Liling Cho,[1] Ph.D.; John A. Reffner,[2] Ph.D.; and David L. Wetzel,[1] Ph.D.

Forensic Classification of Polyester Fibers by Infrared Dichroic Ratio Pattern Recognition*

REFERENCE: Cho L, Reffner JA, Wetzel DL. Forensic classification of polyester fibers by infrared dichroic ratio pattern recognition. J Forensic Sci 1999;44(2):283–291.

ABSTRACT: Using a statistical analysis of infrared dichroic ratio data and fiber morphology, 32 polyester fiber samples were classified into 22 unique individual fiber groups and five paired fiber groups. This classification was based on discriminant analysis of infrared dichroic spectra, differences in fiber diameters, and variations in cross-sectional shapes. Using only the infrared dichroic data, the fibers were sorted systematically into 13 infrared groups. A model for discriminant analysis was derived and tested using 2640 infrared dichroic ratios calculated from 5280 quantitative absorbance measurements from single fiber spectra. A tentative protocol is recommended for fiber sorting. The 32 different polyester fibers that were analyzed represented five U.S. manufacturers. Because polyester fibers are the most common synthetic fibers, differentiating single fibers is important in comparisons of forensic trace evidence.

KEYWORDS: forensic science criminalistics, fiber analysis, Fourier transform infrared (FT-IR) microspectroscopy, polarization, dichroism, infrared, discriminant analysis

Individualization of undyed fibers within a generic class is the ultimate challenge to the forensic fiber analyst. In some cases, physical characteristic and other microscopical features are used to distinguish fibers, but rarely is it possible to reach the goal of individualization. When chemical differences occur in the polymer or on the fiber's surface, single fiber infrared microspectroscopy (IMS) may reveal those differences (1,2). The problem of classification is exacerbated for the generic class of polyester (polyethylene terephthalate, PET) for which, with only a minor exception, the chemical composition is unvaried. In this case, conventional infrared spectroscopy has been of little help. The work reported here demonstrates the potential of using polarized IMS to differentiate among PET fibers.

While the chemical composition of a fiber can be determined from its infrared absorption spectrum, its processing history can be revealed in the fiber's orientation. The dichroic ratio at a particular infrared absorption band results from orientation of macromolecules with respect to each other and with respect to the longitudinal axis of the fiber. Previously, we reported the results of systematic infrared dichroism studies of these effects on single polyester and other polymer fibers elongated under carefully controlled drawing conditions on the microscope stage (3,4). Polymers previously studied elsewhere by infrared dichroism include polyester, acrylic, polypropylene, and nylon (5–11).

[1] Ph.D. student and professor, respectively, Kansas State University, Microbeam Molecular Spectroscopy Laboratory, Shellenberger Hall, Manhattan, KS 66506.

[2] Spectra-Tech Inc., 2 Research Drive, Shelton, CT 06484.

* Contribution no. 97-380-J from the Kansas Agricultural Experiment Station, Manhattan, KS.

Received 19 Nov. 1997; and in revised form 16 March 1998; accepted 6 July 1998.

Experimental

The equipment used in this project was an integrated FT-IR microspectrometer (IRμs® Spectra-Tech, Shelton, CT). The IRμs® was equipped with a 600 lines/mm, zinc selenide wire grid polarizer. The angular position of the polarizer was adjusted manually with a dial micrometer attached to a rack and pinion drive. Fibers were placed in the optical beam unsupported. For each fiber the infrared (IR) spectrum was scanned from 4000 cm^{-1} to 600 cm^{-1}. Two hundred fifty-six scans were coadded, and the optical resolution had a nominal value of 4 cm^{-1}. The sample area for single fiber measurement was 12 $\times$ 48 μm. The same aperture size was used for both the fiber and the background. The ratio of the single-beam spectrum obtained from the fiber to the background spectrum obtained for the respective polarizer orientation was calculated. Spectra were plotted in either transmittance or absorbance (12–14).

The dichroic ratio was obtained for each absorption band of interest by dividing the parallel absorbance by the perpendicular absorbance (11). The absorbance value was measured as the peak height after baseline correction. The absorbance at selected wavelengths was obtained with the polarizer perpendicular to the longitudinal axis of the fiber. Subsequently, without changing the position of the fiber, the polarizer was rotated 90 deg so that it was parallel to the fiber axis. Previous experimentation with single fibers of PET revealed eight useful absorption bands (Fig. 1) for the measurement of dichroic activity. These included 876 cm^{-1} (phenyl C—H band out-of-plane), 973 cm^{-1} (C—O stretch of *trans* ethylene glycol unit), 1376 cm^{-1} (CH_2 wagging), 1455 cm^{-1} (CH_2 bending), 1505 cm^{-1} (phenyl C—C stretch, in-plane), 1579 cm^{-1} (phenyl C—C stretch), 1960 cm^{-1} (1,4-substituted phenyl overtone), and 3435 cm^{-1} (C═O stretch overtone). Because of the fiber thickness, many of the mid-infrared absorption bands (1724 cm^{-1}, 1408 cm^{-1}, 1338 cm^{-1}, 1261 cm^{-1}, 1017 cm^{-1}) were too highly absorbing to be used for quantitative measurements (15,16).

Fiber Samples

A collection of 80 different PET fibers was obtained including those manufactured by five different companies in the United States. These included different deniers ranging from 1.5 to 18, with most of the fibers within the range of 1.5 to 7.5 denier. This set represented a range of commercial fibers expected in fiber evidence.

From this large collection, a calibration subset of 33 fiber types was selected to construct a discriminant analysis model (Table 1).

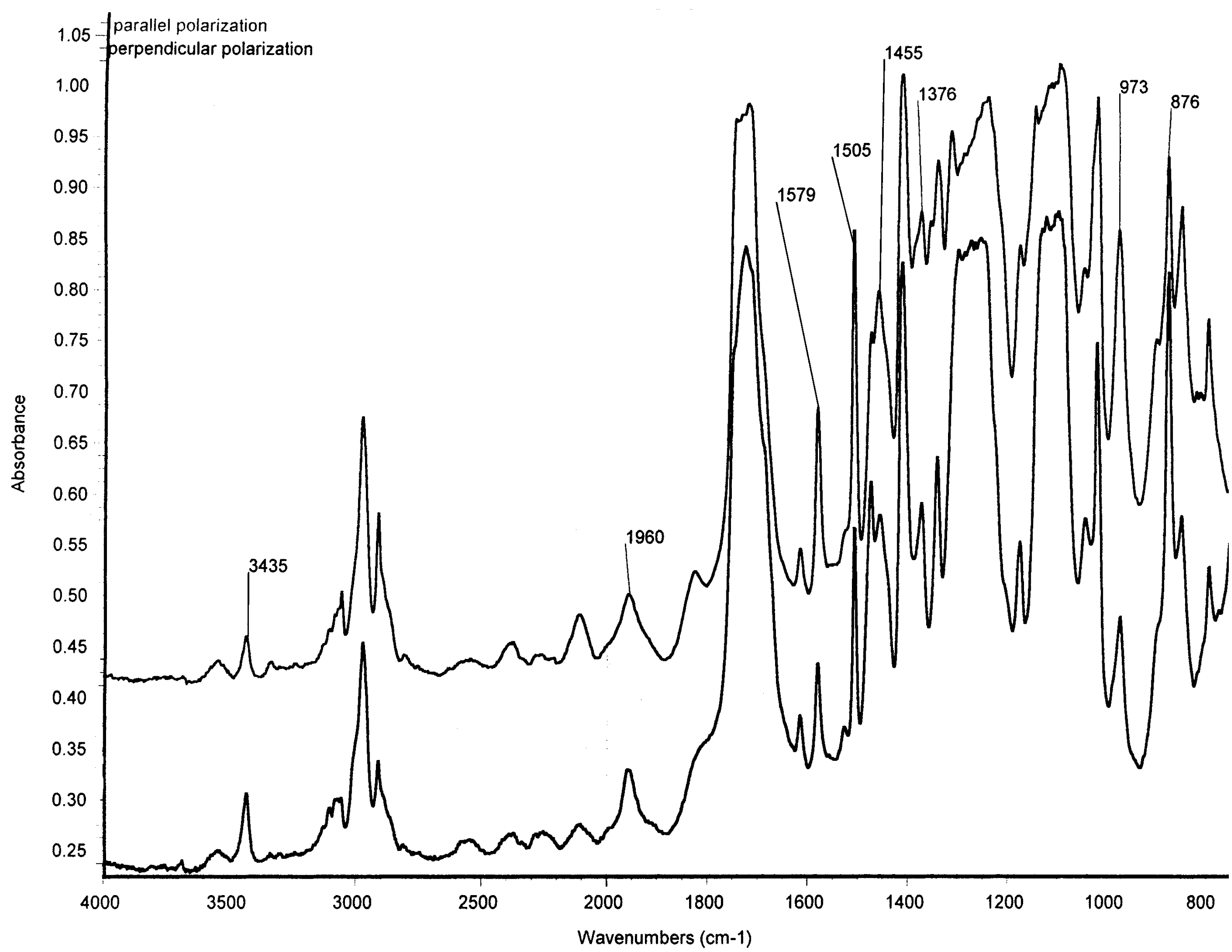

FIG. 1—*Polarized infrared spectra of single polyester fiber with the polarization rector oriented parallel* (upper) *and perpendicular* (lower) *to the fiber axis.*

The goal was to determine if PET fibers from U.S. sources could be sorted into subgroups by discriminant analysis. Fibers from each manufacturer with a range of the denier values was selected. An attempt was made to have proportional representation of the fibers by their manufacturer. As a result, some large manufacturers with widely distributed products had a higher proportional representation than smaller manufacturers who have a smaller market share in the United States. Because the polyester fibers had different deniers, a range of different diameters was represented in the calibration set. In addition to fibers with a round cross section, the collection included those with trilobal, triangular, doughnut, and pentalobal shapes. Whenever more than one shape was present within one denier, then all the shapes were included. Because dyed fibers are classified by their color, the polarized spectroscopic database used here included only undyed PET fibers. This subset of 33 fibers was considered to represent the variables found in the master collection.

Dichroic Spectral Data Collection

Infrared dichroic spectral data were collected using the following procedure. Each of the 33 samples consisted of a bundle of fibers. Ten single fibers were separated from each bundle and mounted on a special fiber sample holder. The 25 $\times$ 75 mm sample holder was fabricated from a 1 mm thick plastic sheet. A row of ten holes (2 mm diameter) was drilled in it. The underside of each hole has a 90° counter-sink opening. The ends of each single fiber were taped down on both sides of the hole. Each of the ten single fibers spanned its own hole on the mounting device. Care was taken not to stretch the fiber while mounting to avoid changing its optical polarization characteristics.

When mounting individual fibers, the fiber axis was aligned parallel to the vertical crossline of the eyepiece reticule. In this orientation, the fiber axis is parallel to the infrared polarization direction. The spectrum of each fiber was collected with the infrared polarizer in one orientation, then the polarizer was rotated 90° to the opposite orientation, and the spectrum was collected again. Reference background spectra, collected previously at both polarizations, were used appropriately to determine ratios and obtain absorbance spectra at each polarizer position. In a similar manner, polarized spectra of each of the other nine single fibers from the same fiber bundle were collected. This procedure was repeated for each of 33 samples to produce 660 spectra (one of each polarization) and 330 dichroic ratios for each of the eight absorption bands of interest.

TABLE 1—*Polyester fibers from which polarized spectra were obtained by single-fiber FT-IR microspectroscopic techniques.*

Sample No.	Manufacturers	Type	Denier	Diameter, μm	Shape
1	DuPont	57	2.1	13–16	round
2	DuPont	76	15	45	doughnut
3	DuPont	278	4.4	24	doughnut
4	Hoechst	270	6.0	26	round
5	Hoechst	296	4.7	24	round
6	Allied	N43-30	5.2	25.1	round
7	Allied	N43-30	12	38.1	round
8	Celanese	T-728-2	2.0	15.6	round
9	DuPont	56	4.4	20–22	round
10	Celanese	T-708	2.7	18	trilobal
11	Allied	N44-100	5.2	25.1	round
12	Celanese	T-278-1	2.0	15.6	trilobal
13	Celanese	T-700	4.6	23.4	round
14	BASF	8380	2.2	16.3	round
15	BASF		2.5	17.4	round
16	Hoechst	220	3.0	19.0	round
17	Allied	N32-32	6.8	28.6	round
18	Hoechst	294	15	42.6	pen-talobal
19	DuPont	232	4.4	18–32	round
20	Allied	N23-30	7.0	29.0	round
21	DuPont	55	2.1	15.0	round
22	DuPont	62	2.1	15–19	trilobal
23	Hoechst	141	2.3	16.5	trilobal
24	Hoechst	625	4.7	23.8	pen-talobal
25	Allied	N25-5	7.1	29.4	round
26	BASF	7151	3.1	19.4	triangular
27	BASF	7444	3.1	19.3	round
28	BASF		5.0	24.6	round
29	Celeanese	T-777	2.0	15.3	round
30	DuPont	54	2.3	16.5	round
31	DuPont	56	2.2	15.5	round
32	Allied	N51-33	5.2	25.1	round
33	Hoechst	618	4.7	23.8	pen-talobal

Note: This collection was assembled before the merger of the Hoechst Corp. and Celanese.

Note: Even though diameter measurements are not typically used to designate the size of noncircular, they were provided by Collaborative Testing Services, Inc. and, therefore, are included in this study for information purposes.

Because of variations in fiber geometry, manufacturing defects, mechanical damage and sample preparation, a single measurement is generally insufficient for quantitative evaluation in single fiber infrared analysis. Single fiber dichroic ratio data of individual fibers from a single sample illustrate the issue of precision (Fig. 2). If a single fiber measurement deviates outside specific limits of variation from the mean values, then it is defined as a spurious data point. Spurious data points are revealed using both a *k*-nearest neighbor and a simple mean with standard deviation computation function applied to the full eight-dimensional experimental data set. Either of these statistical tools could be used as a preliminary data-filtering step prior to discriminant analysis.

A single infrared measurement of a fiber's dichroic ratio may be spurious, placing it into the wrong group. When the same Mahalanobis distance calibration equation was applied to the average value of five dichroic ratio measurements for each fiber sample, false group assignments were eliminated. Therefore, averaging the five dichroic ratio measurements is necessary to produce a reliable data point for group assignment for any sample. It is important to emphasize that in case work, a minimum of five replicate measurements of the dichroic ratio must be averaged to refine the data and detect any spurious measurements. If a single fiber shows no evidence of mechanical deformation or unusual optical retardation patterns, and is more than 1 mm long, then the five replicate measurements may be made on this fiber. Replicate measurements can detect spurious data points and eliminate erroneous group assignment.

Statistical Analysis

Dichroic ratio data calculated from polarized infrared single fiber spectra were statistically analyzed using the Mahalanobis distance discriminant analysis routine developed and discussed by Mark (17) [Bran + Luebbe Analyzing Technologies, (formerly Technicon Industrial Systems) IDAS software, Version 1.40, Revision D]. Canonical variables and stepwise discriminant statistical analysis procedures, available in the SAS/STAT® statistical program (18), also were used to test the discriminant analysis. *K*-nearest neighbors (SAS/STAT®) also was employed.

Results

Discriminant Analysis Applied to Multivariate Dichroic Ratio Data

Discriminant analysis is a statistical method for separating complex data into correlated data sets (17). When a discriminant analysis routine is used, the group to which each member of the training set belongs must be designated. In cases where specific information is known, groups can be assigned. In this case, no advance information, such as draw ratios or relative wind-up speeds, was available from the fiber sources. Without such information, only empirical spectroscopic polarization data resulting from this experimentation were used for the training set group designation. A ''bootstrap'' approach to group selection was applied.

A simple plot of the dichroic ratio data was made to observe the distribution of the dichroic ratios for each of the eight selected absorption bands (Fig. 3). The dichroic ratios are greater than 1 for some bands and less than 1 for other bands. At the absorption band of 973 cm^{-1}, the dichroic ratios ranged from 1.12 to 3.07. At the 3435 cm^{-1} band, the dichroic ratios ranged from 0.35 to 0.89. Preliminary observation led us to list the data in order of dichroic ratios and to observe a reasonable spread in the values. Subsequently, two-dimensional scatter plots were made to look for a natural clustering. This was done for each combination of absorption bands. Four absorption bands displayed significant groupings (Fig. 4). From a three-dimensional plot (Fig. 5) involving the dichroic ratios of three infrared absorption bands (973 cm^{-1}, 876 cm^{-1}, and 3435 cm^{-1}), a preliminary division into eight groups was made.

Application of the Mahalanobis Distance Discriminant Analysis

The Mahalanobis distance was used to further classify the polyester fibers. Dichroic ratio data calculated from polarized IR spectra of each of the 33 fiber samples were used to calculate the Mahalanobis distances. These are the distances in standard deviation units from each point to the centroid of each group in multidimensional hyperspace. The preliminary division of eight groups (Fig. 5) gave a reasonable percentage of ''hits'' on the first attempt to apply the discriminant analysis expression produced to each member of the training set. For this discussion a ''hit'' is defined as a Mahalanobis distance of three or less. From the preliminary

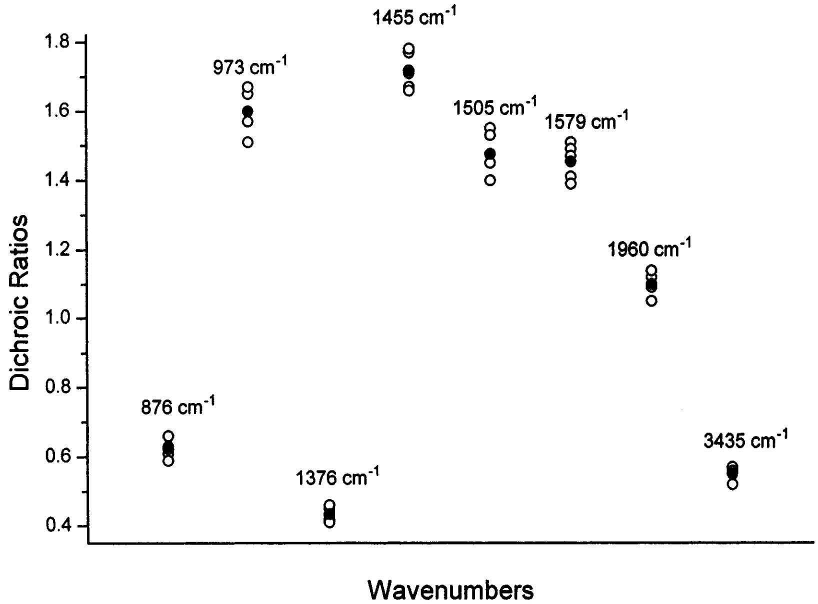

FIG. 2—*Dichroic ratios of five replicates for eight dichroic absorption bands showing the precision of one particular fiber sample. The dark circle is the average of five replicates.*

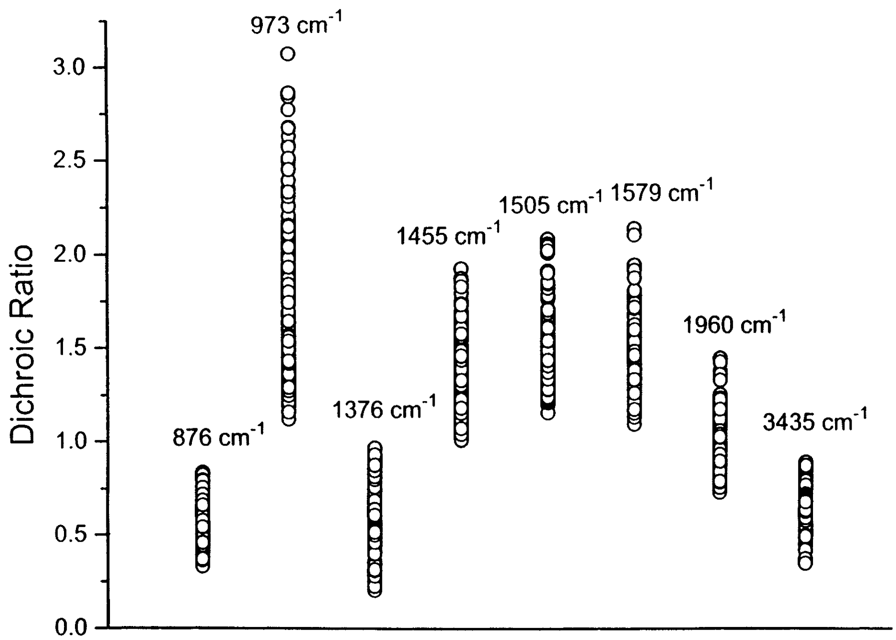

FIG. 3—*Dichroic ratio distribution for five replicates of 33 fiber samples. Each data point is one replicate.*

test, seven rather than eight groups were formed, and some members of the initial groups were redefined to the other groups. Several iterations were involved. After each selection of groups, the discriminant analysis search routine was used to select the absorption bands that served best to discriminate among polyester fibers. A calibration equation was produced.

The Mahalanobis distance from each of seven groups was found for each of 160 dichroic ratio data sets (i.e., 5 replicates of 32 samples). A fiber was considered a member of a particular group when its Mahalanobis distance from that group was the minimum value and less than three (Table 2). Also, it was considered to be definitely excluded from any group when its Mahalanobis distance was greater than three. Of the 33 fiber samples in the calibration set, the dichroic ratio data for sample 32 were highly variable and this sample was excluded from the set. Of the remaining 32 fiber samples, three were considered as individual groups.

Using the 29 remaining fibers samples, a new calibration equation was calculated. In this first stage, the dichroic ratios of three absorption bands were selected. The 145 dichroic ratio sets for each of the eight absorption bands (i.e., 5 replicates of 29 samples) were used to generate the calibration equation coefficients. This produced a Mahalanobis distance of each of the 145 fibers (corresponding to 29 samples) from the centroid of each of the seven groups. Discriminant analysis of dichroic ratios at these three

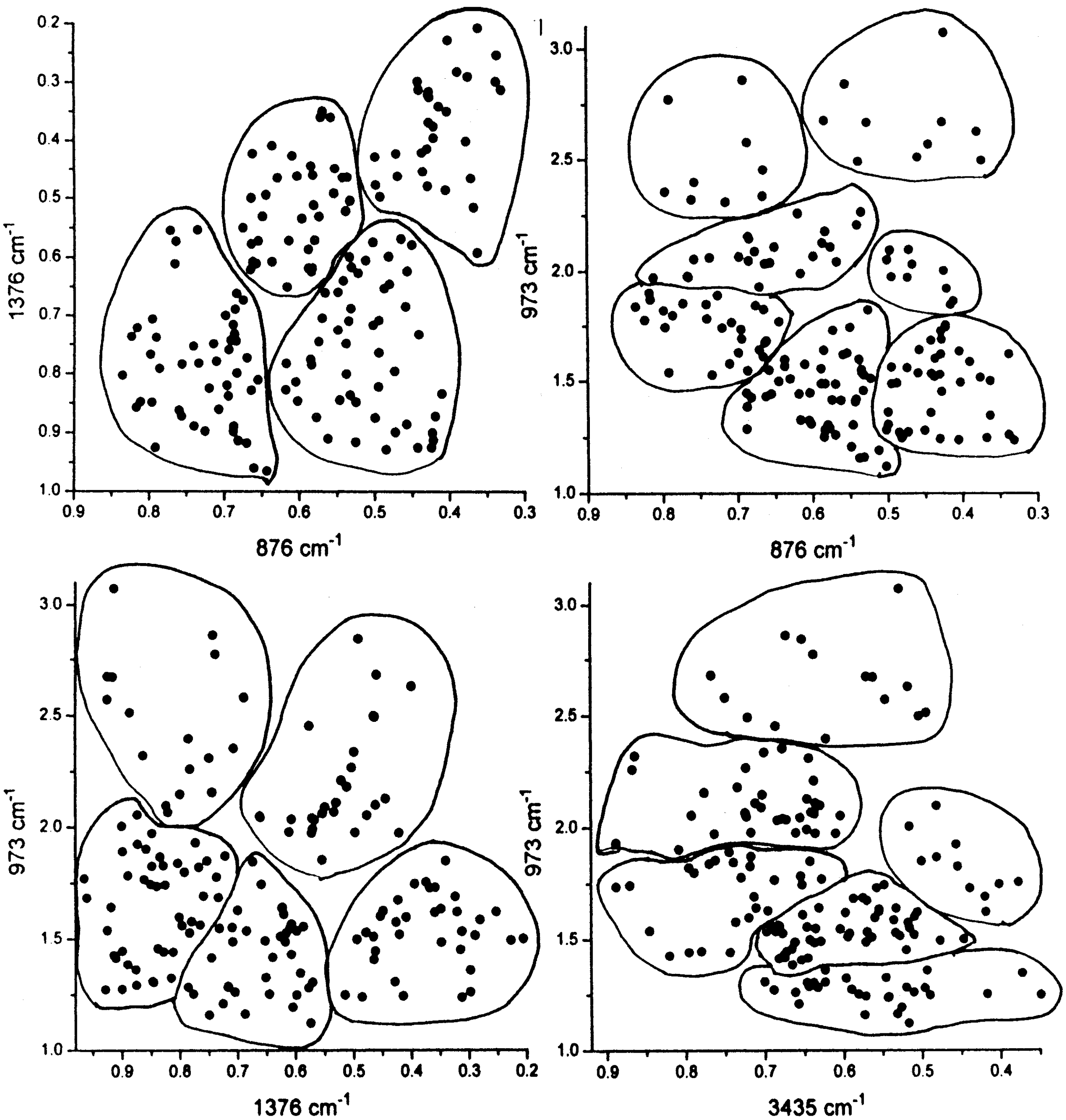

FIG. 4—*Two-dimensional scatter plot showing initial grouping based on the dichroic ratios for each individual replicate. A: 1376 cm^{-1} vs. 876 cm^{-1}, B: 973 cm^{-1} vs. 876 cm^{-1}, C: 973 cm^{-1} vs. 1376 cm^{-1}, D: 973 cm^{-1} vs. 3435 cm^{-1}.*

absorption bands with the seven newly defined groups produced 133 hits in 139 tries (when only dichroic ratio data of individual fibers were used).

The classification based on the lowest numerical value of Mahalanobis distance was correct, and 29 hits for 29 tries were obtained using one subset (when average data of five replicates were used). Also, 100% hits resulted when this classification scheme was tested with the validation subset. When all Mahalanobis distances for both sets of data (Tables 2 and 3) were compared, we are confident in all of the assignments with the exception of samples no. 2 and no. 5. The classification of these samples into group G-1 was marginal, because they also had Mahalanobis distances fairly close to another group, E-1. The classification among five of seven primary groups was excellent. Although potential overlap existed between two of the seven primary groups, misclassification did not occur.

Because three of the seven initial primary groups were close together, all samples assigned to groups D-1, E-1, and F-1 were pooled for a second-stage discriminant analysis. The 55 dichroic ratio data sets were divided into six new groups by using the iterative process previously described. Using these six new groups, a second-stage calibration of Mahalanobis distances was made. Starting with the eight different absorption bands having significant dichroism, a new three-absorption band calibration equation was generated. This new discriminant analysis equation was applied to the 11 samples (i.e., averages of five replicates of each sample), 100% hits occurred. At this point, the two-stage discriminant analysis scheme produced ten separate groups including the four from the initial set (groups A-1, B-1, C-1, and G-1 in Fig. 6) and six from the subgroup designed as a-2, b-2, c-2, d-2, e-2, and f-2 (Fig. 7). Data from averaged replicates are plotted to show four

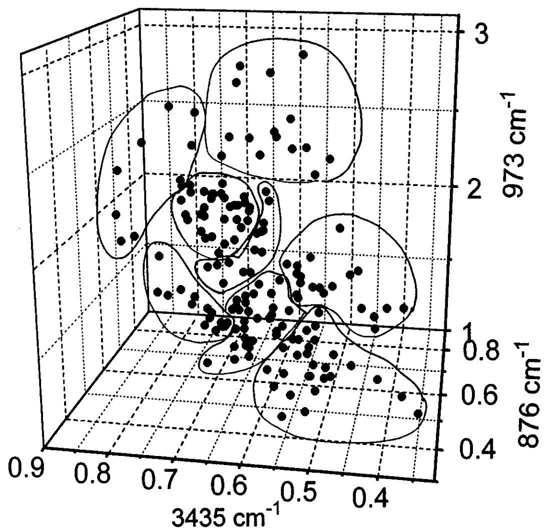

FIG. 5—*Three-dimensional plot of dichroic ratios at 3435 cm^{-1}, 876 cm^{-1}, and 973 cm^{-1} based dichroic ratios from five replicates of 33 fiber samples. Eight preliminary groups were selected.*

separate and three pooled groups from stage one (Fig. 6) and the six separate subgroups from stage two (Fig. 7).

When the two-stage discriminant analysis routine was applied to the averaged data from five replicates of all 29 samples, each fiber sample was placed in its correct group, resulting in 100% hits. The same two-stage scheme applied to the verification set (the averaged value of the last five replicates of the same fiber) also resulted in 100% hits.

The three individual fiber groups excluded from the two-stage analysis were tested by a third-stage discriminant analysis. The resulting expression involved the same absorption bands as the first stage but different coefficients. Because these samples produced dichroic ratios that were far removed from the other 29 in the first-stage analysis, they were assumed to be one-of-a-kind samples. A third-stage discriminant analysis reaffirmed the individual grouping previously inferred for each of these three samples by the first-stage operation. These resulting individual sample groups are shown in Fig. 5 as H-1, I-1, and J-1.

Discriminant Analysis Using Canonical Variables

Dichroic ratio data from 145 spectra were used to calculate canonical variables (CVs). Given a classification variable (groups) and several quantitative variables (the dichroic ratios for eight absorbance bands), the SAS/STAT® statistical program calculates CVs that summarize between-class variations (18). Canonical variables are linear combinations of the quantitative variables. In running this analysis, the initial seven groups, previously chosen and employed in the Mahalanobis distance routine, were used along with dichroic ratio data of the eight absorption band to calculate CVs. From this calculation, six canonical coefficients were assigned to each of the 145 fibers.

The SAS/STAT® routine also produced two-dimensional CV plots. We selected those involving the first three CVs (CV1 vs. CV2, CV1 vs. CV3, and CV2 vs. CV3). On each plot, the individual fiber data were denoted with a letter corresponding the predefined groups, and the plots were examined for potential overlap. Each of the CVs is a composite incorporating all eight dimensions, and this analysis also produced separation of the initial seven groups with no overlapping.

TABLE 2—*Mahalanobis distance from primary groups.*

Sample No.	C-1	G-1	D-1	E-1	F-1	A-1	B-1
1	0.81*	6.75	3.65	4.17	5.72	2.84	5.97
	0.94*	6.44	3.63	3.93	5.54	3.18	5.97
2	6.97	1.87*	4.56	2.24	3.14	8.13	11.87
	7.29	2.01*	4.76	2.56	3.22	8.38	12.20
3	4.83	2.86	3.36	1.26†	2.84	6.28	9.22
	4.83	2.85	3.33	1.22†	2.82	6.27	9.24
4	5.35	2.59	4.01	1.29†	3.73	6.89	10.34
	5.26	2.64	4.02	1.29†	3.79	6.84	10.24
5	5.63	1.95*	5.18	2.23	4.54	7.74	9.90
	5.55	1.94*	5.04	2.07	4.43	7.63	9.89
6	7.56	1.74*	6.84	3.79	5.73	9.67	11.85
	7.64	1.79*	6.93	3.88	5.80	9.76	11.91
7	8.03	1.95*	5.37	3.40	3.11	9.11	12.43
	8.18	1.89*	5.54	3.50	3.29	9.29	12.63
8	4.78	3.78	1.91	1.26†	2.07	5.46	9.70
	4.75	3.79	1.87	1.27†	2.01	5.42	9.63
9	0.83*	7.89	5.27	5.53	7.29	3.47	4.72
	0.79*	7.81	5.24	5.47	7.24	3.51	4.69
10	0.79*	7.00	3.74	4.43	5.83	2.64	5.65
	0.87*	7.16	3.74	4.57	5.90	2.44	5.61
11	5.35	1.94	4.56	1.55†	4.00	7.28	9.88
	5.07	2.20	4.31	1.33†	3.90	6.97	9.66
12	3.95	5.10	0.85†	2.46	2.64	4.11	8.62
	3.99	4.97	0.95†	2.35	2.55	4.23	8.66
13	4.30	11.20	6.70	8.50	9.23	2.69*	4.87
	4.31	11.22	6.74	8.53	8.98	2.74*	4.77
14	3.02	8.49	3.62	5.77	6.10	0.82*	6.17
	3.15	8.62	3.71	5.90	6.19	0.76*	6.21
15	5.65	7.17	1.90†	4.74	3.73	4.20	10.07
	5.64	7.21	1.93†	4.77	3.45	4.22	9.89
16	1.14*	6.28	4.40	4.02	6.04	4.07	5.91
	1.07*	6.36	4.43	4.09	6.09	4.02	5.83
17	7.45	1.25*	6.16	3.21	4.94	9.26	12.05
	7.34	1.23*	6.04	3.10	4.85	9.14	11.96
18	7.12	3.34	3.57	2.80	1.16†	7.55	11.76
	7.22	3.34	3.66	2.88	1.27†	7.66	11.88
19	2.95	7.54	2.56	4.75	5.17	1.52*	7.16
	3.00	7.63	2.63	4.84	5.24	1.45*	7.17
20	4.55	11.08	8.88	9.06	10.83	6.19	2.19*
	4.60	11.20	8.92	9.15	10.90	6.16	2.16*
21	7.26	13.01	10.51	11.16	12.15	7.93	2.46*
	6.98	12.65	10.18	10.81	11.79	7.70	2.36*
22	4.71	11.43	8.35	9.21	10.39	5.28	1.09*
	5.13	11.90	8.77	9.66	10.84	5.58	1.10*
23	1.21*	8.44	5.41	6.00	7.58	3.06	4.41
	1.26*	8.50	5.47	6.05	7.64	3.10	4.37
24	8.91	2.38*	7.10	4.72	5.06	10.48	12.79
	8.93	2.36*	7.10	4.72	5.05	10.49	12.82
25	4.16	4.83	1.07†	2.28	2.35	4.44	8.76
	4.16	4.93	1.01†	2.39	2.38	4.37	8.74
26	4.51	3.89	1.98	1.22†	2.47	5.28	9.52
	4.51	3.84	2.00	1.17†	2.46	5.31	9.51
27	3.71	8.66	3.46	5.86	6.09	1.14*	7.37
	3.54	8.71	3.58	5.91	6.21	0.89*	7.12
28	6.02	4.47	2.09	2.80	0.60†	6.03	10.49
	6.08	4.46	2.20	2.80	0.52†	6.13	10.53
29	6.38	4.66	2.45	3.20	0.66†	6.31	10.71
	6.42	4.55	2.54	3.16	0.59†	6.41	10.75
30	3.64	6.42	3.56	4.08	4.05	3.59	7.13
	3.57	6.55	3.58	4.17	4.17	3.44	7.04
31	4.86	6.67	5.80	5.64	6.37	6.21	6.40
	4.84	7.00	5.94	5.72	6.45	6.30	6.12
32	7.04	3.26	7.28	4.51	6.45	9.49	10.36
	6.88	3.43	7.25	4.53	6.49	9.36	10.12
33	4.71	3.98	1.72	1.88	1.83	5.34	9.26
	4.66	4.12	1.67	1.78	1.83	5.20	9.26

* Primary group assignment.

† Assignment deferred to second stage.

Note: Each MD is calculated from average dichroic ratios of five replicates.

Note: The bottom row of MD beside each sample number was from the verification set of measurement and the average of five replicate dichroic ratios.

Samples 30, 31, 32—for third stage analysis.

Sample 33 had a bad precision.

TABLE 3—*Mahalanobis distances from secondary groups.*

Sample No.	a-2	b-2	c-2	d-2	e-2	f-2
3	2.09*	3.54	6.30	3.49	5.62	5.76
	1.80*	3.92	5.88	3.23	5.33	5.48
4	4.30	7.36	4.62	0.60*	6.31	5.47
	4.35	7.43	4.59	0.59*	6.38	5.59
8	1.37*	5.77	4.05	2.85	3.71	3.75
	1.15*	5.59	4.20	3.00	3.68	3.81
11	3.69	6.37	5.00	0.60*	6.34	5.85
	3.58	6.10	5.16	0.94*	6.39	5.99
12	4.88	0.00*	9.65	6.86	7.91	8.29
	5.09	0.24*	9.86	7.01	8.09	8.44
15	2.02*	6.84	6.18	5.88	3.26	4.42
	1.98*	6.93	6.13	5.86	3.24	4.43
18	4.29	8.29	4.75	5.63	2.33	0.00*
	4.38	8.27	4.95	5.66	2.52	0.24*
25	1.75*	6.33	3.78	4.60	3.21	4.50
	1.84*	6.38	3.81	4.74	3.18	4.52
26	4.88	9.65	0.00*	4.78	4.67	4.75
	4.84	9.61	0.04*	4.75	4.45	4.74
28	3.99	8.53	3.80	6.26	0.87*	2.49
	4.06	8.58	3.84	6.31	0.88*	2.48
29	3.47	7.34	5.20	6.45	0.89*	2.49
	3.47	7.35	5.20	6.45	0.89*	2.49

* Secondary group assignment.

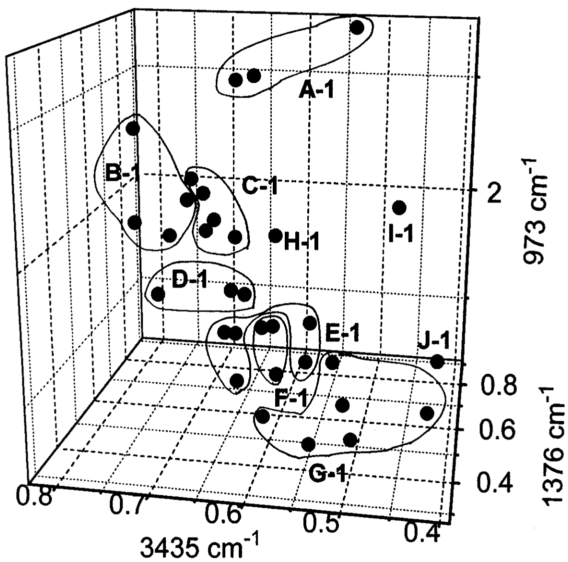

FIG. 6—*Seven groups identified from first-stage discriminant analysis based on three absorption bands. Each data point is the average of five replicates.*

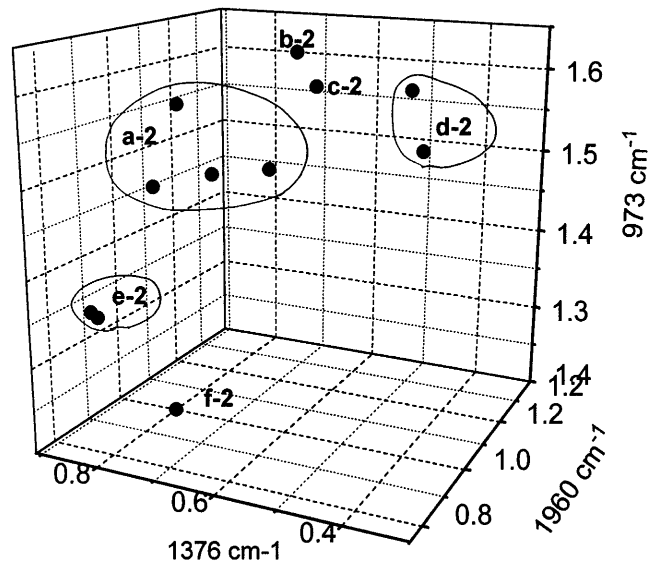

FIG. 7—*Six subgroups classified by second-stage discriminant analysis of data pooled from groups D-1, E-1, and F-1 resulting from the first-stage discriminant analysis separation shown in Fig. 6.*

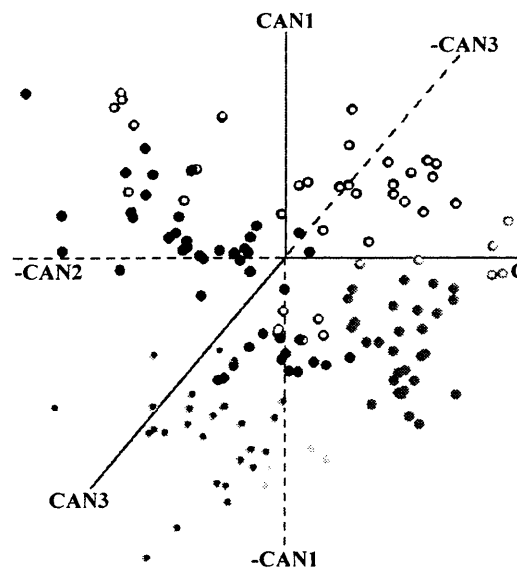

FIG. 8—*Three-dimensional plot of three canonical variables (CV1, CV2, CV3) showing the same seven groupings that were used in the first-stage Mahalanobis distance discriminant analysis.*

Among the seven primary groups that were successful for Mahalanobis discriminant analysis, a three-dimensional (3-D) plot of CV1, CV2, and CV3 (Fig. 8) illustrates obvious group definition and good separation of those groups. This independent result supported the grouping previously used for the Mahalanobis distances discriminant analysis procedure. Thus, incorporating the eight-dimensional information into CVs supported the earlier assignment of groups based on dichroic ratios of three absorption bands of each fiber.

Stepwise Discriminant Analysis in SAS/STAT® Statistical Program

In a stepwise discriminant analysis, the significance of the eight absorption bands that provides the best discrimination can be decided by a forward selection process. Forward selection began with no variables in the model. It then built a model by selecting variables (dichroic ratio by absorption band). The variable entered in the model was dependent on the level of significance it contributed to the discriminatory power of the model. Only one variable could be entered into the model at each step. The forward selection process stopped when the new variables could not meet the entry criterion to improve the discrimination of the samples (17).

Results of applying this statistical procedure further supported the order of importance of the absorption bands that we used in our method development. Stepwise discriminant analysis (18) selected dichroic ratio data from the same four absorption bands (973 cm^{-1}, 1376 cm^{-1}, 3435 cm^{-1}, and 1960 cm^{-1}) and ranked them in order of their significance. These are the same four absorption bands independently selected by Mahalanobis distance discriminant analysis search routines. This coincidence of selection of discriminators added support for the results from our multistep Mahalanobis distance discriminant analyses. Of the absorption bands selected in that analysis, the first three were employed for the first-stage discriminant analysis, and the first two and the fourth were employed for second-stage analysis. Both the CVs and stepwise discriminant analysis data support our Mahalanobis distance analysis protocol, including the choice of absorption bands and the group assignments.

Classification Combining IR Grouping and Morphology of the Polyester Fibers

From Mahalanobis distance discrimination analysis based on the infrared dichroic ratio data, ten multiple-sample groups plus three individual groups were defined. Because of different diameters and cross-sectional shapes of these 32 samples, further classification of PET fibers was made (Table 4). Six different diameter groups and five different cross-sectional shapes were used to separate the samples in the IR groups. For example, four different samples were classified in the A-1 group based on their dichroic activity. When the diameter and cross-sectional shape were considered, these four fiber samples were separated into four different final groups. These final group assignments are listed in Table 4. Following this scheme, the 32 fiber samples were assigned to 27 final groups. Among those groups, five contained two samples each. These five sample pairs could not be separated by this analysis. Because 22 of the 32 fiber samples were grouped separately, these formed unique classifications among the set of 32 PET fibers.

TABLE 4—*Individual classification of polyester fibers.*

Sample No.	IR Grouping	Diameter Grouping	Shape	Final Grouping Assignment
13	A-1	3	R	1
14	A-1	1	R	2
19	A-1	6	R	3
27	A-1	2	R	4
20	B-1	4	R	5
21	B-1	1	R	6
22	B-1	1	T	7
1	C-1	1	R	8
9	C-1	2	R	9
16	C-1	2	R	9
10	C-1	1	T	10
23	C-1	1	T	10
2	G-1	5	D	11
5	G-1	3	R	12
6	G-1	3	R	12
7	G-1	5	R	13
17	G-1	5	P	14
24	G-1	3	P	15
3	a-2	3	D	16
8	a-2	1	R	17
15	a-2	1	R	17
25	a-2	4	R	18
12	b-2	1	T	19
26	c-2	2	Tri	20
4	d-2	3	R	21
11	d-2	3	R	21
28	e-2	3	R	22
29	e-2	1	R	23
18	f-2	6	R	24
30	H-1	1	R	25
31	I-1	3	R	26
32	J-1	3	R	27

Note: Diameter grouping assignments: 1 = 16 ± 2 μm, 2 = 20 ± 2 μm, 3 = 25 ± 2 μm, 4 = 30 ± 2 μm, 5 = 40 ± 5 μm, 6 = vary.

Note: Shape grouping assignments: R = round, D = doughnut, T = trilobal, P = pentalobal, Tri = triangular.

Summary

A discriminant analysis sorting procedure using infrared dichroic ratio data provided a method for differentiating undyed PET fiber samples. In a set of 32 PET fiber samples, the statistical analysis of dichroic ratio data generated 13 groups. The PET fiber classification was extended further when the fiber microstructural morphology was used in addition to infrared dichroic ratio data as discriminating factors. These fibers were separated into six different groups by their fiber diameters and five groups by their different cross-sectional shapes. When all factors were considered, 27 separate group classes were defined. When the 32 fiber samples were assigned to these final groups, 22 unique individual fiber groups and five paired fiber groups were found. For PET fiber samples assigned to the 22 unique groups, this final grouping provided unique classification. Fiber samples assigned to each of the five remaining groups could not be differentiated between the paired fibers.

Spectra of ten single fibers were taken at both polarizations for each of the 33 samples. The absorbance values were calculated for eight absorption bands (876 cm^{-1}, 973 cm^{-1}, 1376 cm^{-1}, 1455 cm^{-1}, 1505 cm^{-1}, 1579 cm^{-1}, 1960 cm^{-1}, and 3435 cm^{-1}) at both polarizations, providing 5280 quantitative absorbance measurements. Examining the dichroic ratio data showed which absorption bands produced the greatest difference. In particular, 2640 data points involving dichroic ratios were generated, of which 1320 data points were used in a discriminant analysis search.

A dichroic three-absorption band Mahalanobis distance equation used the absorption bands 973 cm^{-1}, 1376 cm^{-1}, and 3435 cm^{-1} for the first-stage discriminant analysis. The second-stage discriminant analysis used dichroic ratios of the 973 cm^{-1}, 1960 cm^{-1}, and 3435 cm^{-1} absorption bands. When the averaged dichroic ratio data for replicate measurements of validation samples were used, 100% correct assignment of groups resulted from the two-stage discriminant analysis procedure. Dichroic ratio data for five replicates of the same fiber samples were averaged at each of the individual absorption bands. The same procedure used on a verification data set from the pool of another 1320 dichroic ratios also produced 100% hits. To avoid spurious data, a statistical means of looking for outliers among the replicates was employed. Group assignments used in the Mahalanobis distance method that we developed for PET fibers were supported by resulted of CV analysis, for which dichroic ratio data of all eight absorption bands were used. The order of importance of absorption bands for discriminating PET fiber samples established from the Mahalanobis distance method was also supported by SAS/STAT® stepwise discriminant analysis results.

This classification method for PET fibers depends on measuring infrared dichroic ratios, the selection of proper infrared absorption bands, and a two-staged statistical analysis of the data. In casework, it is important to note that a minimum of five replicate measurements of the dichroic ratio must be averaged to refine the data and remove any spurious measurements. If a fiber shows no evidence of mechanical deformation or unusual optical retardation patterns, and is more than 1 mm long, then replicate measurements may be made on this single fiber.

By obtaining 100% hits for this exemplar set of PET fiber samples, the present method demonstrates the potential of this approach to PET fiber classification. Because PET polyester fibers are the most commonly used commercial fibers in the world, the ability to separate the polyester into different classes is a significant contribution to examination of trace fiber evidence. It should be noted that these results were obtained using undyed fibers. Effects of dyeing or laundering could be important factors in actual casework fiber comparisons. The present data do not address any such potential effects.

References

1. Grieve MC. Fibers and forensic science—new ideas, developments, and techniques. Forensic Sci Rev 1994;6:59–80.
2. Tungol MW, Bartick EG, Montaser A. Analysis of single polymer fibers by Fourier transform infrared microscopy: the results of case studies. J Forensic Sci 1991;36(4):1027–43.
3. Cho L, Wetzel DL. Polarized microbeam FT-IR analysis of single fibers. In: Bailey GW, Corbett JM, Dimlich RVW, Michael JR, Zaluzec NJ, editors. Proceedings of Microscopy and Microanalysis; 11–15 Aug. 1996; Minneapolis, MN. San Francisco, CA: San Francisco Press, Inc., 1996;206–7.
4. Cho L. Single fiber analysis by FT-IR microspectroscopy. PhD. dissertation, Manhattan, KS: Kansas State University, 1997.
5. Chase DB. Dichroic infrared spectroscopy with a microscope. In: Messerschmidt RG and Harthcock MA, editors. Infrared microspectroscopy: theory and applications. New York: Marcel Dekker, Inc., 1988;93–102.
6. Church SP, Khan N. Infrared dichroism of liquid crystalline terephthalate and biphenyldicarboxylate polyesters. Polym Bulle 1993; 30:559–66.
7. Fraser RDB. Interpretation of infrared dichroism in fibrous proteins—2 μ region. J Chem Phys 1956;24(1):89–95.
8. Kaito A, Kyotani M, Nakayama K. Orientation distribution of liquid-crystalline polyester sheets studied by polarized infrared spectroscopy. J Polym Sci: Part B: Polym Phys 1993;31:1099–108.
9. Samanta SR, Lanier WW, Miller RW, Gibson ME. Fiber structure study by polarized infrared attenuated total reflection spectroscopy: orientation development of nylon 66 at various spinning speeds. Appl Spectrosc 1990;44(7):1137–42.
10. Yazdanian M, Ward IM, Brody H. An infrared study of the structure of oriented poly(ethylene terephthalate) fibers. Polymer 1985; 1779–90.
11. Griffiths PR, de Haseth JA. Fourier transform infrared spectroscopy. New York: John Wiley and Sons, Inc. 1986.
12. Wetzel DL. Microbeam molecular spectroscopy of biological materials. In: Charalambous G, editor. Food flavors: generation, analysis process influence. Amsterdam: Elsevier Science, 1995;2039–108.
13. Wetzel DL. Microbeam molecular analysis. Microscopy and analysis 1996;(5):17–19.
14. Reffner JA, Martoglio PA. Uniting microscopy and spectroscopy. In: Humecki HJ, editor. Practical guide to infrared microspectroscopy. New York: Marcel Dekker, Inc., 1995;41–86.
15. Wetzel DL, Cho L. Single fiber characterization by polarization FT-IR microspectroscopy. Mikrochim Acta 1997;14(suppl):349–51.
16. Tungol MW, Bartick EG, Montaser A. Forensic examination of synthetic textile fibers by microscopic infrared spectrometry. In: Humecki HJ, editor. Practical guide to infrared microspectroscopy. New York: Marcel Dekker, Inc., 1995;245–86.
17. Mark H. Principles and practice of spectroscopic calibration. New York: John Wiley and Sons, Inc., 1991.
18. SAS/STAT® user's guide. 6.03 ed. Cary, NC: SAS Institute, 1988.

Additional information and reprint requests:
Prof. David L. Wetzel
Microbeam Molecular Spectroscopy Laboratory
Kansas State University
Shellenberger Hall
Manhattan, KS 66506