

Forensic Discrimination of Dyed Textile Fibers using UV-VIS and Fluorescence Microspectrophotometry

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ABSTRACT

Ultraviolet-visible (UV-VIS) and fluorescence microspectrophotometry (MSP) offer direct, relatively inexpensive, and informative means of characterizing dyed textile fibers. Visual comparisons among the fiber spectra have been supplemented by multivariate statistical analysis to confirm the statistical validity of discrimination observed. Overall, UV-VIS and fluorescence microspectrophotometry are valuable tools for the discrimination of fibers, in particular for discrimination of fibers of similar color but different dye composition.

INTRODUCTION

Fibers are often encountered as trace evidence in incidents involving personal contact, such as homicide, assault, and sexual offenses, as well as hit-and-run accidents and other crimes.¹⁻³ Fibers can also be found in, or on, objects peripherally associated with crimes, such as weapons or cars involved in armed robberies.² Knowledge of the chemistry of fibers and fiber dyes is important to understanding both the basis of fiber identification and the forensic relevance of various fiber/dye combinations.⁴⁻⁷

Analytical methods used for characterizing fibers and/or dyes include polarized light microscopy (PLM)⁸, energy-dispersive X-ray analysis, thin-layer chromatography^{2,3,6,9}, high performance liquid chromatography^{2,3,6,10}, pyrolysis gas chromatography^{3,11-14}, Fourier transform infrared spectroscopy^{3,15-24}, and Raman spectroscopy.^{22,25-27} Nondestructive spectroscopic methods maintain integrity of the original sample, prevent sample contamination, minimize sample handling, and decrease overall analysis time. Visible (VIS), ultraviolet (UV)/VIS, and fluorescence microspectrophotometry offer direct, relatively inexpensive, and informative means of characterizing dyed fibers.^{3,28-33} Single fibers have been analyzed using both visible and UV spectrophotometry.^{28,29} Suzuki *et al.*³⁰ used UV-VIS microspectrophotometry to study single cotton fibers dyed with vat dyes such as indigo and indigo derivatives. Gaudette recommended ultraviolet, violet, blue, and green excitation regions for comparing the fluorescence of fiber and dye samples.³ He also pointed out that for dyed fibers, fluorescence may not only come from the fiber itself, but also the dye. This means that dyed fibers have more discriminating power than undyed fibers.

Carroll³² reports that differences in the fluorescence of fibers are consistently correlated with manufacturer, thus suggesting increased discrimination from the use of fluorescence measurements. Cantrell *et al.*³³ reported the analysis of 3,025 textile fibers collected from movie theater seats, using fluorescence microscopy in the green, blue, and ultraviolet spectral regions for the analysis of certain classes of fibers. This study confirmed that, even though fibers are mass-produced, most fibers exhibit high variability. Fluorescence, in particular, was found to add considerable discrimination even within common fiber class/color combinations.

This paper presents the results of selected fiber comparisons using UV-VIS and fluorescence microspectrophotometry to evaluate the discrimination of dyed fibers.

EXPERIMENTAL

Samples of dyed and undyed cotton, polyester, acrylics (at least 85 % acrylonitrile), and nylon obtained from various textile companies. Fiber samples are referenced by their fiber identification numbers listed here. Single fibers were positioned on a microscope slide using micro tweezers. Spectral grade glycerin (Spectrum Chemical Mfg. Corp., Gardena, CA) was used as the mounting medium with spectral grade quartz slides and cover slips (CRAIC Technologies, Altadena, CA, and Esco Products Inc., Oak Ridge, NJ).

Spectra were obtained using a QDI 1000 microspectrophotometer (MSP) (CRAIC Technologies, Altadena, CA) using GRAMS/AI 7.00 software (Thermo Galactic, Salem, NH) for data acquisition. The MSP was operated in transmission (xenon source) and fluorescence (mercury source) modes using a 15x collecting objective. Spectra were collected by taking an average of 100 scans over the spectral range of 200-850 nm at a bandwidth of 10 nm. The integration time for the charge coupled device (CCD) detector was set to ~4 ms in transmission mode and to 200 ms in fluorescence mode, except when noted otherwise. Fluorescence spectra were acquired using excitation wavelengths of 365, 405, 436, and 546 nm.

RESULTS AND DISCUSSION

The discriminating power of UV-VIS microspectrophotometry for analyzing samples that appear very similar was evaluated. The UV-VIS spectra were recorded for four randomly selected yellow fibers for each of the four generic fiber types. Yellow fibers were chosen to test the discriminating power of UV-VIS microspectrophotometry because shades of yellow are sometimes difficult to distinguish visibly. Figure 1 shows the first of ten replicate UV-VIS spectra taken for each fiber. Note that these spectra are plotted as percent transmittance.

Groups of spectra were analyzed using multivariate data analysis. The combination of principal component analysis (PCA) and linear discrimination analysis (LDA) provides efficient modeling of relationships among a large number of spectra with more than one feature (intensities measured at different wavelengths) representing each sample. PCA³⁴⁻³⁶ is an unsupervised technique that determines linear combinations of the original variables representing directions of maximum variation (principal components,

or PCs). The first principal component (PC) is the direction that explains the maximum variation in the data set; the second PC describes the second greatest amount of variation, and so on. If the first few PCs are found to explain a substantial proportion of the variation in the data, the projection of points representing the samples in a two- or three-dimensional plot may be informative concerning their similarity.

LDA is a supervised technique to determine linear combinations of features (canonical variates) that best separate the data into two or more predefined groups of samples by maximizing the ratio of the between-groups to within-groups variations.^{35,36} PCA and LDA was performed on absorbance and fluorescence spectra using programs written in *Matlab 7* (The MathWorks, Inc., Natick, MA). The spectra were truncated to the spectral range from 280-850 nm. Spectra were normalized to reduce systematic variation and feature intensities were mean centered to remove the overall mean spectrum. Because LDA requires that the number of features be much less than the number of samples, the projections of the spectra in the first few PCs were used as the input data for linear discriminant analysis. Leave-one-out cross validation was employed to assess classification accuracy: each data point was omitted in turn from the data set while the remaining data was used to generate a LDA projection. Each left-out spectrum was then classified as belonging to the nearest group (using Mahalanobis distances³⁷) and the classification accuracy calculated.

The UV-VIS absorbance spectra for the yellow fibers were analyzed using PCA and LDA. The PCA scores plots for the spectra are shown in Figure 2. The replicate spectra of the same fiber tend to cluster together. Because PCA projections maximize total variability, these plots do not show the best possible discrimination: many of the 95 % confidence ellipses in two PCA dimensions overlap. The cross-validated classification accuracies (a measure of fiber discrimination) based on the PCA projections into the space of the first 8 PCs were 70, 80, 67.5, and 90 % for cotton, acrylic, nylon, and polyester fibers, respectively.

The projections on the first 8 PCs were used as the LDA input. In Figure 3, projections of yellow fiber spectra on the first two linear discriminants show improved group separation compared to PCA results. The cross-validated classification accuracy based on the LDA projections into the space of the first 8 linear discriminants was 100 % for each of the four fiber groups. The two fiber groups in Figure 3D (fibers 204 and 335 in Figure 1D) that are seen to overlap in the two dimensional projection are separated perfectly in higher discriminant dimensions.

UV-VIS microspectrophotometry is often followed by fluorescence microspectrophotometry to investigate further similarities and differences in fibers under comparison. The mercury lamp is used as a light source for fluorescence measurements and filter cubes are employed to select the excitation wavelength. Figure 4A shows that three of the four fibers examined have their maximum fluorescence at different excitation wavelengths. Figure 4B shows fluorescence spectra of a red acrylic fiber (81) using different excitation wavelengths. As expected, the fluorescence intensity depends on excitation wavelength. At the wavelength of maximum excitation for this fiber (546 nm), the integration time for the CCD was reduced from 200 to 50 ms to avoid detector saturation.

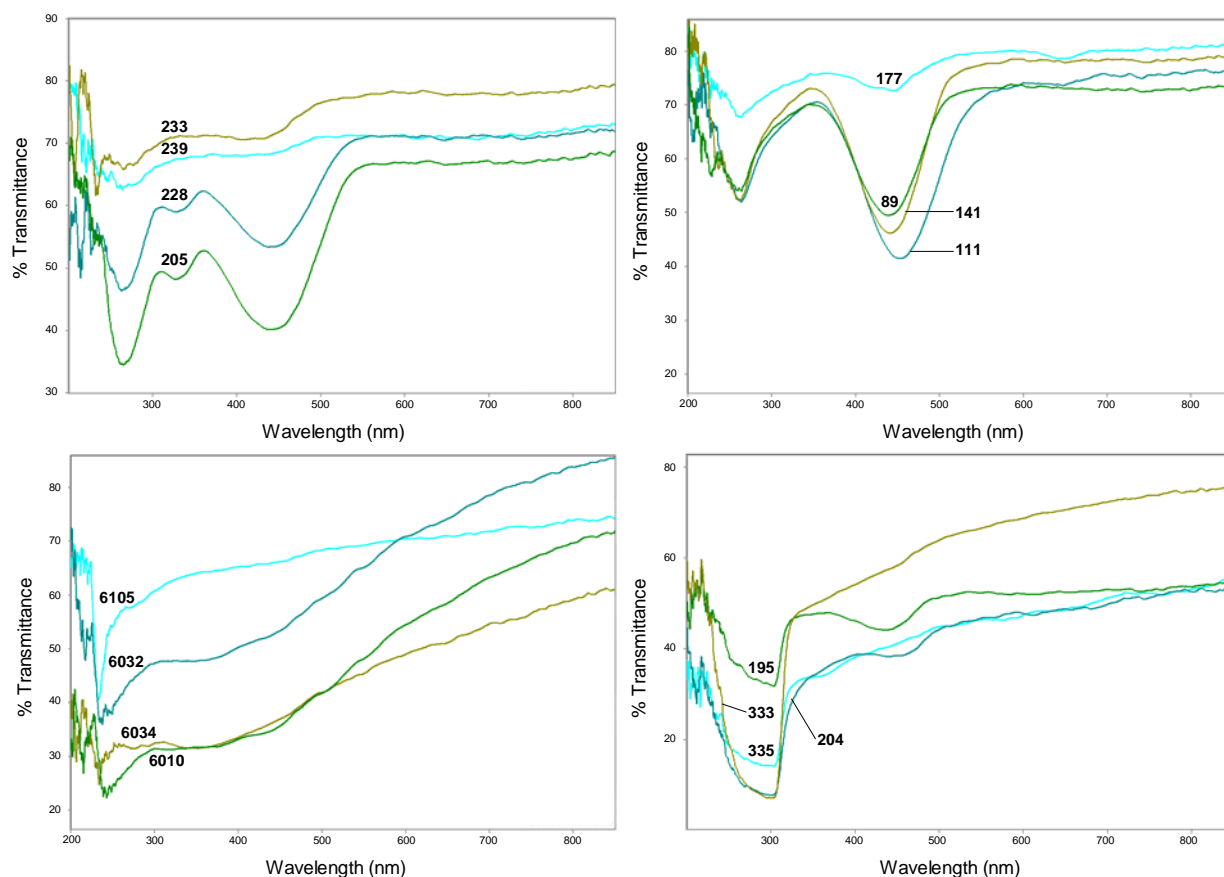


Figure 1. UV-VIS spectrum of yellow fibers mounted in glycerin using quartz slides and cover slips: (A) cotton; (B) acrylic, (C) nylon; (D) polyester.

An evaluation of the differentiation of dyed fibers using UV-VIS versus fluorescence microspectroscopy was performed using three red polyester fibers (337, 338, 339). The three red fibers were similar in appearance when viewed by light microscopy. Two of the fibers (337, 339) were dyed with identical blue, yellow-brown, and rubine dyes; one of the fibers (337) was dyed with an additional pink dye. Polyester fiber 338 was also dyed with the same yellow-brown and rubine dyes as the first two fibers, but had a different blue dye component. The UV-VIS spectra of the fibers (Figure 5A) were similar, although small differences can be seen in certain spectral regions.

Figure 6 presents PCA projections for the 15 UV-VIS spectra of the three red polyester fibers. Note that, although the spectra are plotted as percent transmittance in Figure 5, multivariate analysis was performed using absorbance spectra; projections onto three PCs was used as input to LDA. The absorbance spectra exhibit within-group agreement and between-group separations; the PCA cross-validated classification accuracy for the absorbance data was 86.7 %. Overlap of the 95 % confidence intervals around fiber groups 337 and 339 contributes to the misclassifications by PCA. All groups appear separated by LDA projections of absorbance data; however, the cross-validated classification accuracy was 93.3 % (one spectrum misclassified).

Using the 546 nm excitation wavelength, the fluorescence spectra of the three fibers were quite different (Figure 5B). The groups of fluorescence spectra can be visually distinguished from one another, which can not be done with the UV-VIS spectra. The PCA and LDA projections for the fluorescence spectra are shown in Figure 7. The PCA leave-one-out cross validated classification accuracy was 86.7 %; the LDA leave-one-out cross validated classification accuracy was 100 %. For the discrimination of these three similar red polyester fibers, fluorescence spectra appear to exhibit higher discrimination power than UV-VIS absorbance spectra.

CONCLUSIONS

This preliminary report has summarized techniques for evaluation of the discrimination of dyed textile fibers by UV-VIS and fluorescence microspectrophotometry. Multivariate statistical analysis of spectra of yellow and red fibers was used to evaluate the discrimination between similar fibers of various textile fiber types. The results suggest that, at least for certain fiber/dye combinations, fluorescence measurements provide more discriminating information than do UV-VIS absorbance measurements.

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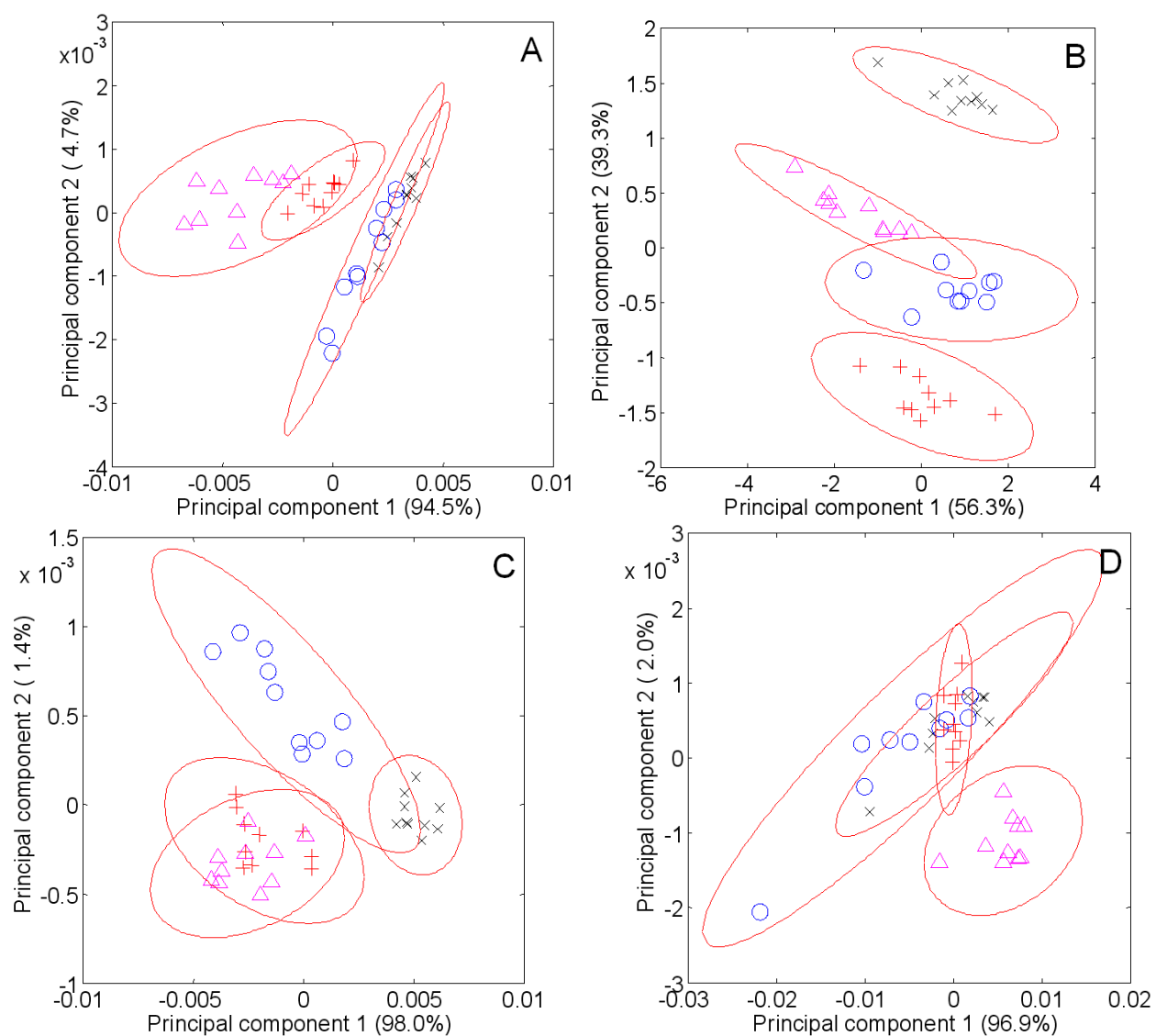


Figure 2. Principal component projections of ten replicate UV-VIS absorbance spectra of yellow fibers: (A) cotton, (B) acrylic, (C) nylon, and (D) polyester fibers. Ellipses represent 95 % confidence around groups.

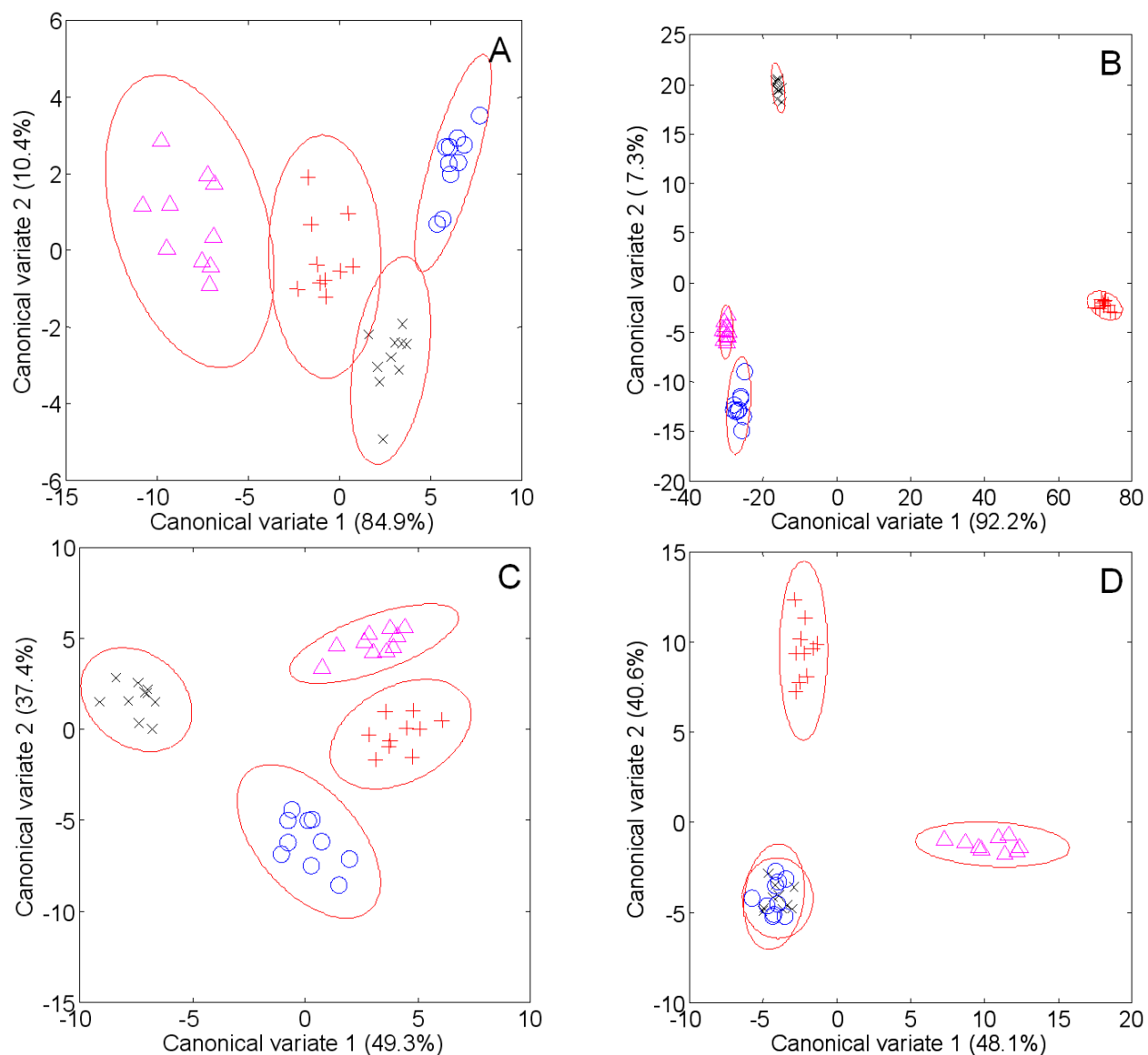


Figure 3. Linear discriminant projections of ten replicate UV-VIS absorbance spectra of yellow fibers: (A) cotton, (B) acrylic, (C) nylon, and (D) polyester fibers. Ellipses represent 95 % confidence around groups.

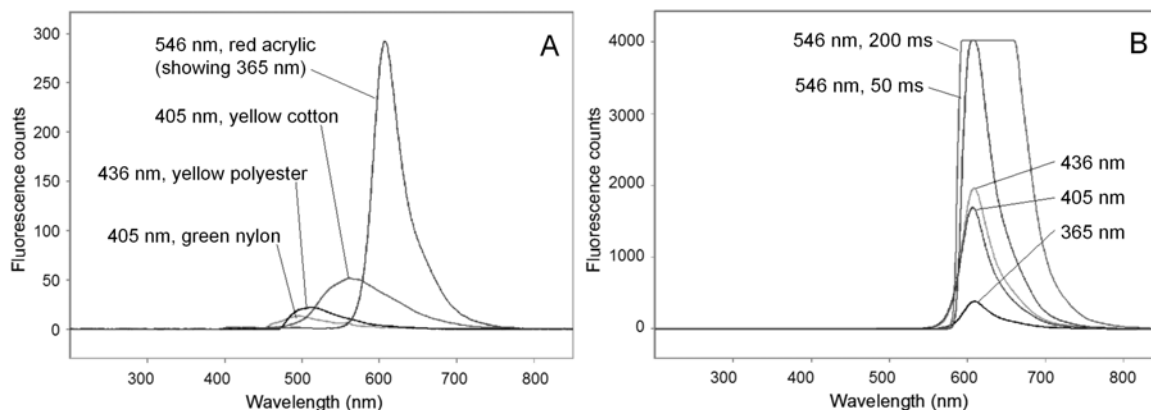


Figure 4. Fluorescence spectra of dyed fibers; (A) spectra of dyed fibers acrylic 81, cotton 205, polyester 195, nylon 6 200; (B) spectra of red acrylic fiber 81 using different excitation wavelengths.

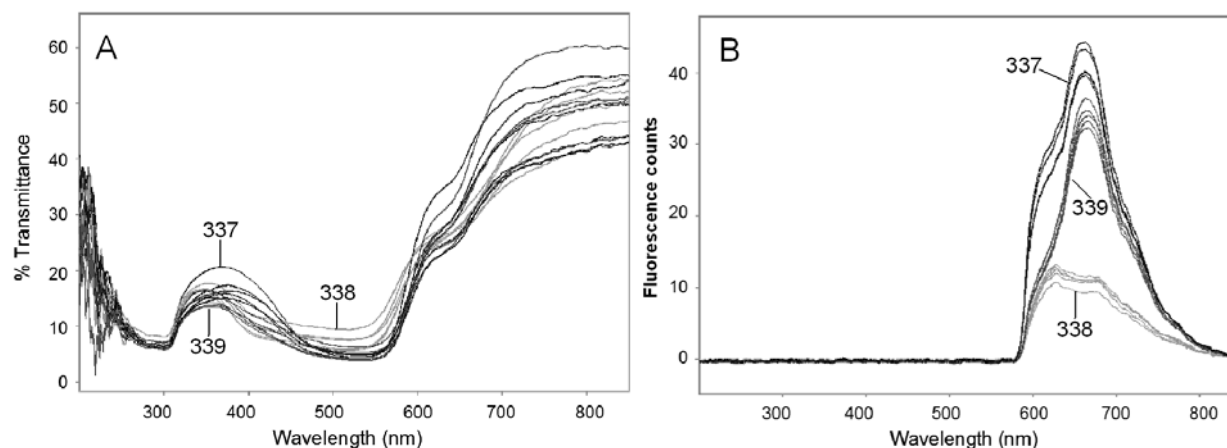


Figure 5. Spectra of three red polyester fibers (337, 338, 339) (A) UV-VIS; (B) fluorescence using 546 nm excitation.

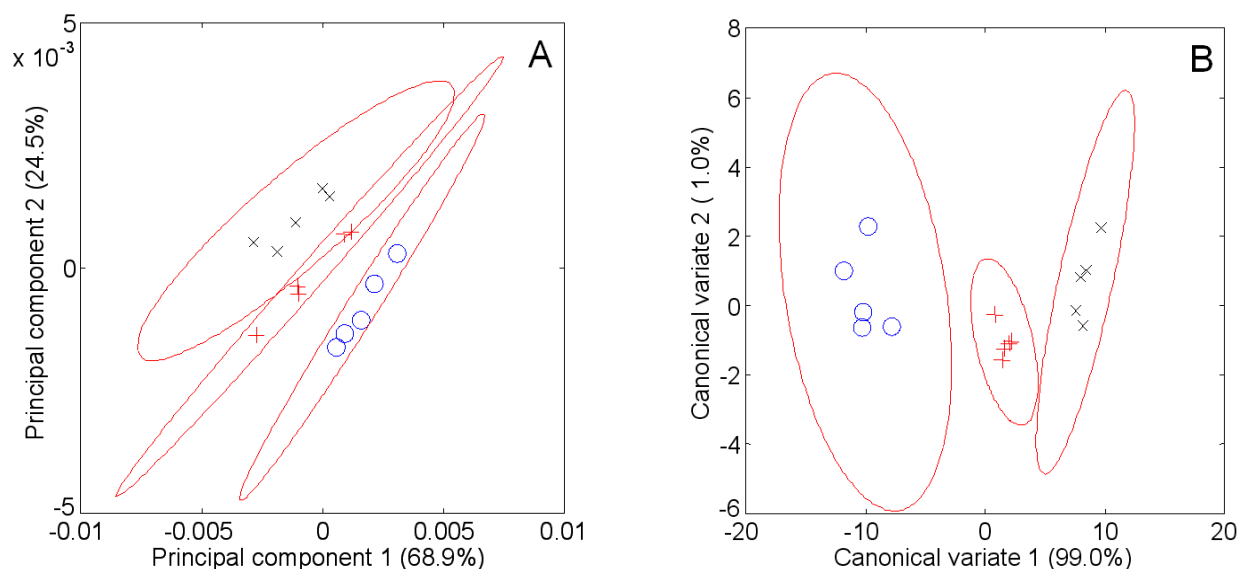


Figure 6. Principal component (A) and linear discriminant (B) projections for five replicate UV-VIS absorbance spectra (280-850 nm) for each of three red polyester fibers. Symbols: 337 = x, 338 = o, 339 = +. Ellipses represent 95 % confidence around groups. The percent variation explained is noted on each axis.

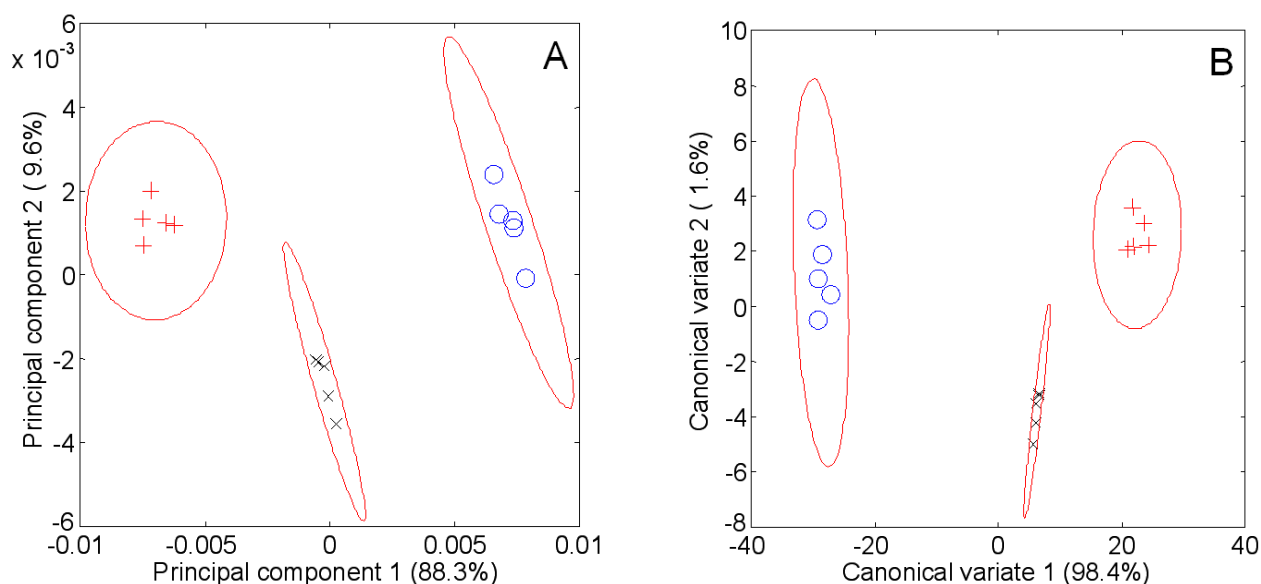


Figure 7. (Principal component (A) and linear discriminant (B) projections for five replicate fluorescence spectra for each of three red polyester fibers (337 = x, 338 = o, 339 = +). Ellipses represent 95 % confidence around groups. The percent variation explained is noted on each axis.