

Analysis of Fiber Blends Using Horizontal Attenuated Total Reflection Fourier Transform Infrared and Discriminant Analysis

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We have investigated the utility of a horizontal attenuated total reflection Fourier transform infrared spectrometer (HATR/FT-IR) for the analysis of fiber and textile blends. The identification of a blended textile can be accomplished by subtracting a reference spectrum of the textile's most abundant component, leading to a difference spectrum that infers the identity of the second constituent of the blended textile. Mathematical post-processing of the spectra employing discriminant analysis provided a useful statistical tool to confirm the fiber blend components.

Index Headings: Fiber blends; Textile blends; Forensics; Horizontal attenuated total reflection; Fourier transform infrared spectroscopy; HATR/FT-IR; Discriminant analysis.

INTRODUCTION

Fiber blends make up a considerable number of fabrics on the market today. They are manufactured by either weaving together different fibers to create a blended yarn or by weaving different yarns to create a textile blend. The classification and examination of fibers and textiles in forensic science has been well studied,^{1,2} but the characterization of fiber blends presents a unique challenge.

Microscopic analysis continues to be the traditional tool when determining whether a trace evidence item is composed of multiple fiber components.³ Fourier transform infrared spectroscopy (FT-IR) is another analytical tool that, when used in fiber analysis, stands out for its robustness, ability to make structural elucidations, ease of sample preparation, and simplicity of operation. For these reasons, FT-IR has become a critical tool in the analysis of synthetic fibers for forensic purposes.^{4,5}

Discriminant analysis (also known as linear discriminant analysis or canonical variates analysis) of vibrational spectra has been successfully used in class character analysis. Examples include bacterial identification,⁶ confirmation of edible oils and fats,⁷ and forensic characterization of printer toners.⁸ Enlow et al.⁹ demonstrated its usefulness in sub-typing nylon polymers. In this study, we present our results of characterizing fibers and textile blends by horizontal attenuated total reflection (HATR) FT-IR analysis with subsequent confirmation by discriminant analysis.

METHODS

A Nicolet, Nexus 470 FT-IR (Omnic v.6 software)¹⁰ with a Smart MIRacle HATR accessory¹¹ was used for developing the fibers database library and to study the spectral properties of fibers and fiber blends. The Smart MIRacle accessory contained a ZnSe single reflection ATR plate with a sampling

diameter of 2 millimeters. Fibers required no sample preparation and were placed directly on the ZnSe window. Textile samples were simply placed on the accessory, whereas fiber samples were oriented in the "east-west" configuration and were aligned with the probing beam in order to minimize unwanted spectral differences due to fiber placement.¹² The micrometer associated with the Smart MIRacle HATR accessory had a straight-edged rubber tip attachment, and each sample was collected while applying approximately 800 psi of pressure. The Nicolet spectrometer contained a KBr beam splitter along with a DTGS KBr detector. The best spectra were obtained when the sampling window (2 mm) was completely covered by the fibers, but reliable data was also produced from a single large diameter fiber (i.e., polyester) or bundles of small diameter fibers (i.e., acrylic) when they covered at least 25% of the sampling window (approximately 0.5 mm in total fiber diameter).

Standard fiber samples were obtained from Microtrace;¹³ wool and silk samples were from the collection of the National Fish and Wildlife Forensic Laboratory. Blended fibers or textiles were obtained from local commercial sources. Collection parameters for the spectral library were optimized to produce high spectral accuracy.⁴ Validation samples were scanned 32 times, whereas the library samples were scanned 256 times under autogain control. The final format of the spectra was $\log(1/R)$ versus wavenumber (cm^{-1}) with a spectral range of 4000–650 cm^{-1} . There was no correction performed on the resulting spectrum. The $\log(1/R)$ for reflection measurements is equivalent to absorbance in transmission measurements.¹⁰ A background spectrum was taken before each fiber was sampled. Discriminant analysis was performed using the TQ Analyst™ v.6.0 software package (Nicolet).¹⁴

RESULTS AND DISCUSSION

Reference Fiber Library Development. The HATR/FT-IR spectra from known standard fibers were collected to assemble a reference library. Each sample was collected using 256 scans, and each spectrum was evaluated for spectral accuracy. Sufficient fibers were selected to completely cover the sampling crystal while ensuring an east-west orientation.¹² Spectra from textile blends that are commonly encountered in commercial trade were also included in the reference library. Textile blends were validated in-house before their inclusion in the spectral library. The validation consisted of confirming the components by polarized light microscopy and by FT-IR analysis as described *vide infra*. The resulting library contained 128 samples (Table I).

Analysis of Blends. The analysis of fibers by FT-IR is straightforward and has been thoroughly reviewed.⁴ When using FT-IR, fiber or textile blends are suspected when (1) the FT-IR spectral library returns a poor match value, (2) multiple

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TABLE I. List of fibers that compose the spectral library.

Fiber/textile	Sample size
Acetate	4
Acrylic	9
Aramid	4
Carbon	1
Chlorofiber	2
Cotton	10
Lyocell	2
Modacrylic	10
Modal 60	1
Nylon 6	10
Nylon 6,6	10
Olefin	7
PBI	1
Polyester	9
Rayon	10
Silk	11
Spandex	2
Sulfar	1
Wool	16
Textile blends:	8
Polyester/wool blend (65:35)	
Polyester/rayon blend (50:50)	
Polyester/cotton blend (40:60)	
Polyester/lycra blend (88:12)	
Polyester/lycra blend (96:4)	
Nylon/lycra (85:15)	
Nylon/lycra (88:12)	
Cotton/Spandex (96:4)	

analyses from various areas of a textile show high spectra variability, or (3) the spectral library provides a good match value for a blend found in the library.

The analysis of blends follows the scheme outlined in Fig. 1. Typically, when a blend is suspected, the library search index provides a match to the most abundant polymer (i.e., generic class such as nylon, polyester, etc.). This match infers the first blend component. Next, a reference spectrum of this component is subtracted from the unknown, and the resulting difference spectrum is again searched against the fiber library. The best match value infers the identity of the second blend component. Confirmation of blends is done by Discriminant Analysis (TQ Analyst™ software). Additional confirmation should include the examination of the unknown spectrum using the “first principle” tables in which typical absorption frequencies for specific fibers are given. Such tables have been compiled by Kirkbride and Tungol.⁴

The example in Fig. 2 demonstrates this process. In this illustration, Fig. 2A is the spectrum of an unknown sample and a library search gives a good match hit to polyester (91.7). We then compared the spectrum of the unknown to that of a polyester standard (polyethylene terephthalate polymer) (Fig. 2B) in order to corroborate that the characteristic frequencies were present (1714, 1243, 1094, 1022, and 730 cm⁻¹).⁴ The presence of these absorptions strongly infers the presence of polyester. However, as the visual examination of the spectrum demonstrates, there are subtle differences when compared to the polyester standard.

In order to characterize the second component, the spectrum of a polyester standard was subtracted from that of the unknown. We used the automatic region subtract option,¹⁰ which allows us to choose which peaks in the spectrum should be eliminated. Polyester has very strong absorption peaks, and the subtraction process eliminates the typical polyester

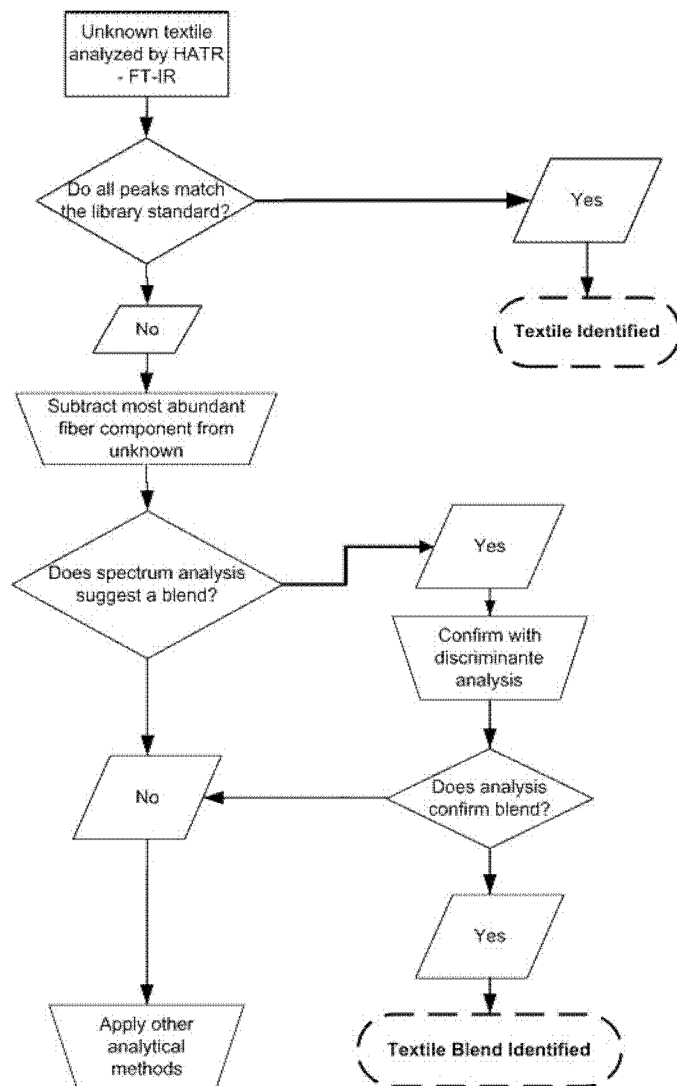


FIG. 1. Scheme used to distinguish the class characters of fiber and textiles by HATR/FT-IR.

frequencies. The difference spectrum (Fig. 2C) was searched against the library and the results suggest cotton as the best match. Although the match value is low (68) the strong peak at 1030 cm⁻¹ in the spectrum (Fig. 2D) is characteristic of the family of cellulose-based fibers (i.e., cotton, kapok, hemp, jute, etc.). If the presence of cotton needs to be corroborated, cellulose-based fibers can be confirmed by microscopic analysis.

In this example, the fiber blend is preliminarily identified as a polyester and cotton blend. In order to confirm the spectral identification, the spectra of a polyester standard and a cotton standard were digitally added to produce the best match to the unknown (Fig. 2E, bottom spectrum), and the resulting spectrum is compared to that of the unknown (Fig. 2E, top spectrum). It can be seen that the two spectra are similar, thus confirming the unknown as a polyester/cotton blend.

Further confirmation uses the statistical power of discriminant analysis. Discriminant analysis is a multivariate statistical method that assists in the classification of spectral data into distinct groups.⁹ The purpose of discriminant analysis in the present situation is to establish discriminant functions from known fiber standards (*n* = 10 each) and then use the

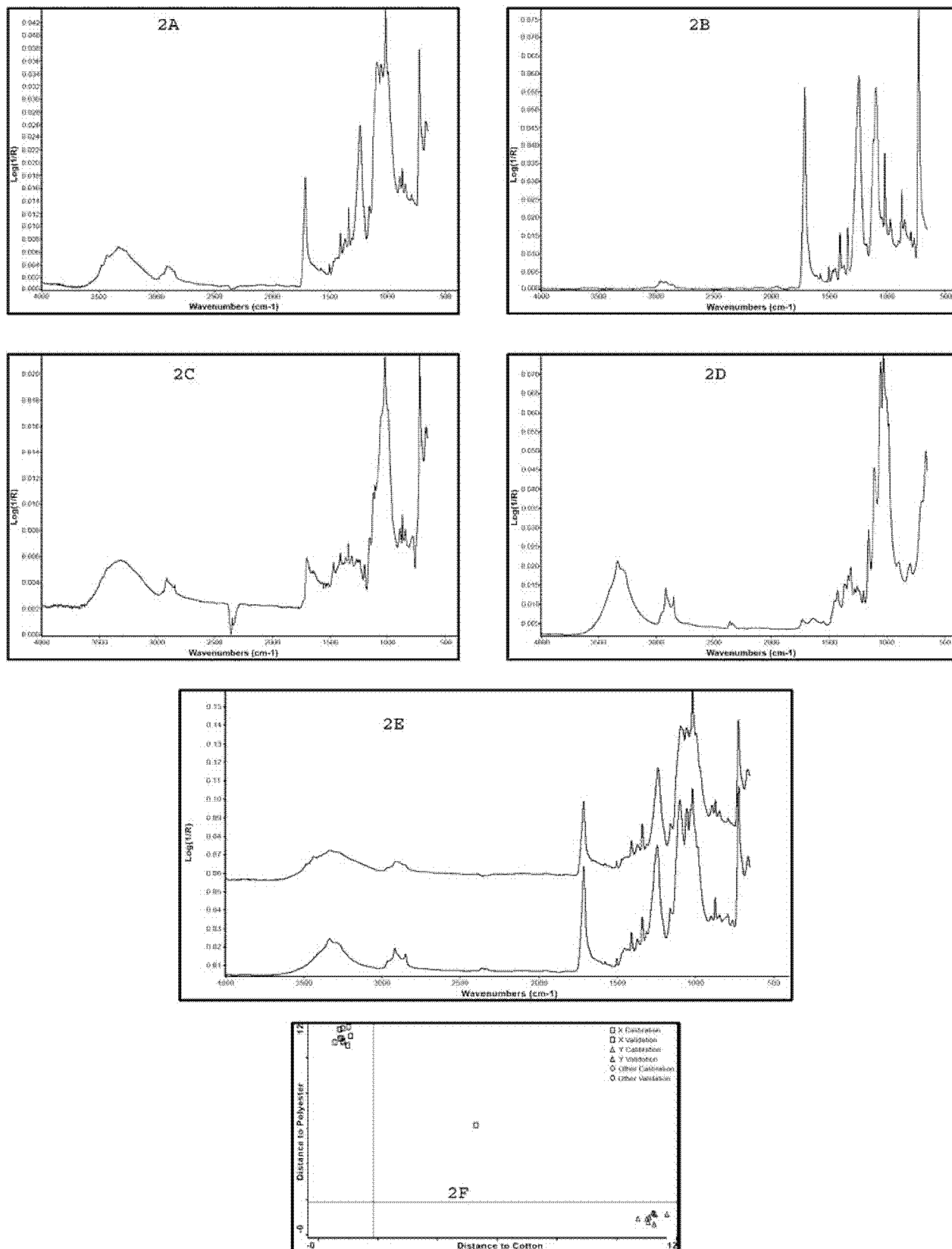


FIG. 2. (A) The HATR/FT-IR spectrum of an unknown (cotton/polyester blend). (B) The spectrum of a polyester standard. (C) The result of subtracting polyester from the unknown. (D) The spectrum of a cotton standard. (E) The bottom spectrum is the result of summing the spectra of polyester and cotton standards; the top spectrum is of the unknown. (F) The discriminant analysis graph. Squares represent the cotton samples, triangles represent the polyester sample, and the square in the middle represents the unknown, confirming it to be a cotton/polyester blend.

discriminant function to classify unknown fibers. TQ Analyst™ compiles an average spectrum from the standards. Each known fiber is then assigned a numerical score based on the variation from the calculated spectrum. These numerical scores are then plotted to provide a graphical representation.

Lastly, each fiber standard is validated by determining the Mahalanobis distance of the sample from the average spectrum. Therefore, each fiber type is assigned to the nearest group centroid based on its calculated Mahalanobis distance. The closer a sample is to a particular centroid class, the higher the likelihood that it will be classified with that particular sample set.¹⁴ In this example, each fiber standard (i.e., polyester and cotton) was correctly classified.

For the example depicted in Fig. 2, our hypothesis is that the spectrum represents a polyester/cotton blend. We conducted a discriminant analysis experiment using 10 samples of polyester and 10 samples of cotton as our reference populations to calculate the discriminant function of each fiber type and to establish the performance index. The performance index is a measure of how well a discriminant analysis method can categorize spectra from calibration standards. The performance index of the discriminant analysis (Fig. 2F) was 96.8%, which is an indication of how well the algorithm can differentiate between polyester and cotton.¹⁴ Reliable categorizations occur when the performance index exceeds 90%.

The score value of the unknown was plotted against the scores of the standards. As demonstrated with the graph (Fig. 2F), polyester and cotton standards are segregated within their corresponding groups, whereas the suspected blend sample is centered between the two distinct groups. The best explanation for this is that the unknown does not conform to either standard. It can be inferred that its chemical nature, as characterized by HATR/FT-IR, is a combination of polyester and cotton.

Figure 3 shows two other examples of blends where the HATR/FT-IR–discriminant analysis strategy was used. Figure 3A is the spectrum of a polyester/rayon textile blend and Fig. 3B is the difference spectrum with polyester removed. Figure 3C is the graphical representation of the discriminant analysis where squares represent the polyester samples and triangles represent the rayon population. The triangle in the middle represents the polyester/rayon textile blend. Figures 3D, 3E, and 3F exhibit the same process but with a rayon/wool fiber example. It is important to note that the spectra of rayon and lyocell are indistinguishable by FT-IR; therefore, the conclusion reached in Fig. 3C is that the sample represents a polyester with rayon and/or lyocell blend.

When using the spectral subtraction procedure, we discovered two sources of potentially spurious results: (1) carelessness in selecting the region to be subtracted and (2) accuracy of the difference (subtracted) spectra.

“Automatic Region Subtract” Process. The automatic region subtraction allows for the removal of the spectrum of a single compound from the spectrum of a blend. This software feature¹⁰ allows one to choose which peak to subtract. The region chosen for subtraction should be a region where the unknown and the standard spectra have a peak in common. Selecting a common peak allows the software to determine a normalization factor by which the rest of the spectrum will be subtracted. Poor selection of common peaks (i.e., a peak not fully resolved to baseline, or a common peak that has an

underlying peak originating from the unknown second component) will lead to spurious results.

Accuracy of Difference Spectra. Subtracted spectra can be especially noisy, and in these cases we obtained reliable results when we used the “squared difference algorithm” and selected data-rich regions for the library queries. The squared difference algorithm tends to accentuate large peaks, and therefore is especially useful with noisy spectra. In those instances where initial spectra were of high quality, we used the default algorithm (i.e., correlation) of the library.

Additionally, when conducting a library search on difference spectra, the Omnic software allows searching the entire spectral range or limits the search to a specific region of the subtracted spectrum. If a difference spectrum is searched over a wide wavenumber area, the results may be spurious given the potential for spectral noise (high signal-to-noise ratio). When the search criterion is focused on a significant peak, the algorithm correctly characterized the second component.

Although in most cases this process was successful in identifying fiber or textile blends, we encountered two instances from eight trials where this analysis faltered. Table II shows a known cotton/spandex textile example where the library correctly identified cotton, but after the spectral subtraction, only noise remained and therefore the secondary identification failed. The most likely explanation for this result is that the spandex fibers (only 4% of the textile) were widely spaced and therefore were not detected in the analysis. A comprehensive sampling strategy of the textile should correct this shortcoming. In the second example, a pashmina/silk textile (pashmina is the trade name given to the wool of goat (*Capra hircus*)), the library correctly identified the blend components, but discriminant analysis failed to separate and correctly categorize the known standards, possibly because the discriminant analysis algorithm could not detect the spectral differences, which can be recognized by careful visual inspection. In both examples, microscopic analysis could assist in completing the analysis.³

CONCLUSION

The HATR/FT-IR technique is an ideal method for obtaining spectra from fibers, yarns, and textiles. The Smart MIRacle attachment is simple to use and does not require sample preparation. It was determined that the components of the fiber blends can be successfully identified using HATR/FT-IR. The scheme presented in Fig. 1 is easy to apply, and the whole process can be accomplished in as little as 15 minutes (though confounding situations may take as long as 1 hour).

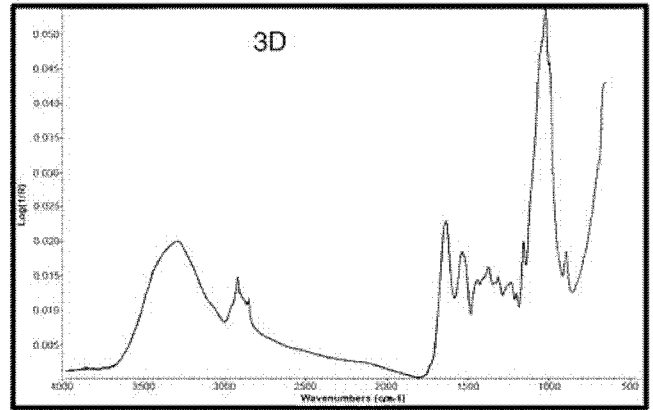
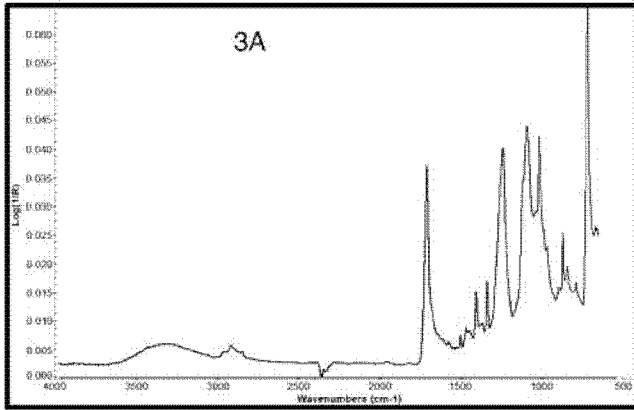
Although HATR/FT-IR analysis provides rapid structural information, it is important to keep in mind the limitations of mid-infrared polymer analysis, already discussed elsewhere.⁴ Additionally, the depth of penetration of the IR beam into the sample with a ZnSe crystal is about 2 micrometers;¹⁵ therefore, if the blend is not represented on the fiber surface or if the 2 millimeter ZnSe window fails to detect the blend (as in the cotton/spandex (96%:4%) example), then the results could lead to spurious conclusions. Therefore, the best-case scenario for the HATR/FT-IR–discriminant analysis scheme would be a homogenous and evenly distributed textile blend.

Spectral library matches operate at a fundamentally different level than discriminant analysis conclusions, but both classification systems are complementary. Library searches are designed to provide the best and closest match to a spectrum,

Polyester/Rayon textile example

Rayon/Wool fiber example

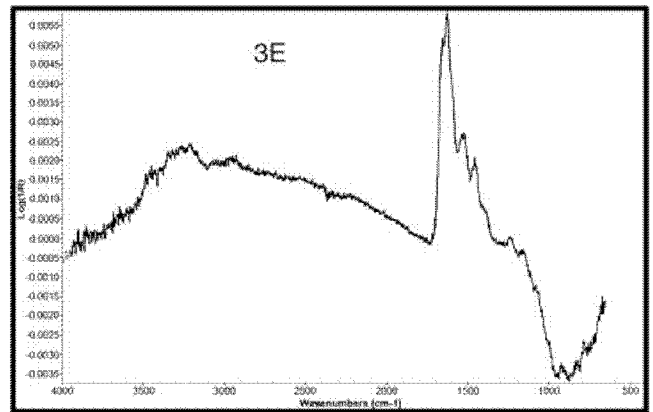
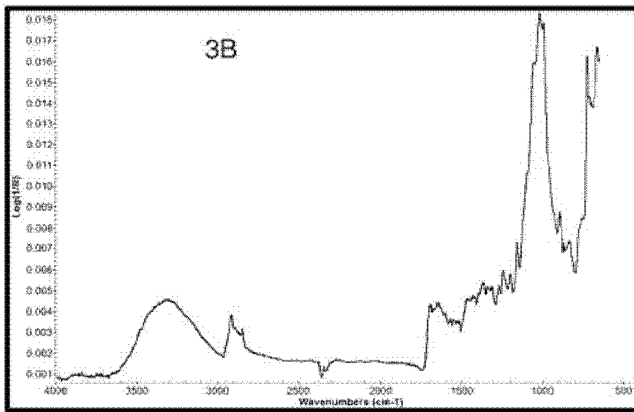
FTIR spectrum of blend



First component identified: Polyester (98% match)

Rayon (94% match)

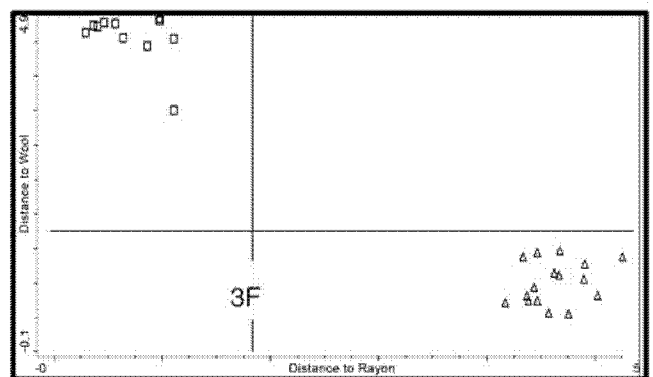
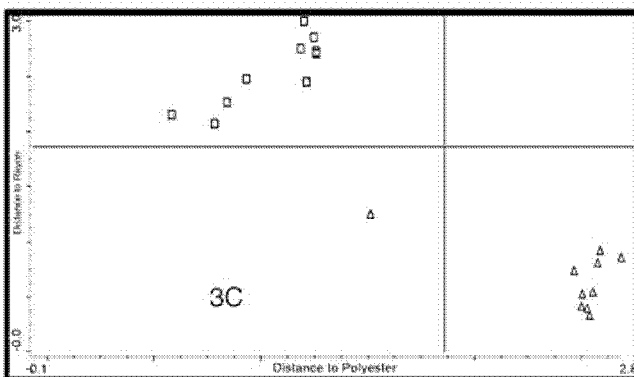
Difference spectra



First component identified: Rayon (75% match)

Wool (39% match)

Confirmation using discriminant analysis



Conclusion: Polyester with rayon and/or lyocell blend

Rayon with wool blend

FIG. 3. (A) The spectrum of a polyester/rayon textile blend. (B) The result of subtracting the polyester spectrum from the spectrum of the exemplar. (C) The discriminant analysis graph. Squares represent the polyester population, triangles represent the rayon population, and the triangle in the middle represents the unknown. (D, E, F) The same process, but with a rayon/wool fiber example.

TABLE II. Selected examples of blends tested and their corresponding library and discriminant analysis results. In one instance (cotton/spandex 96%:4%), the signal-to-noise ratio of the difference spectra did not allow the categorization of the second component, and in one instance (pashmina/silk 50%:50%), the discriminant analysis failed to segregate the standard populations (see discussion).

Blends tested	Library (match value)	Discriminant analysis (performance index)
Polyester/rayon (50%:50%)	Polyester (98.7) Rayon (53.2)	Yes (98.8)
Polyester/wool (65%:35%)	Polyester (97.2) Wool (83.6)	Yes (98.8)
Cotton/polyester (60%:40%)	Polyester (90.9) Cotton (76.6)	Yes (98.5)
Rayon/wool (65%:35%)	Rayon (94.1) Wool (81.7)	Yes (98.5)
Pashmina/silk (50%:50%)	Silk (96.1) Wool (81.5)	Failed to discriminate
Cotton/spandex (96%:4%)	Cotton (92.4)	Noisy difference spectra

and the similarity is rated by a match score. A high match score implies a higher certainty of accuracy than a lower match score. Regardless of the match score, the algorithm always provides a match, even if a visual inspection reveals notable differences. Discriminant analysis of FT-IR spectra of fibers allows for comparing an unknown to a population of fibers. When examining the graphical display of a discriminant analysis, the unknown is compared to a sample set and not to a single spectrum. Therefore, discriminant analysis allows the analyst to assess the unknown against a normal distribution of samples rather than relying on the single best answer from a spectral library.

Given that textile blends constitute a considerable number of the fabrics on the market today, a careless examination of a fiber or textile could lead to a false inference of a single fiber type. Analysts should be especially alert when the results suggest a single fiber form, even with high library match hits. HATR/FT-IR is a useful tool to assist in the elucidation of class characters of fibers and textiles. Examination of a single fiber is a simple matter when using the Smart MIRacle HATR accessory in conjunction with FT-IR analysis. Conversely, the identification of fiber blends requires a keen eye and spectroscopic awareness. Discriminant analysis of FT-IR spectra provides strong inference for confirming fiber or textile blend constituents.

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