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A Study to Investigate the Feasibility of Using X-Ray Fluorescence Microanalysis to Improve Discrimination Between Colorless Synthetic Fibers

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ABSTRACT: The use of X-ray fluorescence microanalysis was investigated to determine if it would allow further discrimination between samples of colorless acrylic and polyester fibers which were indistinguishable using brightfield, fluorescence and FTIR-microscopy. The aim was to determine if this technique could be successfully applied to single fibers of relatively fine titer and whether it would be beneficial to include it into the existing sequence of techniques used to compare colorless fibers. The extent of intra-garment variation and the possible effects of tape and mounting media residues on the elemental analysis were also investigated. The results confirmed the high value of fluorescence microscopy within the existing examination sequence and showed that single fiber analysis using X-ray fluorescence microanalysis is not only feasible, but improved the discriminating power between such colorless samples by about 50%.

KEYWORDS: forensic science, criminalistics, colorless fibers, acrylic, polyester, brightfield microscopy, fluorescence microscopy, fourier transform infrared microspectrometry, X-ray fluorescence microanalysis

In forensic fiber comparisons, the more features that two fibers can be shown to have in common, the greater are the chances that they originated from a single source. In that sense, color is a prime comparative feature, and the recovery and comparison of colorless fibers may therefore prove more difficult. In the absence of results from microspectrophotometry and/or thin layer chromatography, the evidential value of fibers could be reduced. Fiber cases involving the examination of colorless fibers are in the minority. However, under particular circumstances they may become very significant, for example, when they are recovered from an object such as a knife blade or when they are clearly visible as foreign fibers on a dark colored textile surface. The use of additional instrumental analysis methods could be useful in providing additional points of comparison when dealing with relatively featureless fibers.

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Important developments have occurred during the last five years in connection with forensic fiber examination: new brightfield and fluorescence microscopes have been introduced (e.g., Leica DM RX), FTIR-microscopy has been shown to be a powerful analytical tool (1–3), and the elemental analysis of fibers has been tested using X-ray fluorescence microanalysis or other techniques (4–6). There is unfortunately no information on how discriminating power can be improved by the incorporation of such techniques into current analytical schemes.

Material and Methods

Fourty-two samples (15 polyester and 27 acrylic) were selected from the reference collection of authentic manufacturers samples available to one of the authors. These fibers were first classified in five groups (2 PES; 3 PAN) according to polymer composition and their general morphological appearance. In case work, X-ray fluorescence microanalysis is likely to be included in a pool of methods which will only be used in special instances (5). This study was designed to be a demanding test to investigate a particular problem, therefore the samples in each group were deliberately chosen to be as similar as possible and lacking in morphological features. This would minimize their chances of being having been separated using traditional methods (brightfield, fluorescence and FTIR) had they occurred in a case examination and would provide a good test of the potential of X-ray fluorescence microanalysis to discriminate between them. The work of Prange et al. (6) states that the quantitation of titanium dioxide delustrant material using total reflection X-ray fluorescence might prove useful in sample differentiation. In our investigation samples were deliberately chosen to have little or no delustrant, so that the comparisons would be qualitative in nature.

Groups were put together where the fibers: 1. are all undyed; 2. with very few exceptions have the same polymer composition; 3. are either all non-delustred (acrylic) or have a minimal amount of delustrant present (polyester-bright); and 4. have the same cross sectional shape and the titer is the same or very similar.[4]

Details of the samples examined can be found in Table 1.

The selection of the samples involved their examination using brightfield microscopy (×250 and ×400) using a Leica DM RXP microscope also equipped for fluorescence and polarized light examinations. Particular attention was paid to the fiber's cross-sectional shape and to the size and distribution of any delustrant particles. Polyester samples designated as "bright," normally contain a minimal amount (c.0.03%) of delustrant particles.

[4]Titer is a measure of fiber fineness in dtex.

TABLE 1—*Fiber samples analyzed in this study.*

Code	Brand Name	Manufacturer	Group	dtex
73	Trevira 130	Hoechst	1	1.3
71	Trevira 120	Hoechst	1	1.3
74	Trevira 131	Hoechst	1	1.3
18	Trevira 220	Hoechst	1	1.3
101	Terital 10	Montedison	1	1.5
106	Terital 11	Montedison	1	1.5
36	Diolen 11	Enka	1	1.7
35	Diolen 12	Enka	1	1.7
103	Terital 10	Montedison	1	1.7
12	Trevira 270	Hoechst	1	1.7
24	Tergal T110	Rhodiaceta	1	1.6
110	Terital 58	Montedison	1	1.9
13	Trevira 350	Hoechst	2	3.3
6	Vestan X210	Bayer	2	3.3
109	Terital 50	Montedison	2	3.3
1	A201	BASF	A	2.8
3	Courtelle ITA	Courtaulds	A	*
4	Cashmilon A51	Asahi	A	3.3
5	Cashmilon Bico.	Asahi	A	*
6	Beslon AD82	Toho Beslon	A	3.3
7	Courtelle LC	Courtaulds	A	3.3
8	Dolan 26	Hoechst	A	3.3
10	Dralon L	Bayer	B	3.3
11	Leacril flock	Montefibre	B	3.3
12	Acrilan A16	Monsanto	B	3.3
13	Acrilan 16	Monsanto	B	3.3
14	Acrilan B57	Monsanto	B	2.8
15	Dolan 37	Hoechst	C	3.3
16	Dralon X305	Bayer	C	3.3
17	Dolan 20	Hoechst	C	3.3
19	Dralon X100	Bayer	C	3.3
20	Dolan 50	Hoechst	C	3.3
21	Orlon 75	Du Pont	C	3.3
22	Dolan 21	Hoechst	C	3.3
23	Dolan 21	Hoechst	C	3.3
24	Dolan 20	Hoechst	C	3.3
25	Dolan 23	Hoechst	C	3.3
26	Dolan 30	Hoechst	C	3.3
27	Dralon X100	Bayer	C	3.3
28	Dralon X385	Bayer	C	3.3
29	Dralon X820	Bayer	C	3.3
30	Dralon X870	Bayer	C	3.3

*Titer not known, microscopically compatible.

The polymer composition of all the acrylic fiber samples was already on record as a result of them having been examined previously as described in (3). Only examples of methylacrylate and vinyl acetate co-polymers were chosen.

Following the selection of the groups, all of the samples in one group were compared with all other samples in that group, using a Leitz comparison microscope (×400) fitted with a Ploemopak attachment containing Leitz filter blocks A, H3, and N2.1 to permit additional optical comparison by fluorescence microscopy (fluorescence was not measured by micro spectrophotometry).

In the polyester samples, there is a slight variation in fiber diameter within the individual samples. Fibers were deemed to match when the diameter of a fiber in one sample falls within the range of the diameter exhibited by the other sample. It is very difficult to accurately compare delustrant particle size/distribution when only a minimal quantity is present.

Following this, all of the samples were examined using X-ray fluorescence microanalysis (XRFM) as described below: A Kevex Omicron energy dispersive XRFM system was used to perform multielement analyses according to the following conditions: single fibers of 10 to 20 mm in length were stretched between two jaws in the vacuum sample chamber. X-rays from a rhodium tube operating at 40 kV and 1 mA were collimated to form approximately a 2.3 by 3.0 mm spot at the fiber. Secondary X-ray fluorescence from elements present in the fiber was accumulated from 10 randomly selected spots along the fiber, during 1000 s (total accumulation time/fiber = 10,000 s). The spectra were automatically treated by computer using the software provided by the manufacturer: baseline correction, escape peaks subtraction, intensities extraction (by Gaussian deconvolution).

A blank result was obtained by performing an analysis without fiber in the sample chamber. The reproducibility of the analysis was controlled by measuring the same standard at each set of analyses. The homogeneity among a sample was investigated by analyzing six different fibers of the acrylic sample N° 13 (Acrilan 16) and six different fibers from the polyester sample N° 13 (Trevira 350). The analysis of three other polyester fibers from N° 13 was repeated three months later. Because of the high degree of similarity between the spectra, correlation values were computed to rate each spectrum as to its similarity (100 indicates perfect overlap) or dissimilarity (0 indicates no similar peak) to each of the other spectra compared. For this purpose, a correlation value, C, is defined as:

$$C = 100\left[\frac{[(A_1B_1) + (A_2B_2) + \cdots + (A_nB_n)]^2}{(A_1^2 + A_2^2 + \cdots + A_n^2)(B_1^2 + B_2^2 + \cdots + B_n^2)}\right]$$

where A_1, A_2, . . . , and A_n equal relative (sum of the counts of all detected elements = 100%) areas for peaks 1 through n for spectrum A; and B_1, B_2, . . . , and B_n equal relative areas for peaks 1 through n for spectrum B. This correlation analysis was used by Keto (7) for the comparison of pyrograms and is similar to that used routinely for spectral library searches or manipulation of chromatographic data.

The threshold value for C was derived from the results obtained when investigating the homogeneity of the results within a sample. Within-sample comparisons had a mean correlation value of 98.7 with a standard deviation of 0.8. Two fiber samples were therefore considered as discriminated when their correlation value was inferior to 96.3. In other words, assuming a normal distribution, 99.5% of all within-samples comparisons will have a correlation value of 96.3 or higher.

It should be noted that the most useful elements for comparison were Si, P, S, Ti, Cr, Mn, Cu, and Zn because of their relative good reproducibility. On the other hand, some elements were not considered when performing comparisons because their results were not sufficiently reproducible (Na, Ca, Ni, Co) or because they were present in the sample chamber (e.g., Al and Fe of the sample holder).

Subsequent work was carried out in order to investigate using the technique under case work conditions. A blind test was performed as follows: a polyester fiber (Tergal T110), was given to the analyst as the evidence together with three polyester tuft samples (Tergal T110, Trevira 130, and Terital 58) for comparison. This test was repeated with acrylic samples (Dolan 37 to compare with Dolan 37, Dralon X305, and Dolan 21). Information on possible intra-garment variabilities and on the effects of adhesive tape or mounting media were also investigated. Fibers taken from 12 different places within a new white polyester shirt were analyzed; and fibers of the polyester sample N° 13 (Trevira 350) were submitted to seven usual treatments before being analyzed (Table 2).

TABLE 2—*Treatment applied to fibers from the same sample (Trevira 350 No. 13) before analysis.*

Code	Treatment
A	Recovered from adhesive tape (Cellux Sellotape)
B	Recovered from adhesive tape, washed with xylol and water, then dried in a dessicator
C	Recovered from adhesive tape, washed with ethanol and water, then dried in a dessicator
D	Recovered from sample tuft, mounted on a microscopic slide in glycerol:water (1:1), then washed with water and dried in a dessicator
E	Recovered from sample tuft, mounted on a microscopic slide in phytohistol:water (3:1), then washed with water and dried in a dessicator
F	Recovered from adhesive tape, washed with xylol, ethanol and water, mounted on a microscopic slide in glycerol:water (1:1) during 3 weeks, washed with water and dried in a dessicator
G	Recovered from adhesive tape, washed with xylol, ethanol and water, mounted on a microscopic slide in phytohistol:water (3:1) during 3 weeks, washed with water and dried in a dessicator

Results and Discussion

The use of microscopy and FTIR microscopy in the scheme of fiber analysis is well known and accepted. Practical considerations of these techniques are beyond the scope of this paper. For further details the reader should consult the appropriate literature. X-ray fluorescence microanalysis analysis of a single fiber was found to be feasible, but slow, due to the weak intensities encountered. The optimum accumulation time to have an acceptable signal to noise ratio was 10,000 s/fiber. For the same reason, the highest current and source voltage settings were chosen. These analytical conditions produce backgrounds that were low enough in the region where K-lines of the first row transition elements occur to allow detection of most elements of interest. Figures 1–4 show spectra obtained for two acrylic samples (Dolan 37/Dralon X-870) and two polyester samples (Trevira 130/Tergal T110). It should be noticed that the major difference in the elements present in acrylics vs. polyesters was the presence of sulfur in acrylic fibers. This could originate from the following: 1. In suspension polymerization, water soluble redox systems are used as polymerization initiators: for example, sodium sulfate, sodium bisulfate + sodium persulfate (8). 2. In solution polymerization, solvents that can be include: sodium dimethylsulfoxide, sodium thiocyanate (8). 3. Third monomers added to produce acidic dyes sites often contain sulfate: for example, sodium styrene sulfonate, sodium methallylsulfonate (3).

From a total of 205 pairs in the five groups, examination of Tables 3–7 shows that 175 pairs were differentiable. Of these 175 pairs, 81 could already have been discriminated by the usual sequence of examinations (Brightfield-, Fluorescence-, FTIR-microscopy), but were also differentiable using XRFM. A further 73 pairs could be separated by using XRFM where this would otherwise not have been possible. Twenty-one pairs could only be separated using microscopy. Thirty pairs (26 acrylic) remained inseparable despite the use of all techniques.

The possibility of using the results to identify a specific manufacturer was investigated, but without success. The tendencies observed were not sufficiently clear cut: approximately 50%

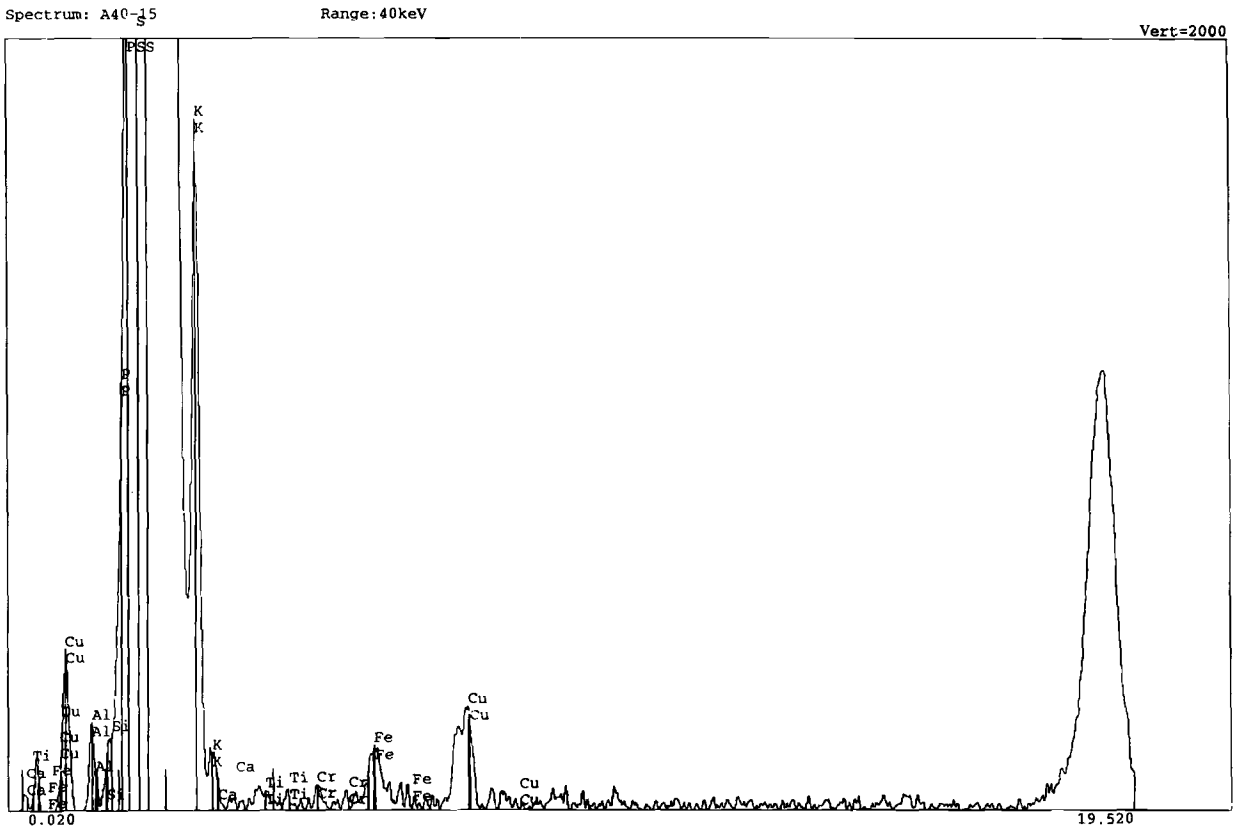

FIG. 1—*Spectrum of Dolan 37 (sample No. 15; group C).*

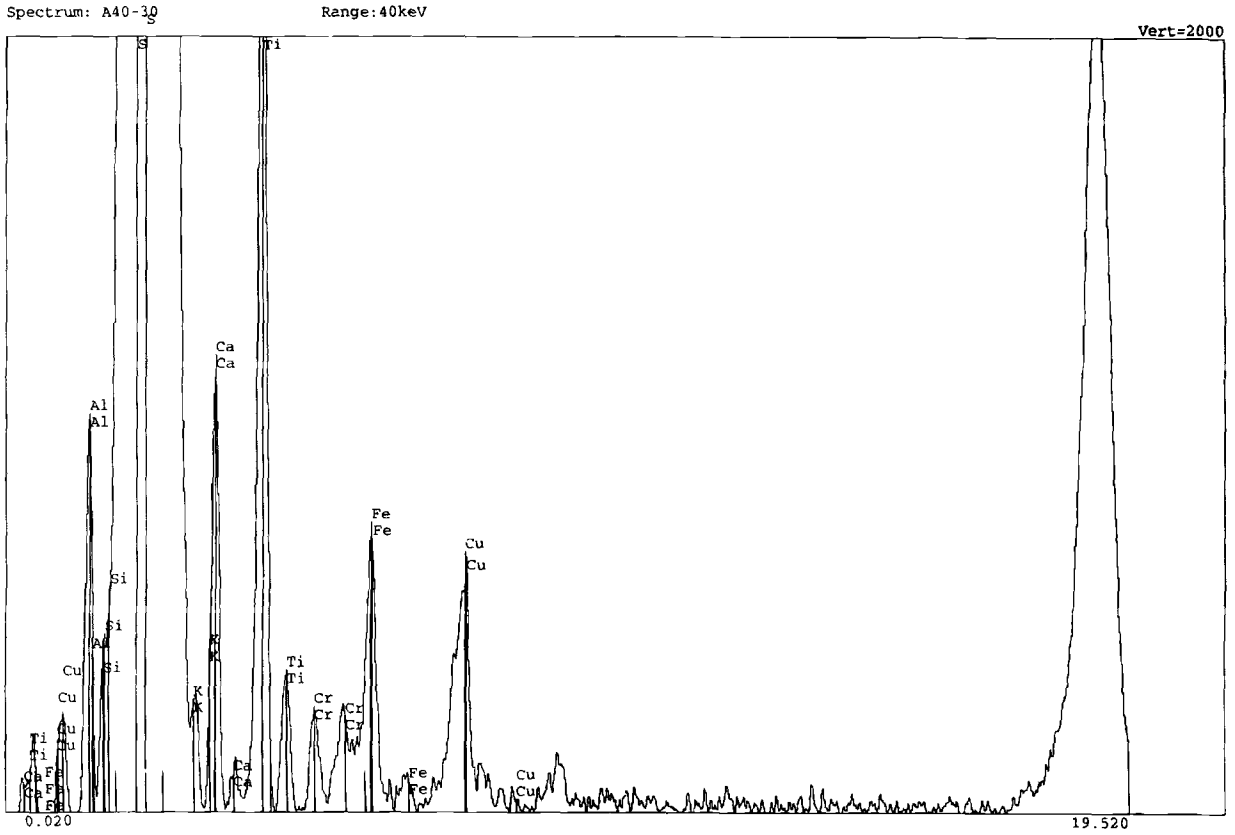

FIG. 2—*Spectrum of Dralon X870 (sample No. 30; group C).*

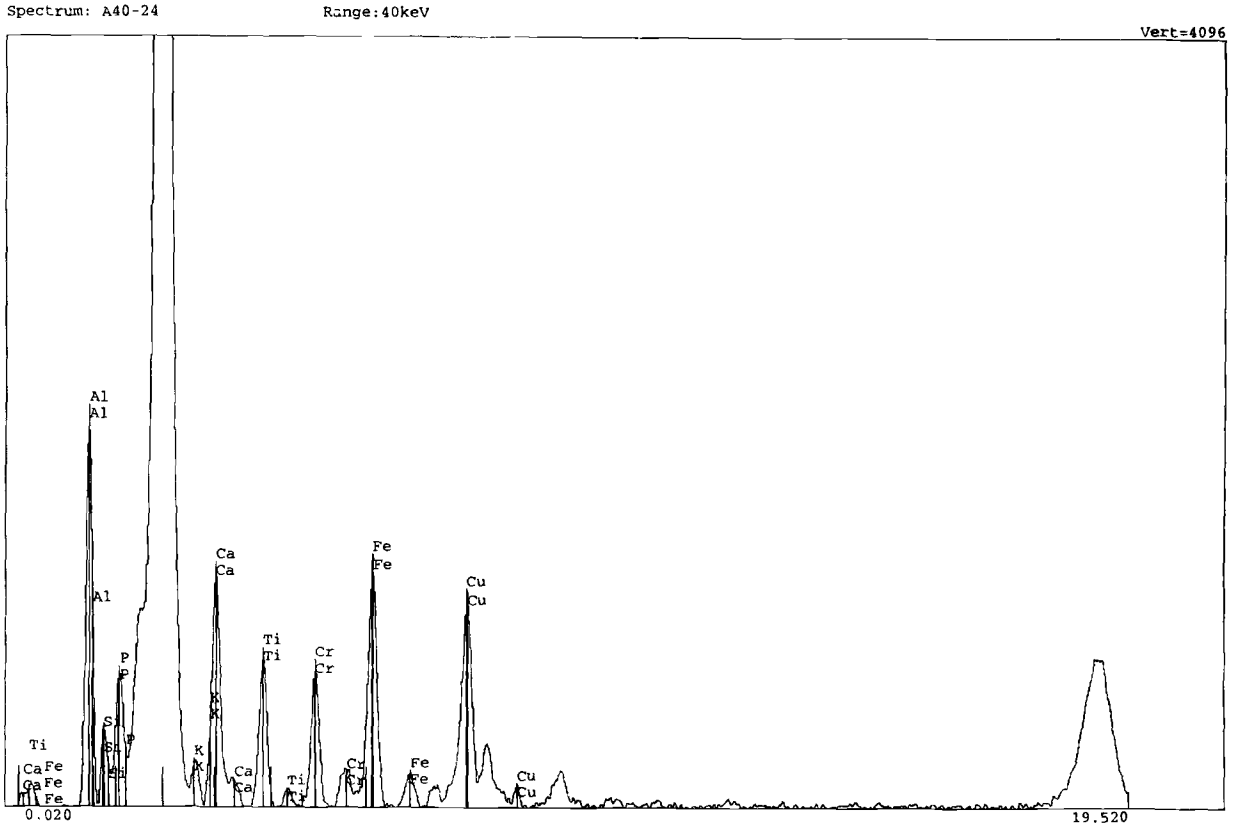

FIG. 3—*Spectrum of Trevira 130 (sample No. 73; group 1).*

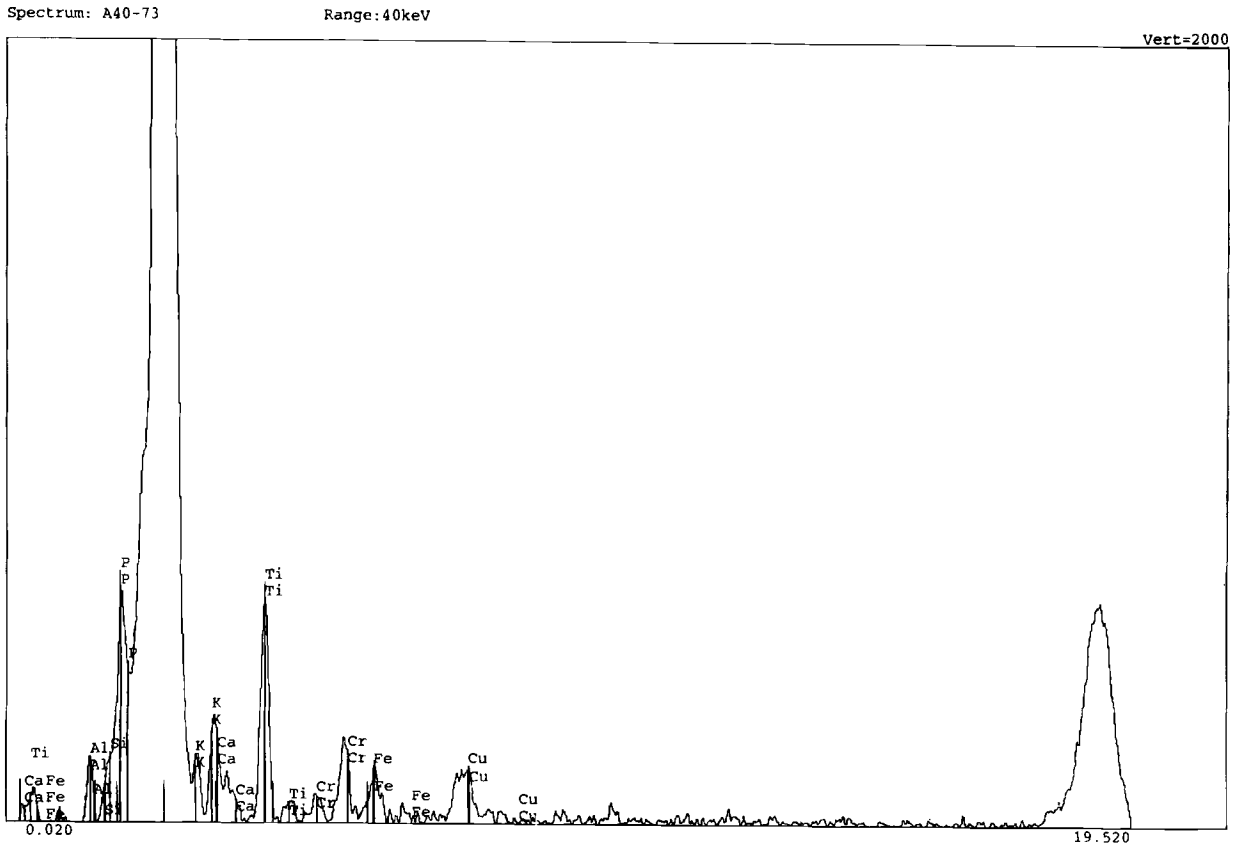

FIG. 4—*Spectrum of Tergal T110 (sample No. 24; group 1).*

TABLE 3—*Overall results.*

1	73	71	74	101	106	36	35	103	12	24	110	18
73		X		X	X	D/X	D/X	T	F/X	X	X	
71			X	X	X	D/X	D/X	T/X	F/X	X	X	X
74				X	X	D/X	D/X	T	F/X	X	X	
101					X	D/X	D/X	X	F/X	X	X	X
106						D/X	D/X		F/X	X	X	X
36							X	D/X	D/X	D/X	D/X	D/X
35								D/X	D/X	D/X	D/X	D/X
103									F/X	X	X	T
12										X	X	X
24											X	X
110												X
18												

Blank = undifferentiable; D = discriminated by delustrant; F = discriminated by fluorescence microscopy; T = discriminated by thickness; X = discriminated by X-ray microfluorescence.

TABLE 4—*Overall results.*

2	13	6	109
13		X	X
6			X
109			

Blank = undifferentiable; X = discriminated by X-ray microfluorescence.

TABLE 5—*Overall results.*

A	1	3	4	5	6	7	8
1		F/IR/X	F/IR/X	F/IR/X	F/IR/X	F/IR/X	X
3			F/IR/X	F/IR/X	F/IR/X	F/IR/X	F/IR/X
4				F/IR	F/IR/X	F/IR/X	F/IR/X
5					F/IR/X	F/X	F/IR
6						F/IR/X	IR/X
7							F/IR/X
8							

Blank = undifferentiable; F = discriminated by fluorescence microscopy; IR = discriminated by FT-IR microscopy; X = discriminated by X-ray microfluorescence.

TABLE 6—*Overall results.*

B	10	11	12	13	14
10			X		X
11			X		X
12				X	
13					X
14					

Blank = undifferentiable; X = discriminated by X-ray microfluorescence.

TABLE 7—*Overall results.*

C	15	16	17	19	20	21	22	23	24	25	26	27	28	29	30
15		F/X			F/X	X	F		F	F/X	F			X	X
16			F/X	X	F		F/X	X	F/X	F/X	F/X	X	X		X
17					F/X	X	F		F	F/X	F/X			X	X
19					X	X	F		F	F/X	F			X	X
20						F	X	F/X	X		X	F/X	F/X	F	F/X
21							F/X	X	F/X	F	F/X	X	X	X	X
22								F				F	F	F/X	F/X
23									F	F/X	F/X			X	X
24										X		F	F	F/X	F/X
25											X	F/X	F/X	F/X	F/X
26												F/X	F/X	F/X	F/X
27														X	X
28														X	X
29															X
30															

Blank = undifferentiable; F = discriminated by fluorescence microscopy; X = discriminated by X-ray microfluorescence.

of the matching pairs (12 of the 26 matching acrylic pairs) were made up of samples originating from the same manufacturer.

Flow charts showing the effectiveness of the different steps in the sequential examination are shown in Fig. 5. The value of fluorescence examinations within the traditional sequence is demonstrated and the effectiveness of XRFM can clearly be seen in the two largest groups where the Discriminating Power has been increased after it's use from 0.45 to 0.94 and from 0.49 to 0.79, respectively.

The results of the two blind tests were correct; the analyst was successful in matching the "suspect" samples to the correct control material in each case.

The following conclusions could be drawn with regard to the possibility of applying the technique in routine case work: The variations between two analyses of the same fiber (reproducibility) were negligible when compared to the variations existing between one fiber and another taken from the same sample (homogeneity). These variations did not increase when fibers from a new polyester shirt were examined, but showed a slight increase (max. + 5%) after various treatments involving adhesive tape and mounting media detailed in Table 2. It should be noted that the wearing or washing of garments may cause more important localized variations (9,10). Therefore the match criteria were certainly a reasonable compromise within the scope of this trial, but should not be spontaneously applied in a case work situation. The use of case specific threshold for the correlation values, taken from at least 10 different locations within the control garment is highly desirable.

Within Group 1, the largest polyester group, only four pairs remained inseparable after using XRFM (see Table 3). It is interesting to note that after using interference microscopy (11) to measure the refractive indices of these four pairs, only one pair (samples 103/106) remained indistinguishable. The combination of these methods increased the differentiating power to 0.98. The value of FTIR-microscopy is shown in Group A where 19 of the 21 samples can be distinguished by this technique due to variation in the termonomer content (3). On the other hand in Group C where all of the fibers contain acrylonitrile/methylacrylate/sulfonate + dimethylformamide residue, it is of no help at all.

Within Group C, a more detailed examination of the cross sectional shape might have allowed additional discrimination, but in a case work situation, if only a very short lengths of recovered fiber are available this could be difficult, so the method was considered as being a last resort. It was interesting to note that some fibers (e.g., Dralon X-870, see Fig. 2) show a high level of titanium, although the fiber is non-delustred. This confirms the observations of Koons (5) who states that the levels of Ti in XRF spectra are not correlated with the delustrant content of the fiber.

Conclusion

In this study, brightfield microscopy, fluorescence microscopy, FTIR microscopy, and X-ray fluorescence microanalysis have been applied in sequence to the analysis of 42 colorless acrylic and polyester fibers. These fibers represented a total of 205 possible pairings divided into five groups.

X-ray fluorescence microanalysis can be successfully applied to single fibers. The use of this technique allowed the separation of an additional 73 pairings which could not be distinguished using the traditional methods. Within the two largest groups the discrimination was increased from 0.45 to 0.94 (round, bright polyesters) and from 0.49 to 0.79 (bean/peanut, bright, methylacrylate co-polymer acrylics).

These results point out that this sensitive and non-destructive technique can be usefully employed to supplement the pool of existing methods that can be applied not only to dyed fibers (5) but also to the comparison of colorless fibers originating from clothing, especially in cases where limitations are imposed by similarities in morphological features. The study also illustrated that time may be saved by avoiding rigid application of a sequence of analytical techniques. Careful consideration of which technique may give the best discrimination under a given set of circumstances may be beneficial, especially in these times of economic restrictions.

Acknowledgment

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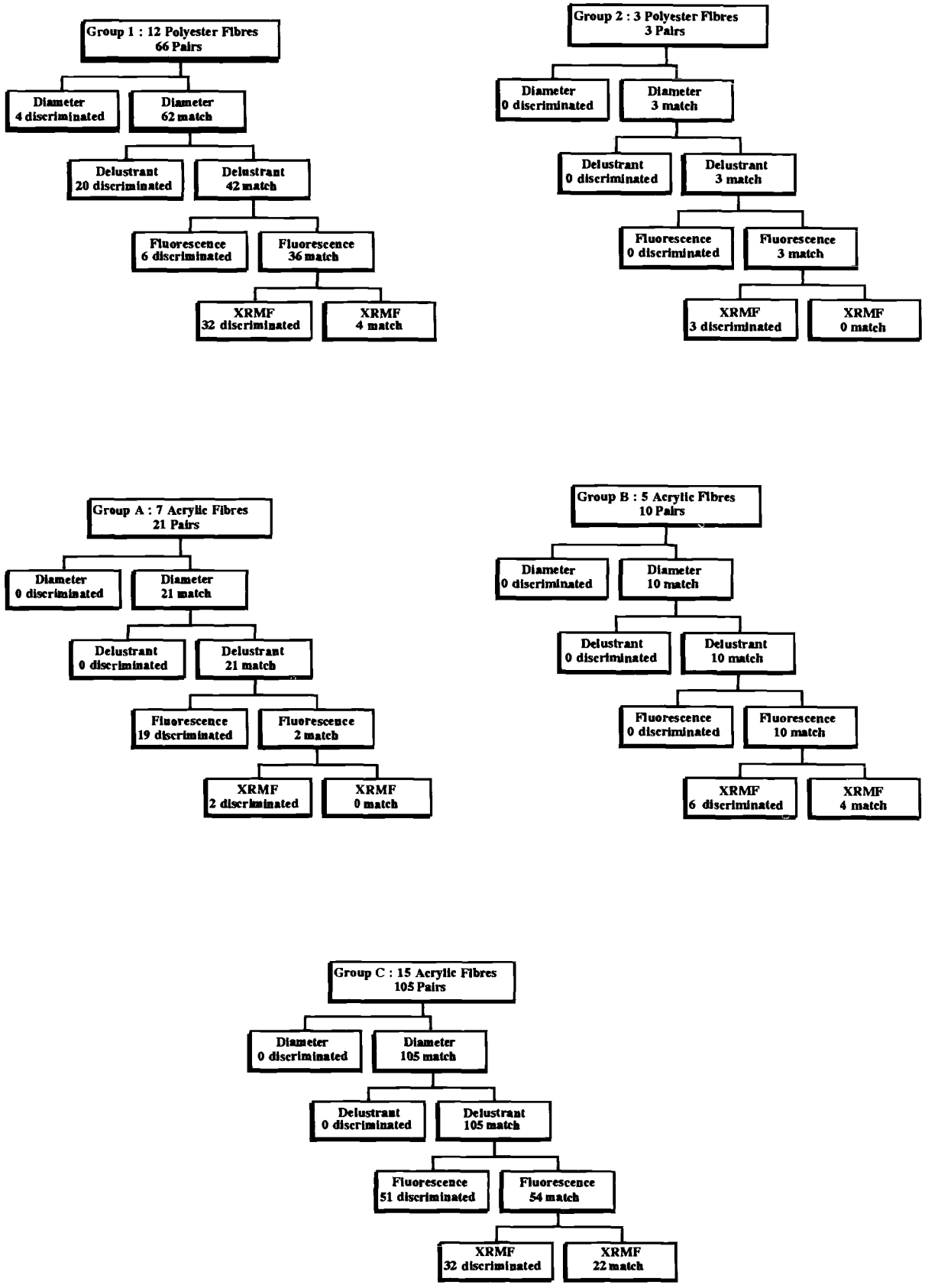

FIG. 5—*Flow charts showing the results obtained for the different steps in the sequential examination.*

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