, the limits of screening (wavelength 214 nm) were obtained by using 0.5 cm × 0.5 cm textile [signal-to-noise ratio (S/N) = 20] or 2.5 mm thread (S/N = 9), so that all the components present at high concentrations can still be monitored reliably in the electropherograms.
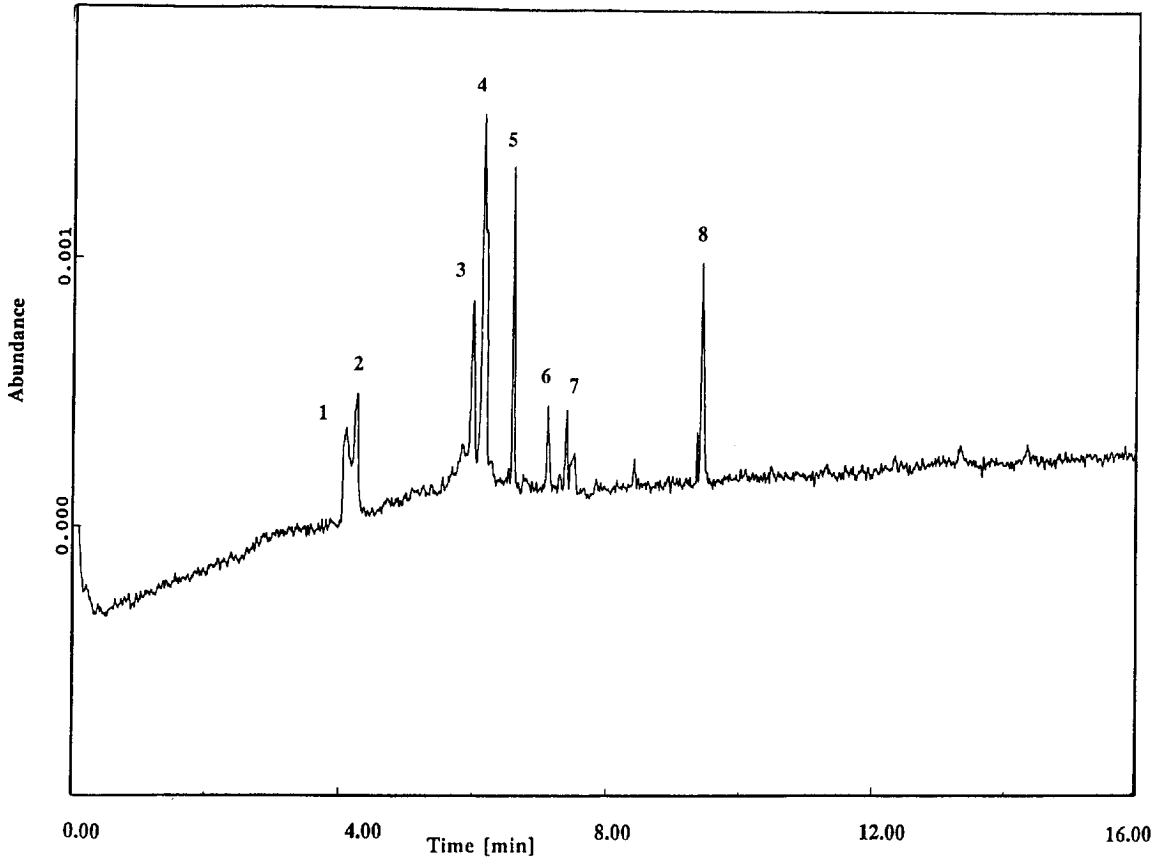
Fig. 4. Electropherogram of a reactive dye from black cotton material (Switzerland) obtained with the Beckman Model 2050 P/ACE instrument.

4. Conclusion

A CZE method with UV detection for screening black dyes from cotton and wool materials has been developed. The method is suitable for the separation processes because of the excellent separation efficiency of CZE. The advantages of the CZE technique could be exploited when the pH method stacking was used.

The recoveries of the black dyes were good (the colour was totally transferred into the solvent), although no reference materials from the manufacturers could be obtained. The repeatabilities of the extraction processes, which were detected for a reference with an UV–Vis

dual-beam spectrophotometer, were also very good.

The calculated results were obtained by two marker techniques using phenylacetic acid, benzoic acid and meso-2,3-diphenylsuccinic acid as the marker compounds. The use of these carboxylic acids increases the reliability of the separation procedures. The migrations of the dye components were repeatable within a day. Therefore, the peaks in the electropherograms could be easily identified according to the index and the UV spectra taken from the two slopes and the apex of the peaks. No systematic changes in migration indices (Table 1) were found, which confirms that the method is accur-
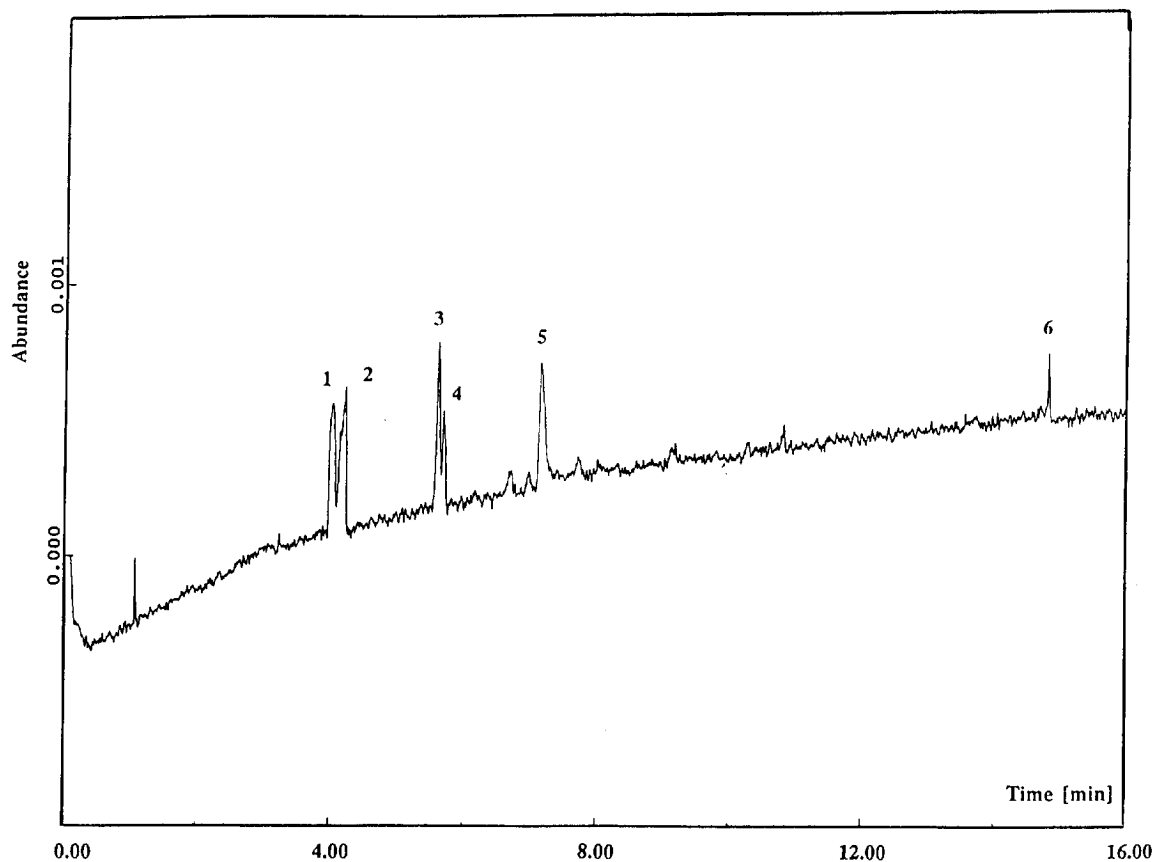
Fig. 5. Electropherogram of an acid dye from black wool material (Finland) obtained with the Beckman Model 2050 P/ACE instrument.

Table 1
Repeatability of the analysis in terms of absolute migration times and migration indices for dye components in black materials

Sample[a]	Compound No.	Absolute migration time (min)	R.S.D. (%)	Migration index	R.S.D. (%)
A	1	4.03	2.32	663.81	0.51
	2	4.20	2.35	691.46	0.22
	3	5.40	2.15	990.32	0.15
	4	6.12	2.02	1060.68	0.24
	5	7.00	0.78	1292.97	0.08
B	1	4.00	0.34	701.10	0.24
	2	4.19	0.38	733.39	0.11
	3	5.61	1.20	983.61	0.07
	4	6.01	0.38	1053.19	0.47
	5	6.73	0.71	1254.99	0.54
	7	7.20	0.35	1342.20	0.14
	8	9.76	0.46	1819.60	0.11

[a] Relative standard deviations within-day (six replicates). A, sample as in Fig. 5; B, sample as in Fig. 4.

Table 2
Average values and standard deviations for absolute migration times and electrophoretic mobilities determined with the marker technique using three aromatic carboxylic acids

Compound[a]	Migration time (min)			Mobility[b] (10^{-8} m^2 V^{-1} s^{-1})		
	$t_{a,ave}$	S.D.	R.S.D. (%)	μ_{ep}(ave)	S.D.	R.S.D. (%)
1	4.06	0.08	1.9	−1.1196	0.0552	0.321
2	4.23	0.06	1.5	−1.2726	0.0492	0.267
3	5.93	0.09	1.5	−1.9265	0.0108	0.258
4	6.10	0.10	1.4	−2.0276	0.0085	0.213
5	6.54	0.08	1.2	−2.3889	0.0072	0.202
6	7.05	0.08	1.1	−2.7296	0.0030	0.109
7	7.35	0.03	1.0	−2.9187	0.0265	0.091
8	9.93	0.07	0.78	−4.1461	0.0072	0.073

Sample as in Fig. 4.
[a] Data obtained with Beckman 2050 instrument.
[b] Calculations according to Ref. [9].

ate. However, good results were only obtained when the samples were analysed fresh within one day, to maintain the accuracy of the results.

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