Journal of Chromatography, 586 (1991) 73–84
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 590

Analysis of dyes extracted from textile fibers by thermospray high-performance liquid chromatography–mass spectrometry☆

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(First received May 14th, 1991; revised manuscript received June 28th, 1991)

ABSTRACT

Thermospray high-performance liquid chromatography was used to analyze a series of disperse dyes extracted from polyester and cellulose acetate fibers, a basic dye from orlon fiber and a vat dye from denim. Molecular characterization of each dye was obtained from the extract of a single fiber, 5–10 mm long. This was achieved by high-performance liquid chromatographic separation followed by thermospray mass spectrometry of the separated dye.

INTRODUCTION

Textile fibers found at a crime scene can be used as physical evidence in a wide range of crimes, such as crimes that involve personal contact in which cross-transfers may occur between the clothing of suspect and victim.

The value of fibers as evidence will depend on the forensic scientist's ability to narrow their origin to a limited number of sources, or even to a single source. The mass production of textiles makes this a difficult task. It is therefore of major importance to be able to define all the possible characteristics of fibers found at the scene of the crime, in order to compare them with fibers found on the suspect.

An important part of forensic fiber examination involves the characterization of textile dyestuffs. Three techniques are commonly used for this purpose: thin-layer chromatography (TLC) [1–4], visible microspectrophotometry [1,3,5] and high-performance liquid chromatography (HPLC) [2,6–8].

There are several limitations in the use of these techniques. Microspectrophotometry is applicable to small fibers, but considers only the spectral characteristics of the dyes, which show considerable variation. In this method chemical and structural differences between dyes are not taken into consideration. TLC requires a relatively large amount of extracted dye, which may not always be available on a single short fiber. Also, the reproducibility of dye separation by TLC is not satisfactory [7]. HPLC has a much better sensitivity and reproducibility than TLC for analysis of dyes, but characterization of a dye is based on retention time only. As hundreds of dyes are used in the textile dying industry, ambigu-

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ous results might be obtained because of overlapping of HPLC peaks and similar retention times for different dyes. Also, some dyes are complex mixtures and most dyes are not chemically pure, resulting in additional chromatographic peaks. Even multi-wavelength detection does not provide an absolute answer to this problem.

Thermospray high-performance liquid chromatography–mass spectrometry (HPLC–TSP-MS) has been found to be a selective technique for separation, identification and quantification of dyes in various matrices [9–15].

Disperse dyes, based on anthraquinone and azo compounds, are the major coloring agents in use with polyester and cellulose acetate fabrics. As synthetic fibers are of major importance in the textile industry, mainly disperse dyes were selected to study the application of HPLC–TSP-MS in the identification of dyes extracted from textile fibers.

EXPERIMENTAL

Samples

Most dyed fibers were taken from pattern cards supplied by the manufacturers. The blue denim fibers were taken from an old pair of blue jeans. Details of the studied samples and structures are given in Table I and Fig. 1. A single fiber, 5–10 mm long, was pushed to the bottom of a 5-cm-long glass capillary tube of 2 mm O.D. and 0.8 mm I.D., previously sealed at one end by heating. For the disperse dyes, 5 μl of chlorobenzene were added, and the tube sealed and heated at 100°C for 15 min [6]. After cooling, the tube was opened and the extract was injected into the HPLC–MS system. For the basic dye, formic acid at room temperature was used, and for the vat dye formic acid with heating at 80°C for 1 min was used. Standards of Indigo (Vat Blue 1) (dye content ~99%) and Disperse Orange 13 (dye content ~15%) were purchased from Aldrich (Milwaukee, WI, USA). They were dissolved in acetone, and 5 μl of each were injected into the HPLC–MS system.

Equipment

The instrument used was a 4510B Finnigan-MAT (San Jose, CA, USA) HPLC–MS system with a thermospray interface and ion source. The HPLC

TABLE I

INVESTIGATED SAMPLES

C.I. = Color Index.

Commercial name of dye	C.I. name	C.I. number	M.W.	Structure[a]	Type of fiber	Manufacturer
1.5% Serisol Fast Yellow GD	Disperse Yellow 3	11855	269	**1**	Diacetate	Yorkshire
2.0% Serisol Fast Yellow PL 150	Disperse Yellow 9	10375	274	**2**	Diacetate	Yorkshire
1.2% Resolin Yellow 5GS	Disperse Yellow 5	12790	324	**3**	Polyester	Bayer
0.72% Dispersol Orange B-A Grains	Disperse Orange 1	11080	318	**4**	Polyester	ICI
0.6% Serilene Orange 5R300	Disperse Orange 1	11080	318	**4**	Polyester	Yorkshire
0.6% Serilene Orange 2RL200	Disperse Orange 25	11227	323	**5**	Polyester	Yorkshire
0.72% Dispersol Orange B-2R 200 Grains	Disperse Orange 25	11227	323	**5**	Polyester	ICI
1% Resolin Orange F3R 200%	Disperse Orange 25	11227	323	**5**	Polyester	Bayer
2.2% Resolin Orange RL	Disperse Orange 13	26080	352	**6**	Polyester	Bayer
0.6% Serilene Yellow Brown 2RL 150	Disperse Orange 37	–	391	**7**	Polyester	Yorkshire
1.5% Serisol Brilliant Red X3B 200	Disperse Red 11	62015	268	**8**	Diacetate	Yorkshire
0.6% Serisol Fast Scarlet BD 200	Disperse Red 1	11110	314	**9**	Diacetate	Yorkshire
0.6% Serisol Fast Crimson BD 150	Disperse Red 13	11115	348	**10**	Diacetate	Yorkshire
0.6% Serilene Red Brown R-FS 150	Disperse Brown 1	11152	432	**11**	Diacetate	Yorkshire
1.5% Serisol Brilliant Blue BGN 300	Disperse Blue 3	61505	296	**12**	Diacetate	Yorkshire
1.0% Resolin Blue BBLS	Disperse Blue 165	–	405	**13**	Polyester	Bayer
1.0% Yoracryl Yellow RL	Basic Yellow 28	–	309	**14**	Orlon	Yorkshire
Indigo	Vat Blue 1	73000	262	**15**	Denim	Levi Strauss

[a] See Fig. 1.

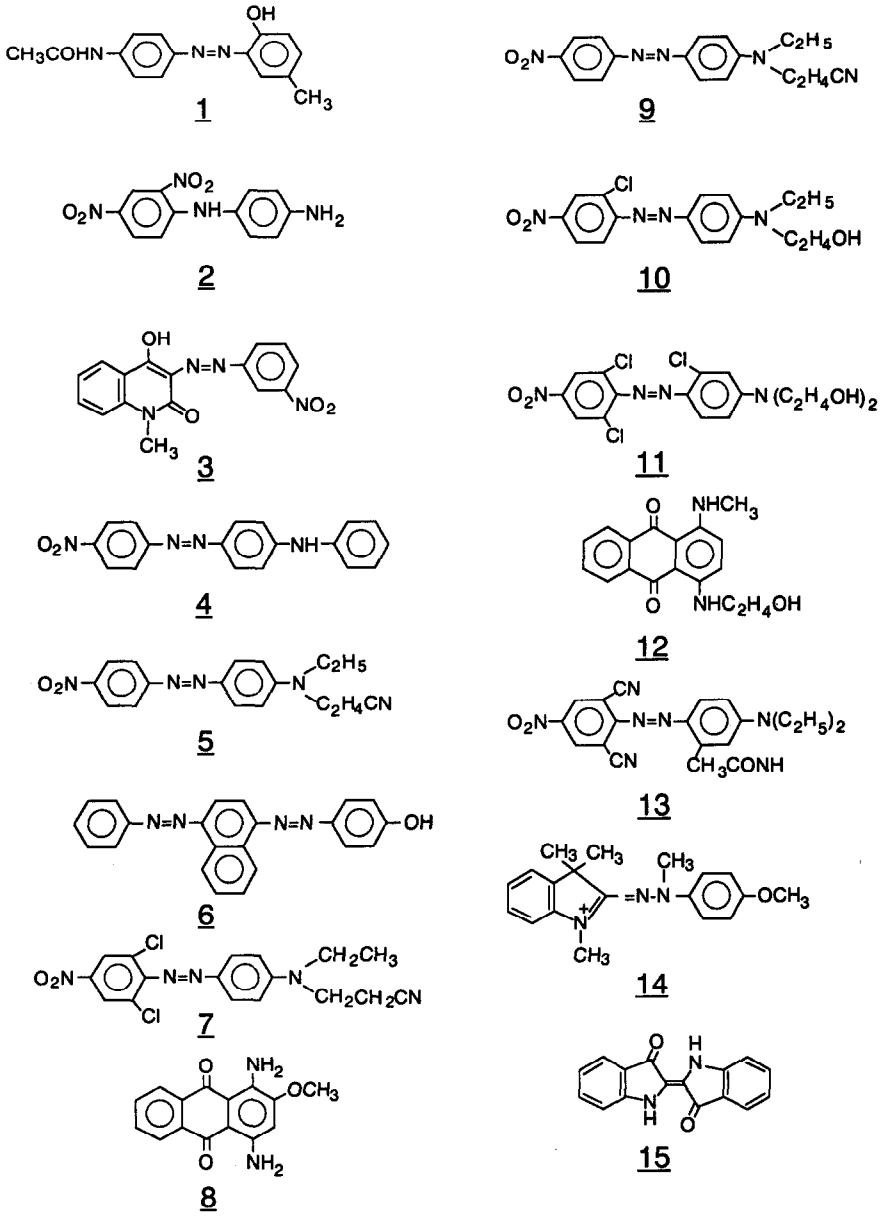

Fig. 1. Structures of compounds **1–15**.

system consisted of a CM4000 LDC Milton Roy solvent-delivery system with a Rheodyne 7125 injector valve fitted with a 5-μl sample loop. The column was a Merck C_{18} column (15 cm × 4 mm I.D.). The chromatograph was operated in the gradient mode, starting at a mobile phase of methanol–water (50:50), changing within 5 min to 100% methanol and staying at that level for 20 min. The flow-rate was 0.9 ml/min. The buffer, 0.1 *M* ammonium acetate, was delivered post-column via the TSP interface into the ion source by a Constametric Bio 3000 Milton Roy delivery pump.

TABLE II

THERMOSPRAY MASS SPECTRAL IONS OF DYES

Dye	M.W.	Structure[a]	Ions observed (percentage relative abundance)
Dispersive Yellow 3	269	**1**	271(17); 270(100)
Disperse Yellow 9	274	**2**	297(32); 292(24); 276(9); 275(100); 245(15)
Disperse Yellow 5	324	**3**	347(15); 326(17); 325(100)
Disperse Orange 1	318	**4**	320(15); 319(100); 289(11)
Disperse Orange 25	323	**5**	346(7); 325(15); 324(100)
Disperse Orange 13	352	**6**	354(21); 353(100)
Disperse Orange 37	391	**7**	396(8); 394(41); 392(100)
Disperse Red 11	268	**8**	270(11); 269(100)
Disperse Red 1	314	**9**	316(15); 315(100)
Disperse Red 13	348	**10**	351(20); 350(11); 349(100)
Disperse Brown 1	432	**11**	437(8); 435(23); 433(20); 301(42); 280(12); 279(100); 231(12)
Disperse Blue 3	296	**12**	298(13); 297(100); 242(11); 241(12); 234(10)
Disperse Blue 165	405	**13**	406(17); 405(31); 404(21); 331(100)
Basic Yellow 28	309	**14**	311(84); 310(100)
Vat Blue 1	262	**15**	264(11); 263(100); 257(13) 245(14); 237(14); 235(16); 234(83); 230(13)

[a] See Fig. 1.

Typical operating temperatures of the thermospray interface were vaporizer, 105–115°C; jet, 250°C; source, 250°C. Repeller was operated at a voltage of 100 V. Scan time was 2.0 s.

RESULTS AND DISCUSSION

In HPLC–MS, in addition to recording exact chromatographic retention times, one is looking at mass chromatograms of characteristic ions, representing the dyes eluted through the column which are ionized in the TSP interface and detected by the mass spectrometer.

Table II represents the positive ions of the investigated dyes and their relative abundance. These TSP mass spectral ions were found to agree with published data [9–11,13,14] and with TSP mass spectra of standard dyes. Mainly MH^+ ions were produced, but sometimes also some fragment or adduct ions. The TSP mass spectrum of Disperse Yellow 9 (Fig. 2) contains two adduct ions: $[M+NH_4]^+$ at m/z 292 and $[M+Na]^+$ at m/z 297. The sodium is an impurity in the ammonium acetate. An $[M+Na]^+$ ion is also observed in the TSP mass spectrum of Disperse Yellow 5, at m/z 347. The TSP mass spectrum of Disperse Orange 1 contains a fragment ion, $[MH-NO]^+$, at m/z 289. The TSP mass spectrum of Disperse Brown 1 contains several ions, including the ion forming the base peak at m/z 279, which probably originate from dibutyl phthalate, which coeluted with the dye. These ions were not observed in the TSP mass spectrum or in the mass spectrometry–mass spectrometry–collision-activated dissociation (MS–MS–CAD) spectrum of Disperse Brown 1 [11].

The ion at m/z 279 also appeared in the mass chromatograms of other dyes (Disperse Blue 3 and Basic Yellow 28), although not coeluting with them. The phthalate eluted at 15.30 min, which was also the eluting time of Disperse Brown 1. Also, in the mass spectrum of Disperse Blue 3 (see Fig. 6), some ions could not be attributed to the dye; they are probably due to impurities. In the TSP mass spectrum of Disperse Blue 165 the base peak is at m/z 331, which can be attributed to the fragment ion $[MH-NO_2-C_2H_5]^+$. This has to be substantiated by MS–MS–CAD. The ions at m/z 405 and 404 are probably due to an impurity coeluting with the dye. The TSP mass spectrum of the Indigo extract (Vat Blue 1) (see Fig. 8) contains some ions due to impurities or other components. Many dyes are blends of several components.

At this stage only the identification of the major dye in each extract was of interest, and not the additives or other components of the fiber which might have been extracted together with the dye. In

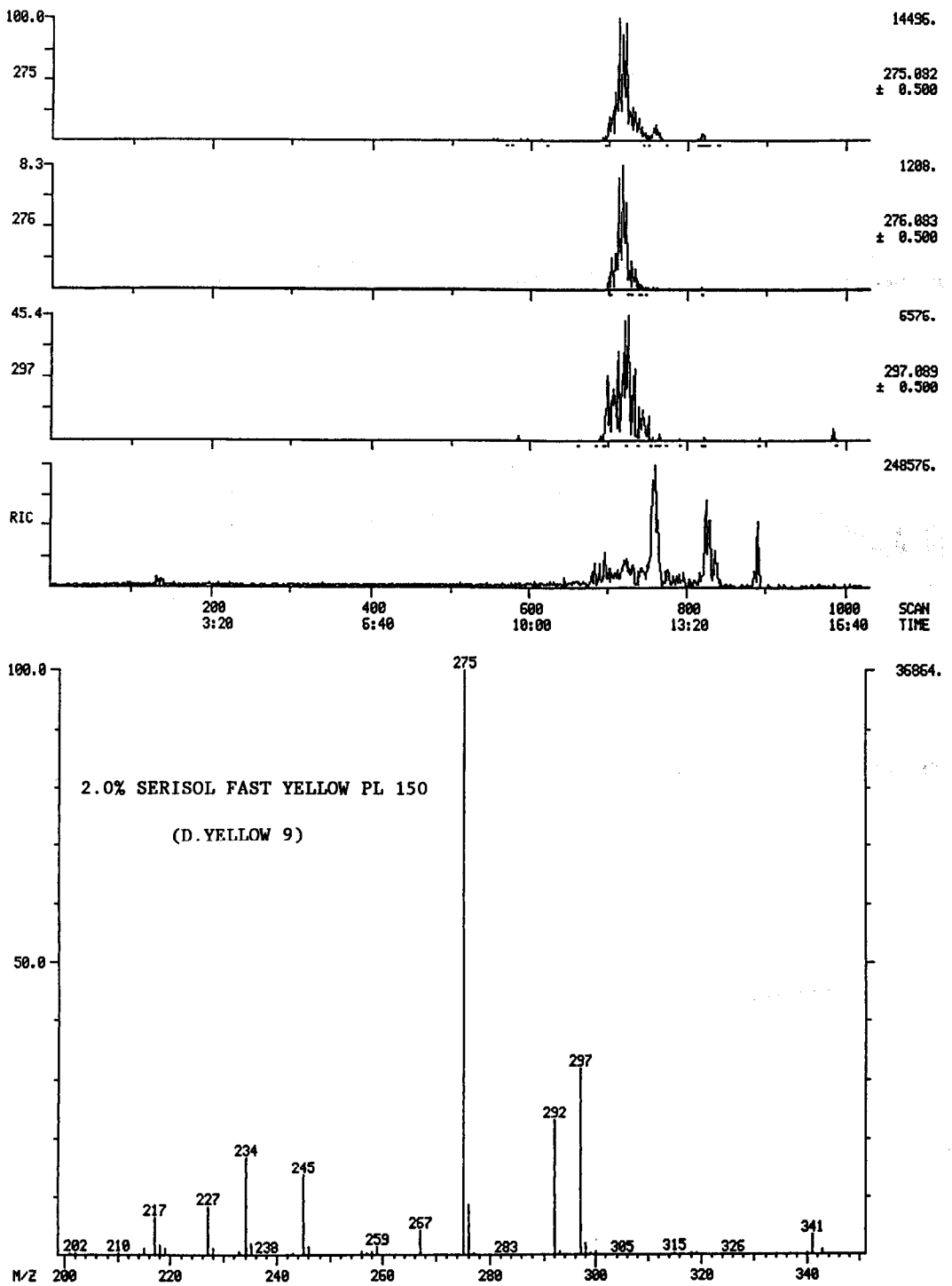

Fig. 2. HPLC mass chromatogram and TSP mass spectrum of 2.0% Serisol Fast Yellow PL 150.

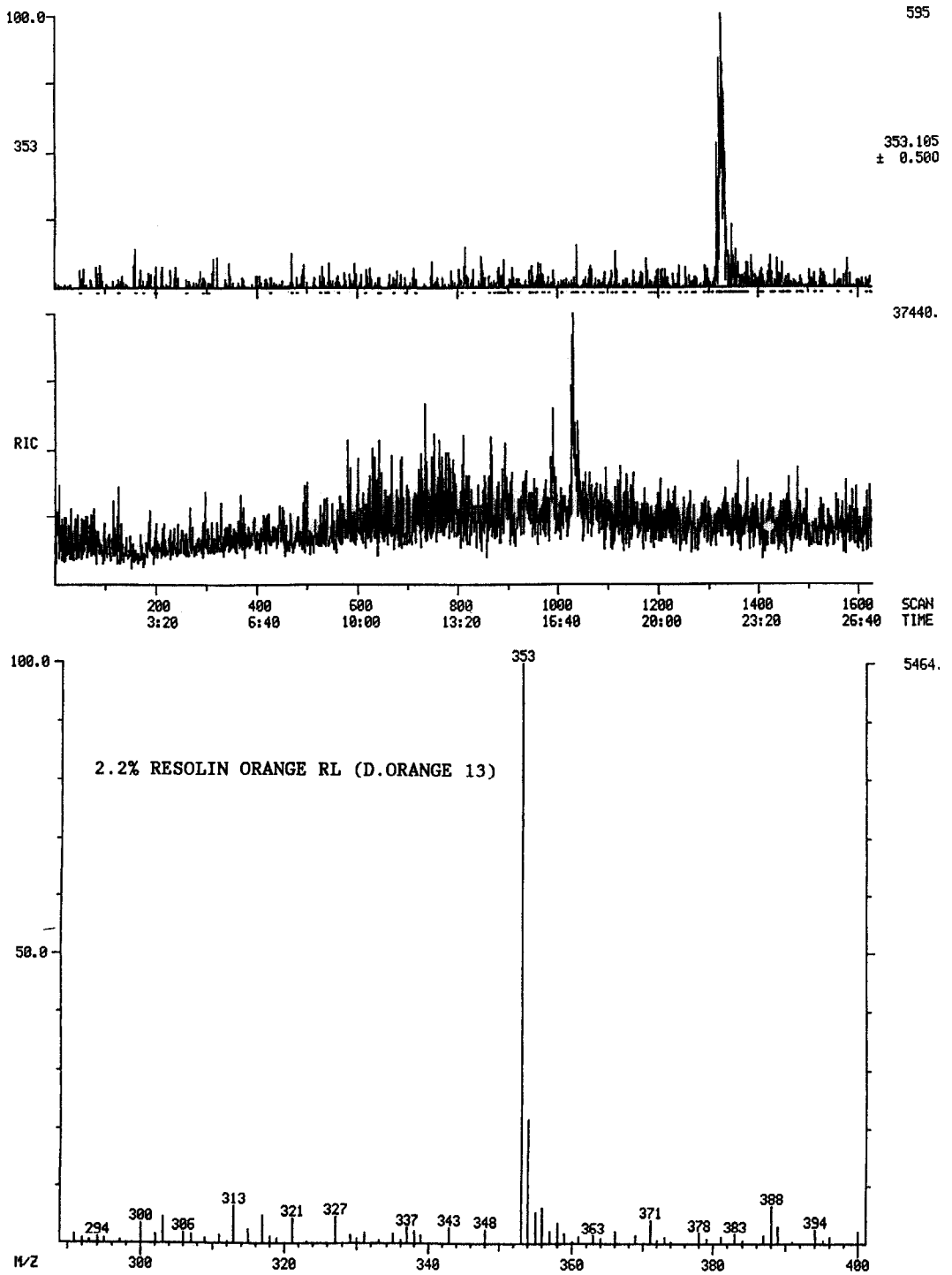

Fig. 3. HPLC mass chromatogram and TSP mass spectrum of 2.2% Resolin Orange RL.

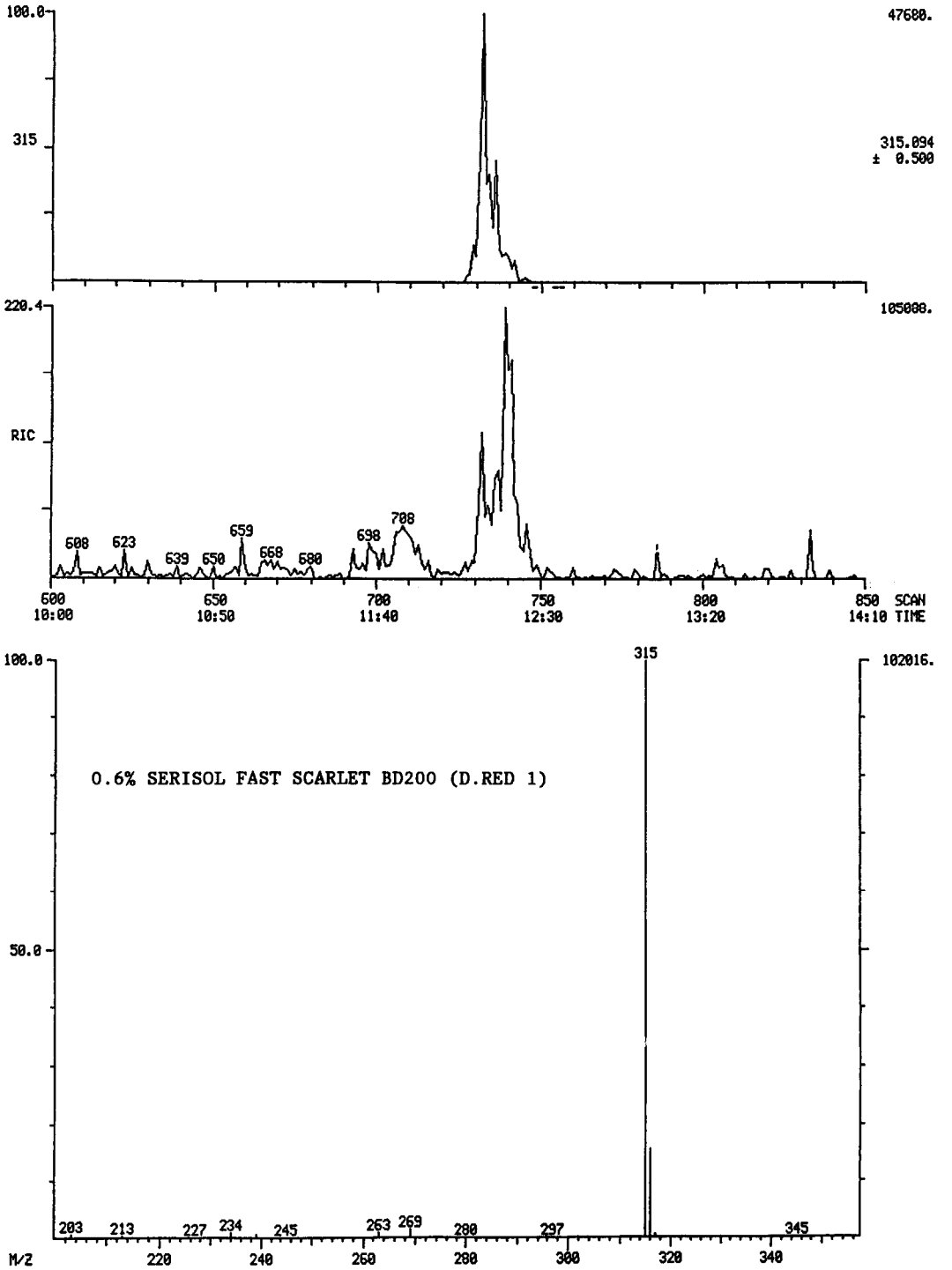

Fig. 4. HPLC mass chromatogram and TSP mass spectrum of 0.6% Serisol Fast Scarlet BD200.

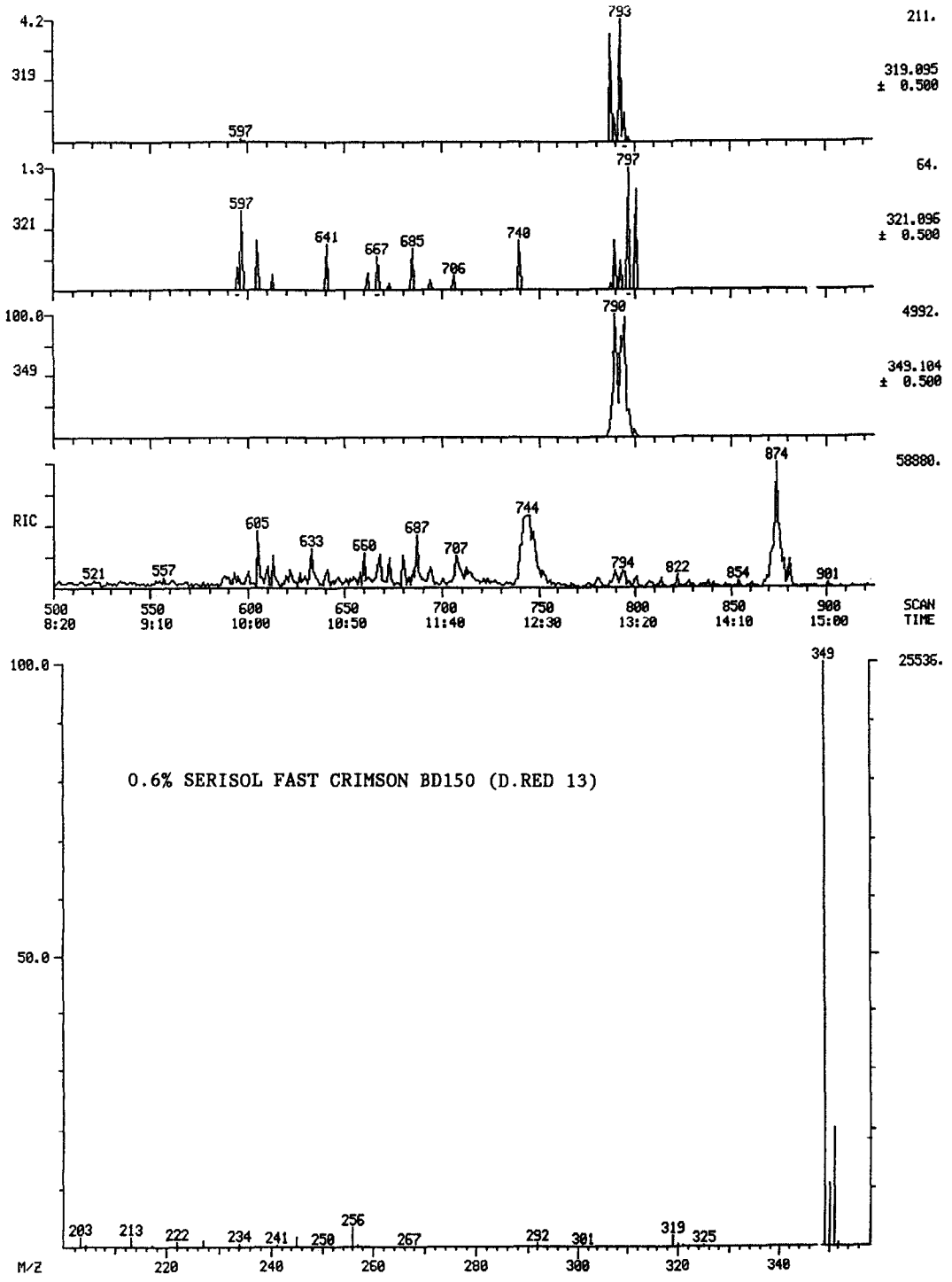

Fig. 5. HPLC mass chromatogram and TSP mass spectrum of 0.6% Serisol Fast Crimson BD 150.

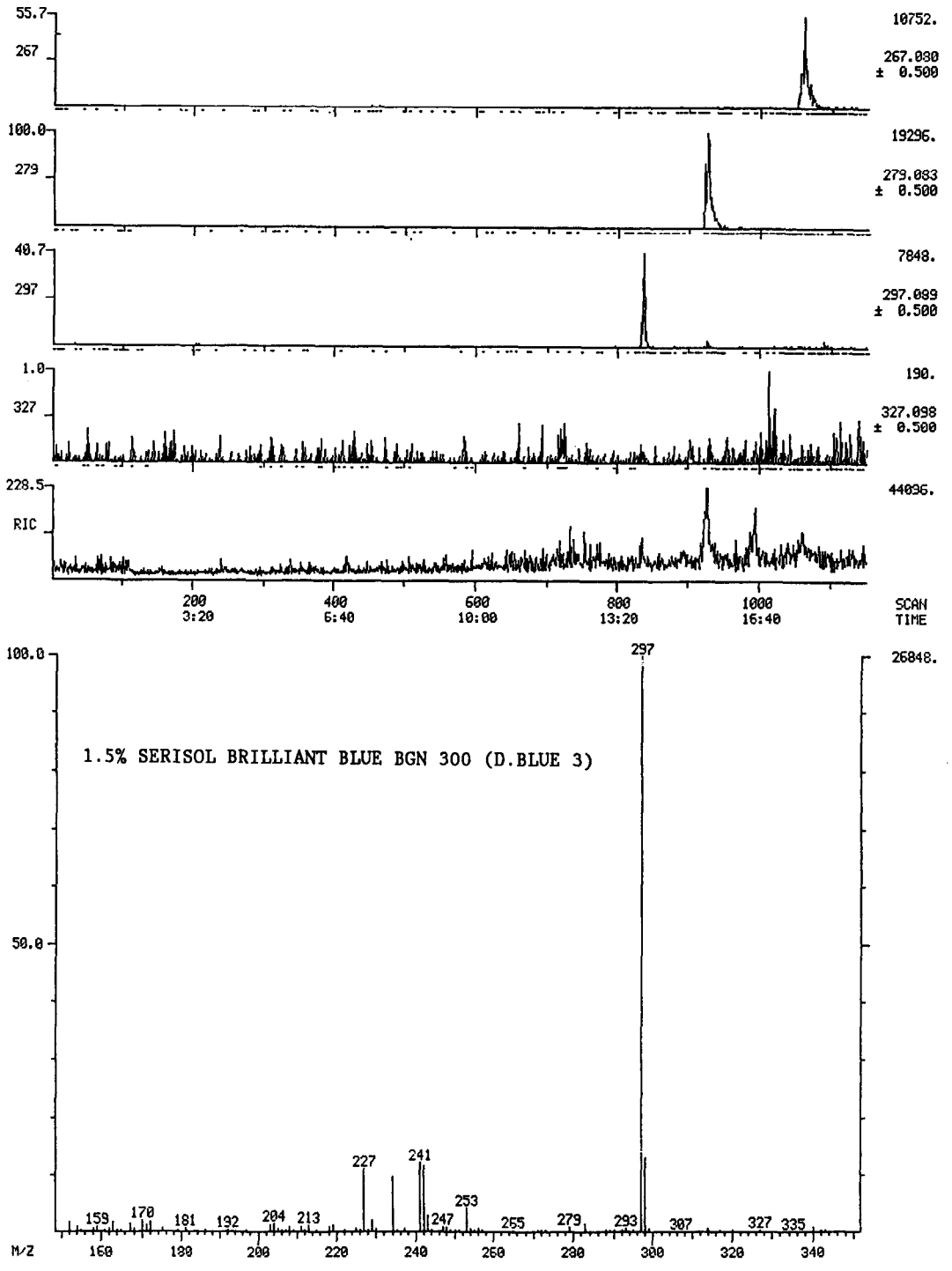

Fig. 6. HPLC mass chromatogram and TSP mass spectrum of 1.5% Serisol Brilliant Blue BGN 300.

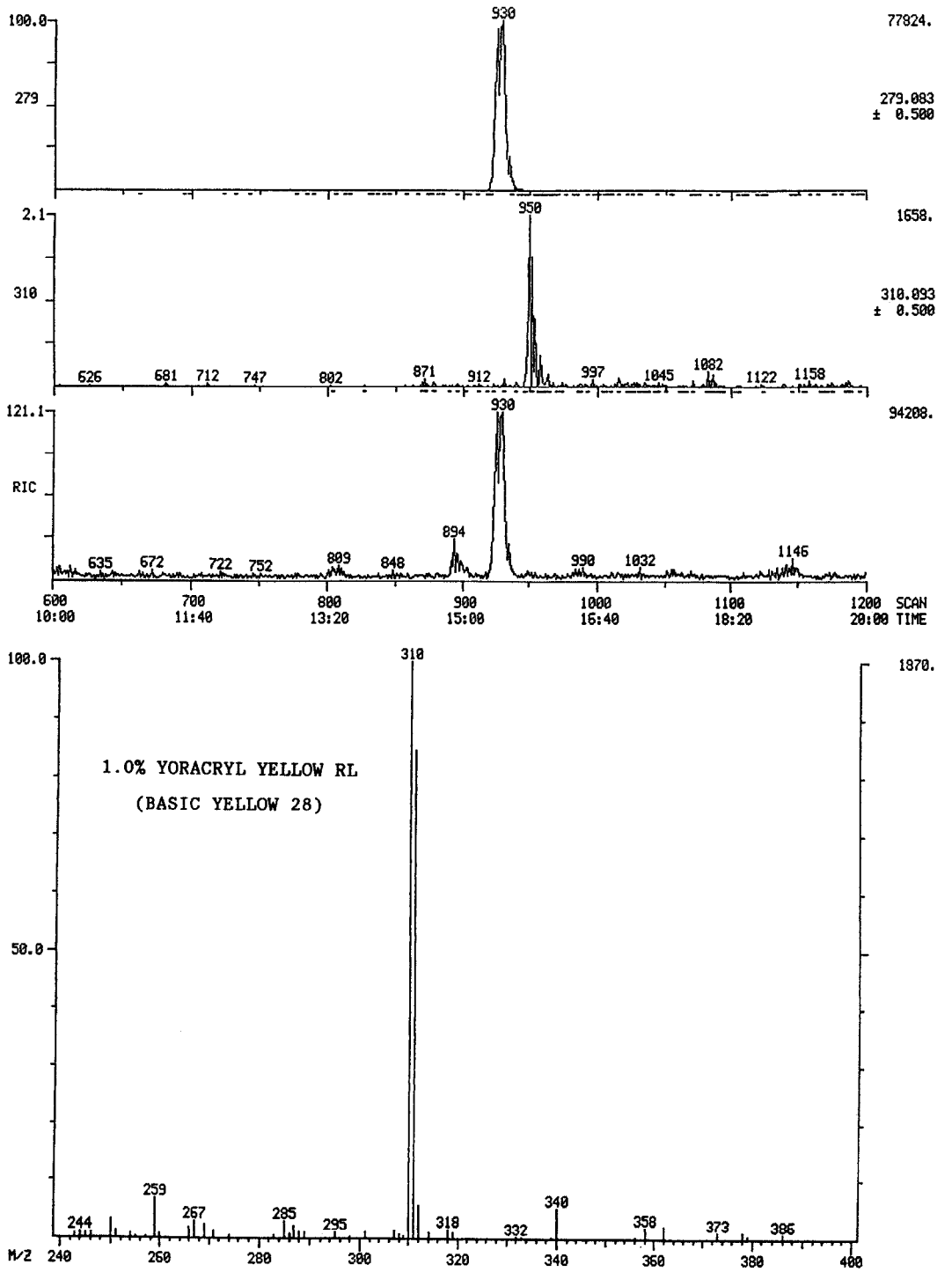

Fig. 7. HPLC mass chromatogram and TSP mass spectrum of 1.0% Yoracryl Yellow RL.

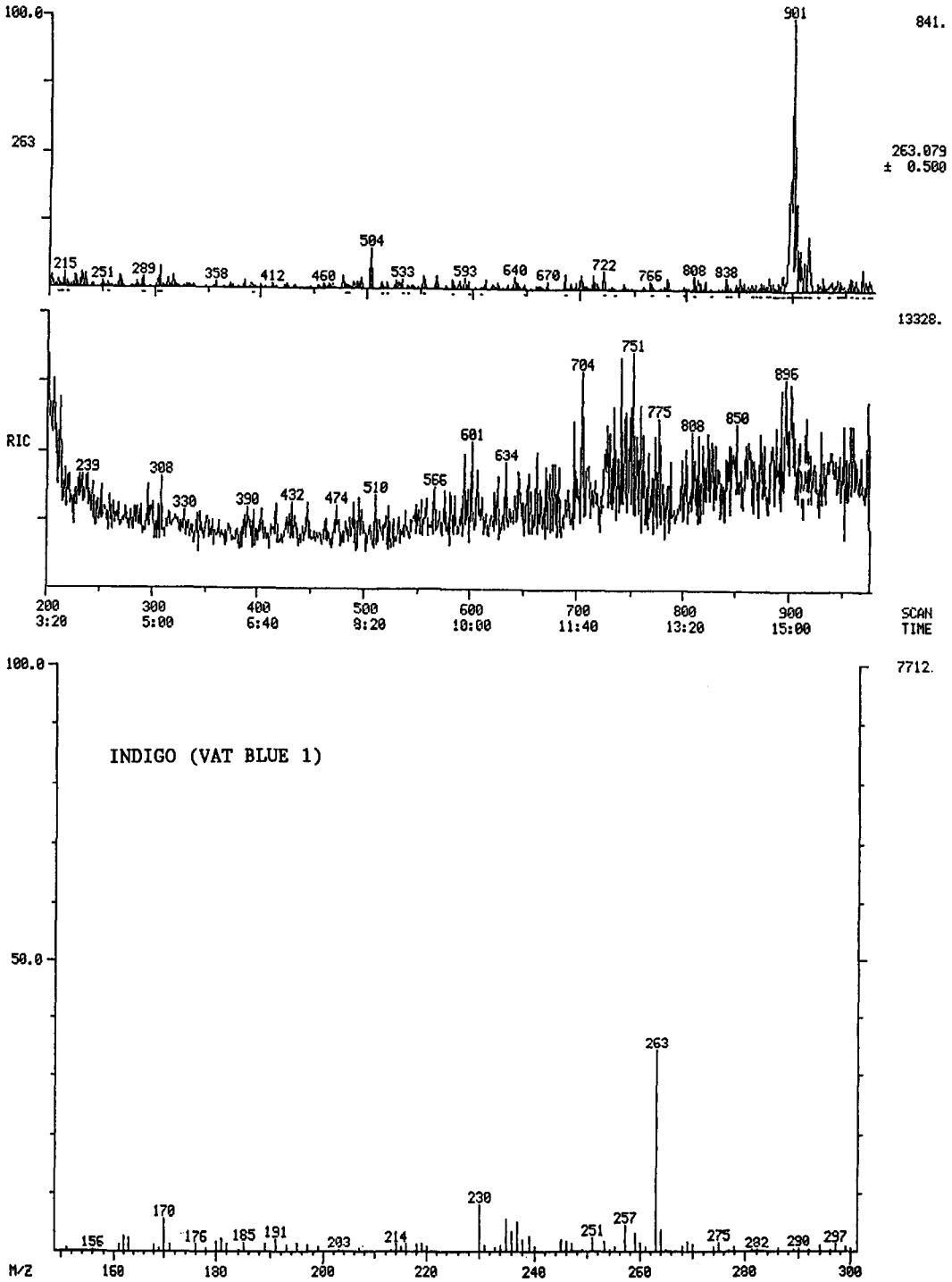

Fig. 8. HPLC mass chromatogram and TSP mass spectrum of Indigo.

order to separate those components from the dye of interest, one has to improve the HPLC separation characteristics.

Figs. 2–8 represent examples of reconstructed total ion current (RIC) and mass chromatograms and TSP mass spectra of seven of the investigated dyes. In most of the chromatograms it can be seen that the dye component is very small relative to the other components present in the fiber extract. Only by using HPLC–MS is it possible to identify characteristic ions of the dye. The chromatogram of 2.2% Resolin Orange RL (D. Orange 13) in Fig. 3 is a typical example which shows how the mass chromatogram of the MH^+ ion of the dye at m/z 353 is singled out from a noisy RIC chromatogram. Such a peak would have been hard to observe in a HPLC chromatogram with a UV detector because of lack of specificity. The amount of dye is very small, as fibers having a length of 2–10 mm contain 2–200 ng of dye, depending on the depth of the dying [16]. The amount of dye also depends on the shade percentage. The lightest shades of the investigated dyes were 0.6% (*i.e.* 600 g of the dye had been used to color 100 kg of fiber).

It is, of course, essential that the dyestuff be efficiently extracted from the fibers, and that the dye remains unchanged during the extraction procedure. The solvents chosen were found to be most suitable from a whole range of solvents suggested [2–4,6].

CONCLUSIONS

From our preliminary study it was found that TSP-HPLC–MS is a method having enough selectivity and sensitivity for identification of dyes extracted from single textile fibers. A library of TSP mass spectra of textile dyes will have to be created to serve as reference library.

Further work is in progress to examine the various components present in commercial dyes, by increasing the HPLC chromatographic separation, and to evaluate the possibility of differentiating between fibers of the same color but with different shades. The list of dyes and type of fibers investigated will be expanded.

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