Imelda P. Keen,[1] *B.App.Sc.; Graeme W. White,*[2] *B.App.Sc.; and Peter M. Fredericks,*[1] *D.Phil.*

Characterization of Fibers by Raman Microprobe Spectroscopy

REFERENCE: Keen IP, White GW, Fredericks PM. Characterization of fibers by Raman microprobe spectroscopy. J Forensic Sci 1998;43(1):82–89.

ABSTRACT: A set of fibers, mainly synthetic, has been examined by Raman microprobe spectroscopy. It was found that high quality spectra, requiring no sample preparation, are easy to obtain and that fibers with different molecular structure have very different Raman spectra. Fluorescence was occasionally a problem with excitation at 632.8 nm, but could be significantly reduced by using a semiconductor laser emitting at 780 nm. Fibers of the same polymer type from different manufacturers have Raman spectra which are only slightly different but which could be distinguished by the multivariate statistical technique of principal components analysis (PCA). Dyed fibers gave spectra with bands due to the polymer, but also with intense bands due to the dye, because of the high Raman cross-section of dye molecules. Extraction of the dye, followed by a spectral subtraction procedure allowed separate spectra of the polymer and the dye to be obtained.

KEYWORDS: forensic science, criminalistics, fibers, Raman spectroscopy, microprobe, dye

The characterization of fibers, both natural and synthetic, is a significant aspect of the forensic analysis of physical evidence (1,2). A wide range of techniques may be used to examine fibers, but in recent years the technique of vibrational spectroscopy, in the form of infrared spectroscopy, has become important. The availability of Fourier transform infrared (FT-IR) spectrometers, which utilize an interferometer in place of the traditional diffraction grating, has increased the speed and sensitivity of the infrared method. In particular, the improved sensitivity of FT-IR spectrometers has allowed the development of FT-IR microscopes (3) which have proven to be very useful in forensic science in general and especially for the examination of fibers (4–12). Infrared spectroscopy has the capability to fingerprint the molecular structure of the fiber giving information which would not be available by other techniques. Fibers may be readily classified according to structural type.

However, there are some difficulties associated with infrared microspectroscopy of fibers. Fibers thicker than about 30 μm may be totally absorbing in all or part of the spectrum. Additionally, the generally circular section of many fibers has a lensing effect which refracts some of the light and severely reduces the quality of the spectrum by decreasing the signal-to-noise ratio. For these reasons, fiber samples are usually prepared for infrared microscopic examination by rolling flat (6,8,9,11) or by flattening under high pressure in a diamond anvil cell (4,5). Apart from the time involved, both these methods have a tendency to destroy the morphology of the fiber and it is possible that subtle information may be lost.

While infrared spectroscopy has found considerable use for fiber characterization, the alternate vibrational spectroscopic technique, Raman spectroscopy, has been little used. There are several reasons for this: the Raman effect is very weak and very sensitive, expensive equipment is required to measure the spectrum; many samples fluoresce under laser irradiation and the weak Raman signal may be swamped; many samples photodegrade when subjected to laser irradiation. In recent years advances in instrumentation have made Raman spectroscopy more attractive for analytical use. The development of Fourier transform (FT) Raman spectroscopy (13,14) which uses an FT-IR spectrometer and a near-infrared laser leading to a substantial reduction in fluorescence, has made Raman applicable to a much wider range of sample types. Another recent advance has been in Raman microprobe spectroscopy (15,16) and the development of benchtop Raman microprobe spectrometers has the potential to contribute to many areas of analytical science.

There have been a number of previous reports of the use of Raman spectroscopy in the study of fibers (9,10,15,16). Several of these reports are relevant to the use of the Raman technique in forensic science. Lang et al. (9) studied the Raman microscopy of some polyester fibers and a polyacrylonitrile fiber using excitation at both 514.5 and 476.5 nm. They concluded that although only a very small sample was required and sample preparation was minimal, the technique was limited by fluorescence. The work of Bouffard et al. (10) was limited to the identification and quantitation of pigment additives in polypropylene fibers using a benchtop microprobe spectrometer equipped with a helium-neon laser emitting at 632.8 nm. They found Raman microscopy to be useful for this purpose, but found some limitations because of fluorescence and sample heating. Bourgeois and Church (17) found that macroscopic FT-Raman with near-infrared excitation at 1064 nm was capable of recording spectra of dyed acrylic fibers, showing bands due to both the fiber matrix and the dye. Spectral subtraction techniques allowed the spectrum of the dye to be isolated. The long excitation wavelength did not induce fluorescence in these fibers. Jurdana et al. (18) demonstrated that spectra of wool fibers can be obtained with a Raman microprobe spectrometer using an exciting line at 514.5 nm. They also studied human hair but were only able to obtain spectra of white/gray hair because of immediate photodegradation of dark hair.

Previous work described above has demonstrated that Raman microprobe spectroscopy may be useful for fiber characterization but no comprehensive study has been reported. This paper describes the application of Raman microprobe spectroscopy to the forensic characterization of fibers.

[1]Graduate student and associate professor, respectively, Center for Instrumental and Developmental Chemistry, Queensland University of Technology, PO Box 2434 Brisbane, Queensland 4001, Australia.

[2]Supervisor, Forensic Chemistry, John Tonge Center for Forensic Sciences, PO Box 594, Archerfield, Queensland 4108, Australia.

Received 10 Feb. 1997; and in revised form 9 June 1997; accepted 11 June 1997.

Methods

Samples

Reference fibers were obtained from the Collaborative Testing Service (CTS) 1987 Reference Collection of synthetic fibers (SF-3). In this report samples have been labeled with their CTS number. The wool sample was commercially scoured Australian merino top of mean fiber diameter 22 μm. The blue-dyed fiber was Item 2 of the CTS Proficiency Testing Program #9607. The two red-dyed polyester fibers were from commercial textiles obtained from a retail outlet.

Raman Spectroscopy

Raman spectra, in the range 3700-200 cm^{-1} of Raman shift, were obtained on a Renishaw Model 1000 microprobe spectrometer. The main elements of the spectrometer are an Olympus microscope to visualize the sample, and to direct the exciting light onto the sample and collect the scattered light, an optical filter to remove the Rayleigh line, a single diffraction grating, and an electrically cooled CCD camera to detect the Raman signal. The microscope is equipped with three interchangeable objective lenses with magnifications of 50, 20 and 10, respectively. Typically the 50 times objective was used giving a theoretical spot size on the sample of 0.8 μm diameter. Two lasers were available: a Spectra-Physics Model 127 helium-neon (HeNe) laser emitting at 632.8 nm, and a Renishaw semiconductor laser emitting at about 780 nm. Both lasers produced a maximum laser power of about 20 mW at the sample. Measurement times were generally in the range 1–10 s. For a small number of fluorescent samples, the sample was left under laser illumination for about 5 min before data collection was initiated. Samples were presented to the spectrometer by taping short lengths, about 1 cm, onto a glass slide or metal plate which was then placed on the stage of the Raman microscope.

Data manipulation, plotting etc. was carried out using the software package GRAMS32 (Galactic Corp, Salem, New Hampshire). Principal components analysis (PCA) was carried out with the software package PLS-IQ (Galactic Corp, Salem, New Hampshire). Pre-treatment of data for PCA included mean-centering, normalization, and automatic baseline correction. PCA was performed using the cross-validation option.

Results and Discussion

Fibers of Different Molecular Structure

Figure 1 shows a series of Raman spectra, obtained using the HeNe laser, of a range of different types of fibers, both synthetic and natural. It can be seen that each fiber type has a distinctive spectrum which would serve to readily distinguish it from any other fiber type. For the synthetic fibers the measurement time to collect a high quality spectrum was in the range 1–10 s. Wool and rayon were much weaker Raman scatterers and a longer measurement time of about 1 min was required. The spectra show some similarities with infrared spectra of the same fiber types. For example, polyester fibers show an ester C═O stretching band near 1700 cm^{-1}, while wool and nylon show the amide C═O stretch near 1650 cm^{-1}. However, one significant difference between infrared and Raman is that vibrations of polar groups such as O—H tend to be very weak in the Raman and strong in the infrared. Hence the Raman spectra of wool and rayon are not dominated by O—H bands as their infrared spectra are. Another point to note is that Raman spectra, in comparison with infrared, tend to have fewer bands which are sharper and less overlapped. It is therefore somewhat easier to distinguish between Raman spectra derived from different sample types.

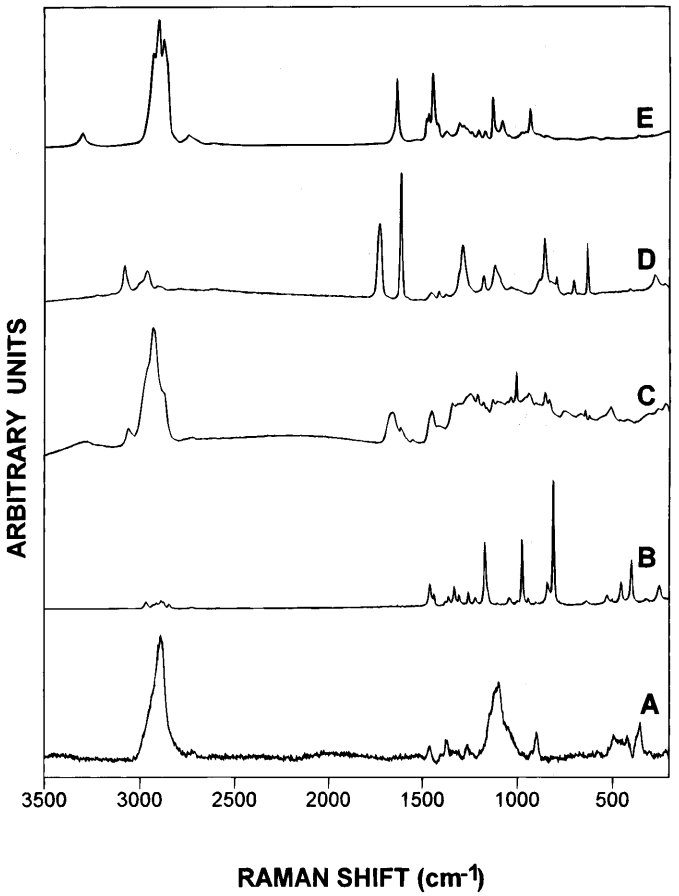

FIG. 1—*Raman microprobe spectra of a range of fiber types using excitation at 632.8 nm. (A) rayon; (B) polypropylene; (C) wool; (D) polyester; (E) nylon.*

Collection of the spectra shown in Fig. 1 was extremely simple and very fast. In contrast to the currently used infrared method, no sample preparation was required. Fibers were merely taped to a glass slide or a small metal plate, placed on the stage of the Raman microscope and brought into focus visually. Laser light was then allowed to fall on the sample and a spectrum collected, often in a matter of seconds. In this work fiber lengths of about 1 cm were used, but as the laser spot size was very small, it would have been possible to use very much shorter lengths of fiber. None of the samples showed any visible damage from irradiation by the HeNe laser and the spectra did not change, except for fluorescence reduction, when the sample was irradiated for longer times.

Fluorescence

Previous reports (9,10) show that fluorescence is a significant problem and can swamp the Raman signal. In this work most samples from the CTS Reference Collection showed little fluorescence. Sometimes a broad fluorescence background could be seen in the spectrum, but the Raman spectrum was usually clearly visible above the background. Often, the fluorescence would diminish as data collection proceeded. This phenomenon is well-known and is caused by the photodegradation of the fluorescing species. Only for a few samples was there significant fluorescence which

swamped the Raman spectrum. Figure 2 shows the Raman spectrum, in the range 1800-300 cm^{-1} Raman shift, of a polypropylene fiber collected with excitation from a HeNe laser emitting at a wavelength of 632.8 nm. A substantial fluorescence band can be seen with a maximum around 1250 cm^{-1}, and the Raman bands of the polypropylene are present but quite weak. Figure 2 also shows the Raman spectrum of the same polypropylene sample collected with excitation at a wavelength of 780 nm from the semiconductor laser. In this case the fluorescence background is much weaker and the Raman bands of polypropylene are clearly visible. In moving the excitation from 632.8 nm to 780 nm the energy of the exciting light is reduced and can no longer generate fluorescence in this sample to the same degree. Fluorescence would be further reduced with a even longer wavelength such as the 1064 nm used in FT-Raman. However, this wavelength would not be compatible with the CCD camera and it would not be possible to measure much of the normal spectral range. 780 nm excitation allows Raman data to be collected in the spectral region 200—around 3000 cm^{-1}, although the bands near 3000 cm^{-1} such as C—H stretching bands, are much reduced in intensity because of the poor detector characteristics at this wavelength. Despite this, 780 nm excitation does represent a useful compromise between fluorescence reduction and compatibility with the CCD camera. In our work, very few samples were found to fluoresce with 780 nm excitation, and we suggest that this would be the excitation wavelength of choice for forensic applications.

A further disadvantage of excitation at longer wavelengths is that the intensity of Raman scattering is inversely related to the fourth power of the exciting wavelength. Hence, when 780 nm excitation is used in place of 632.8 nm, the intensity of Raman scattering will be reduced by $(632.8/780)^4$, i.e., a factor of 2.3. However, this deficiency is readily compensated for by a small increase in the measure time, which in most cases would still remain in the range 2–10 s.

Fibers of Similar Molecular Structure: Polyesters

One of the important factors in forensic analysis is the capability to distinguish between different, but similar samples. To investigate this aspect of Raman microspectroscopy, spectra of four samples of polyester fibers, from different manufacturers, were compared. The generic description "polyester" usually refers to fibers of the polymer poly(ethylene terephthalate). Figure 3 shows the spectra which can be seen to be very similar. However, there are differences in the relative intensities of bands particularly near 1100 and 350 cm^{-1}. In order to highlight these differences the technique of principal components analysis (PCA) was employed. PCA is a multivariate statistical technique (19,20) which reduces a data set of (for example) spectra by calculating a common set of factors, a linear combination of which will regenerate the original data. By allowing for the noise in the spectra, a fewer number of factors is required to fit the data than there were spectra in the

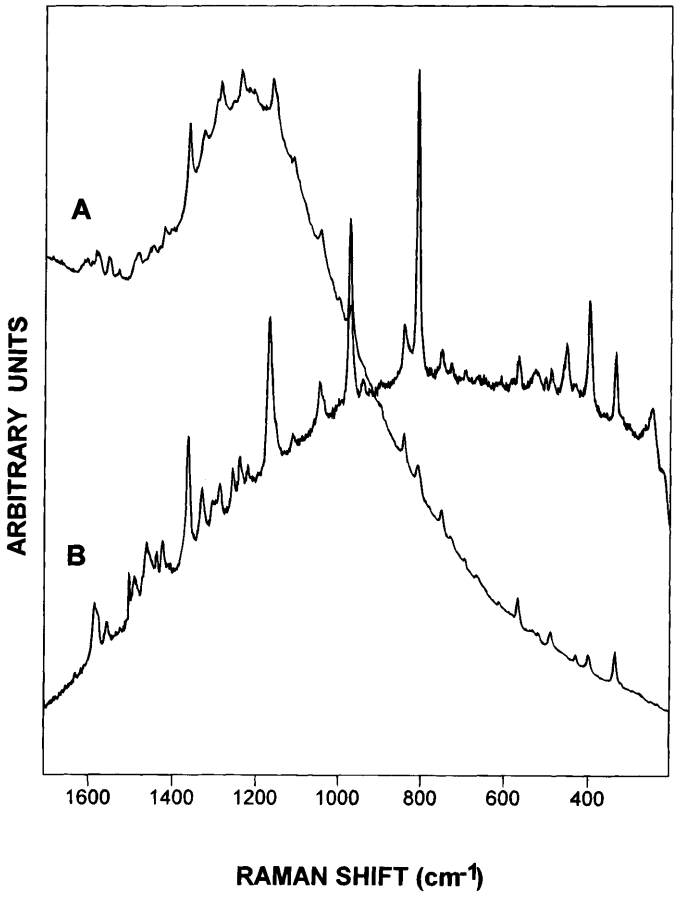

FIG. 2—*Raman microprobe spectra of a polypropylene fiber showing fluorescence reduction with longer wavelength excitation light. (A) 632.8 nm excitation; (B) 780 nm excitation.*

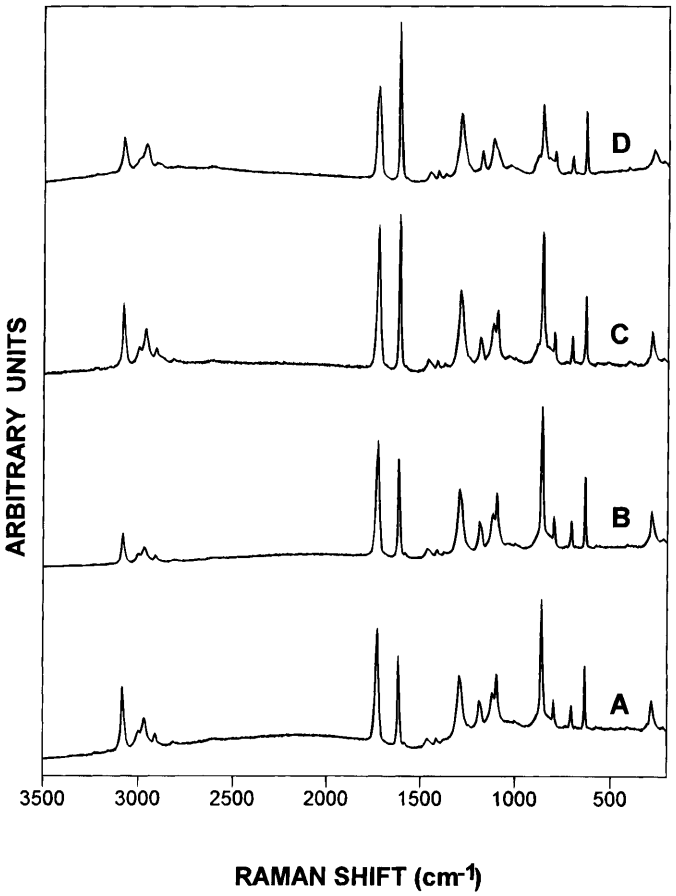

FIG. 3—*Raman microprobe spectra (632.8 nm excitation) of a set of polyester fibers from different manufacturers. (A) Allied (AO196); (B) Firestone Fibers (AO421); (C) Hoechst (AO243); (D) Tolaram (AO333).*

data set. The coefficients required for the linear combination of factors in order to reproduce a particular spectrum are known as its "scores." Spectra may therefore be more easily compared by examination of PCA scores, which form a much reduced data set, rather than the original spectral data.

For the polyester fibers, the spectral data set consisted of 4 measurements each of four samples. Each measurement was made at a different point on the fiber. PCA was carried out on this data set and a scores plot for Factor 1 vs Factor 2 for each of the spectra in the data set is shown as Fig. 4. Clearly, the spectra fall into four distinct groups indicating that there are real and reproducible spectral differences between each group. The spread within each group is a measure of the reproducibility of the Raman spectrum of that particular sample. The Raman spectra of the four polyester fibers are therefore reproducibly different. A benefit of the PCA approach, particularly applicable to forensic analysis, is that the spectrum of an unknown sample of one of the four polyesters, could be subjected to the same PCA model and its scores calculated. It could then be plotted in the same way and would be seen to belong unequivocally to one of the four groups. While PCA is a very powerful comparative tool, it does not eliminate the need for a forensic scientist to make direct physical comparison of the spectra.

Fibers of Similar Molecular Structure: Polyamides (Nylons)

The polyamides, known commercially as nylons, are an important group of fibers with many uses in textiles, furnishings, ropes etc. A range of different molecular structures is possible. Self-condensation of an ω-amino acid leads to a range of "single number nylons" which, in practice, have carbon chain lengths in the range 3-11. Perhaps the most common structure of the single number nylons is nylon-6. Condensation of a diamine with a diacid gives a range of possible structures known as the "double number nylons," for example nylon-6,6. Like many commercial polymers nylons have a tendency to fluoresce under laser illumination and they have therefore been difficult to study by Raman spectroscopy. However, recently systematic studies of both single number and double number nylons by FT-Raman spectroscopy have been reported (21,22). These authors have found that Raman spectra of nylons can be acquired routinely with near-infrared excitation without interference from fluorescence, and that the technique is useful to distinguish many of the different nylon structures.

Figure 5 shows a series of Raman microprobe spectra, taken with 632.8 nm excitation, of nylon fibers from the CTS fiber collection. An expansion of the spectra in the region 1700-500 cm^{-1} is given in Fig. 6. The spectra are broadly similar and show the expected features of polyamide spectra such as the N-H stretch at 3300 cm^{-1}, and the amide C═0 stretch near 1650 cm^{-1}. The spectra are also similar to the previously reported FT-Raman spectra of nylons (21,22), but not identical as there are considerable differences in band intensities. Careful examination of Fig. 5 shows that there are many small differences between the spectra which could be used to distinguish between the different fibers. For example, the exact position of the band near 940 cm^{-1} (assigned to the C—CO stretching mode) varies from 929 cm^{-1} for nylon-6, 953 cm^{-1} for nylon-6,6, to 946 cm^{-1} for the nylon-6,12 fiber. Similarly, the position of the amide C═O stretching band also varies from 1636 to 1641 cm^{-1} among these spectra. There are also many variations in band intensities. Clearly, Raman microprobe spectroscopy has demonstrated a similar ability to distinguish between nylon structures in fibers as was previously reported for FT-Raman spectroscopy (21,22) of nylon pellets and films. The advantage of the microprobe is that small fiber samples, commonly encountered in forensic casework, require no special mounting techniques, are non-destructively analyzed, are easier to handle, and that high qual-

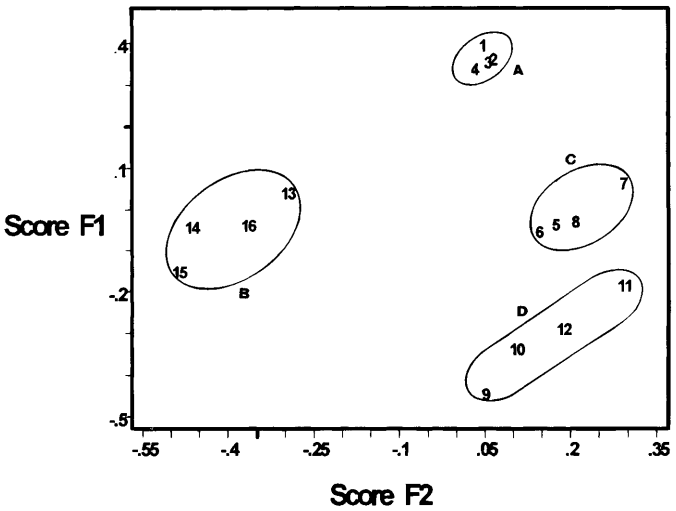

FIG. 4—*A principal components analysis (PCA) scores plot for the spectra of the polyester fibers shown in Fig. 3. Repeat spectra for each sample are circled.*

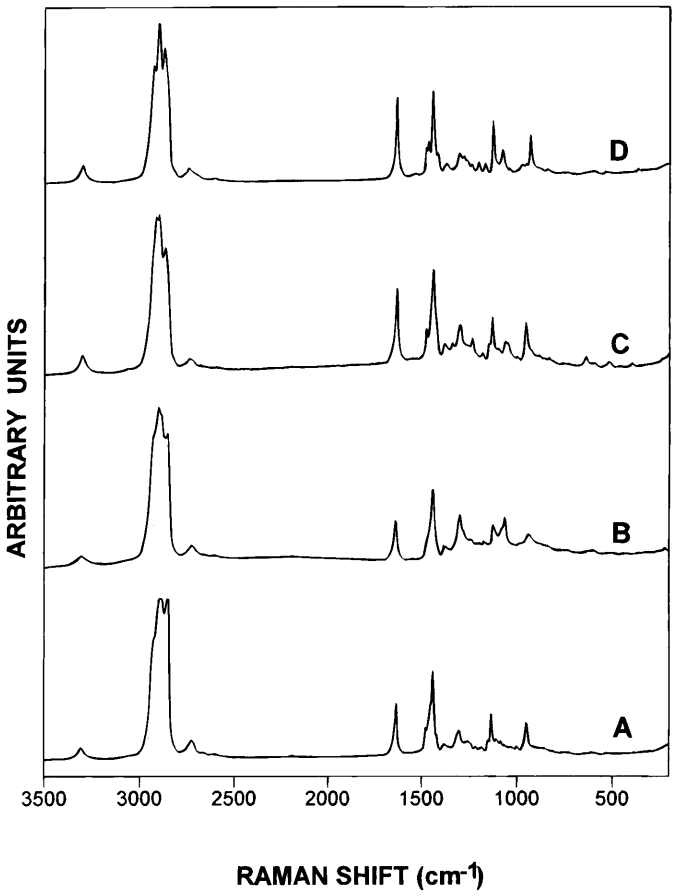

FIG. 5—*Raman microprobe spectra (632.8 nm excitation) of a set of nylon fibers of different molecular structure. (A) nylon-6,12 (AO464); (B) nylon-6,11 (AO302); (C) nylon-6,6 (AO330); (D) nylon-6 (AO208).*

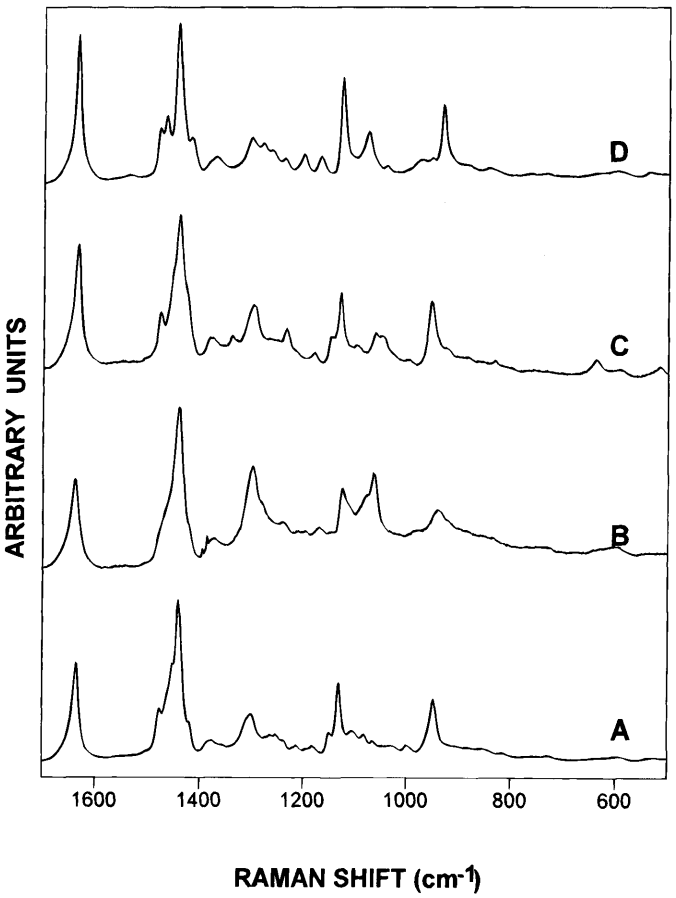

FIG. 6—*As for Fig. 5 but showing an expanded spectral region 1700-500 cm*$^{-1}$.

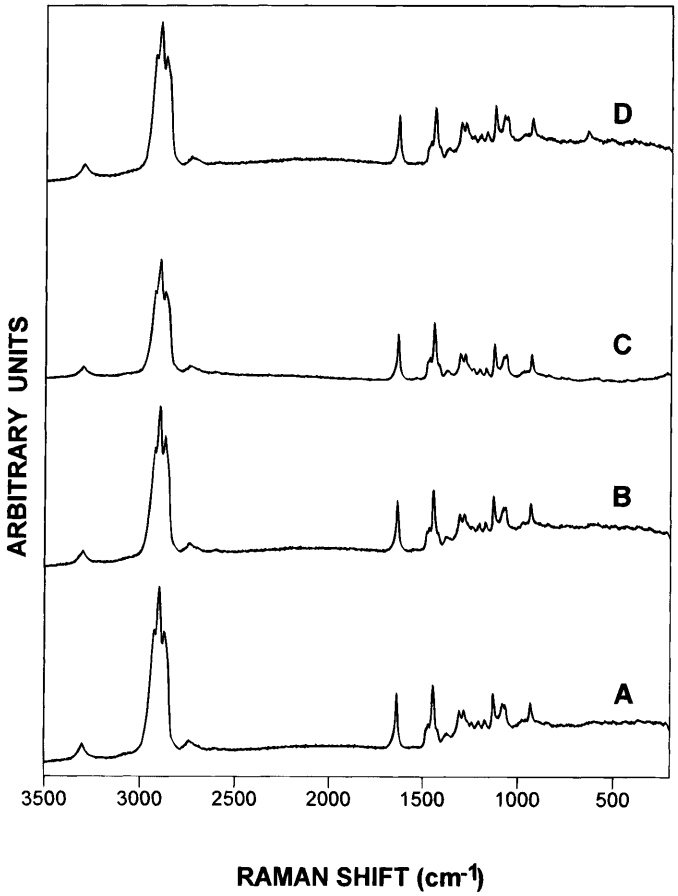

FIG. 7—*Raman microprobe spectra (632.8 nm excitation) of a set of nylon-6 fibers from different manufacturers. (A) Badische (AO163); (B) Berkley and Co. (AO410); (C) Allied (AO207); (D) Albany International (AO463).*

ity spectra are obtained in a matter of seconds. Figure 5 shows that fluorescence is not a problem with these fibers despite the fact that the excitation was in the visible region of the spectrum.

When the nylon fibers are of the same structural type, the Raman spectra are expected to be much more similar. Figure 7 shows a suite of 4 samples of nylon-6 fibers each produced by a different manufacturer. Only very minor differences in peak width and intensity can be seen between the spectra, which are more similar than those shown above for polyester fibers (Fig. 3). Principal components analysis (PCA) was applied to these spectra in the same manner as the polyester fibers and a scores plot is shown as Fig. 8. Repeat spectra, taken at different points on each fiber sample, are grouped close together on the scores plot showing that the spectra are reproducible. The groups of spectra for each of the different nylon samples are well separated indicating that each sample has a distinctly different spectrum. Again, the capability of the PCA technique to distinguish between similar spectra is demonstrated. This is made possible because the Raman microprobe spectra are very reproducible which is probably due to the minimal sample preparation necessary to obtain the spectra.

Dyed Fibers

All fibers previously discussed were taken from the CTS reference collection and are free of dye. Of course many real fiber samples are dyed and it is necessary to determine how this affects the Raman spectrum. Dyes are typically aromatic and/or unsaturated molecules and hence are generally excellent Raman scatterers. However, these same structural features also make dye mole-

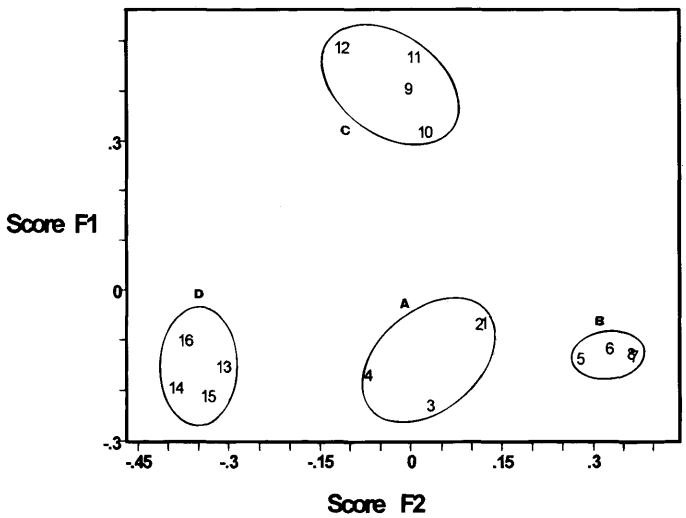

FIG. 8—*A principal components analysis (PCA) scores plot for the spectra of the nylon-6 fibers shown in Fig. 7. Repeat spectra for each sample are circled.*

cules tend to be fluorescent under laser irradiation. It has been previously reported by Bourgeois and Church (17) that FT-Raman spectroscopy utilizing near-infrared excitation at a wavelength of 1064 nm is a useful method to characterize dyestuffs in acrylic fibers. Their work was carried out in the normal macroscopic sample compartment of the FT-Raman spectrometer using a specially designed cell to hold the fiber sample. The long wavelength of the exciting line allowed Raman spectra to be collected without interference from fluorescence.

In our work we used a Raman microprobe spectrometer to investigate dyed fibers, consequently no sample preparation or special cell was required. As fluorescence posed a problem with 632.8 nm excitation, the longer wavelength light, 780 nm, from the semiconductor laser was used and fluorescence was avoided. Figure 9 shows the Raman microprobe spectra of two different red-dyed polyester fibers. The spectra show bands due to both the polyester itself (marked with asterisks) and the dye compound. Note that these bands are similar intensity despite the fact that the proportion of dye present is very low compared with the polyester. As mentioned before, this is a result of the high Raman cross-section of typical dye molecules compared with typical polymers. Raman spectroscopy is therefore a particularly useful technique for studying dyes on fibers, and much superior to infrared spectroscopy which would show spectra dominated by polymer absorptions. The other point to note is that although the fibers visually had similar colors, the Raman bands due to the dyes are quite different, indicating different dye compounds.

The nature of the polymer for a dyed fiber may not always be known. In this case it is possible to obtain separate spectra of both the fiber and the dye. Figure 10A shows the spectrum of a blue dyed fiber in the region 1650-450 cm^{-1}. At this stage it is not clear which bands may be assigned to dye vibrational modes and which to polymer (fiber) modes. The dye was extracted from the fiber at elevated temperature by a solvent consisting of a mixture of water and pyridine. The Raman microprobe spectrum of the fiber, after removal of the dye, is shown as Fig. 10, spectrum B. The fiber can now be identified as a nylon by comparison with the spectra in Fig. 5. This identification could be performed automatically by computer searching of a database of Raman spectra of fibers. Subtraction of spectrum 10B from 10A should give the spectrum of the dye alone (spectrum 10C).

A standard method for characterizing dyes is thin layer chromatography (TLC) (23). In this case the dye solution was spotted onto a high performance TLC plate. The Raman spectra of the dye spot and the clean HPTLC plate were obtained and are shown as Fig. 11, spectra A and B, respectively. The difference spectrum, Fig. 11, spectrum C, is the spectrum of the extracted dye on the HPTLC plate. The spectrum is essentially identical to the spectrum of the dye obtained by spectral subtraction (Fig. 10, spectrum C). The great sensitivity of the Raman microprobe for dye compounds has enabled a spectrum of the dye to be obtained with very little effort. Again, it might be possible to identify the dye by computer searching of a spectral database of dye spectra. This would have to be assembled by the user, as currently none is commercially available.

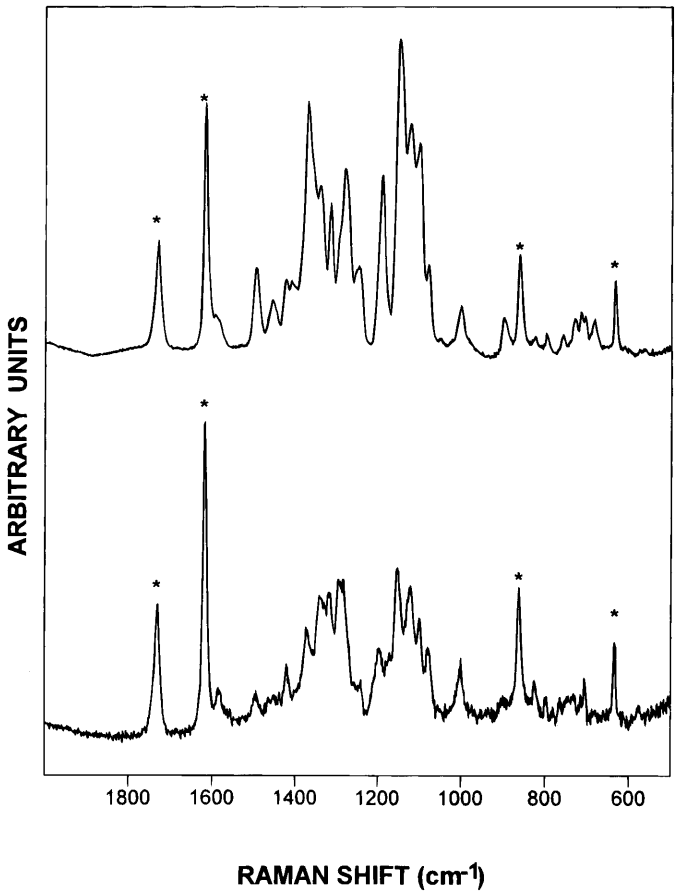

FIG. 9—*Raman microprobe spectra (with 780 nm excitation) of two different red-dyed polyester fibers. Polyester bands are marked with an asterisk.*

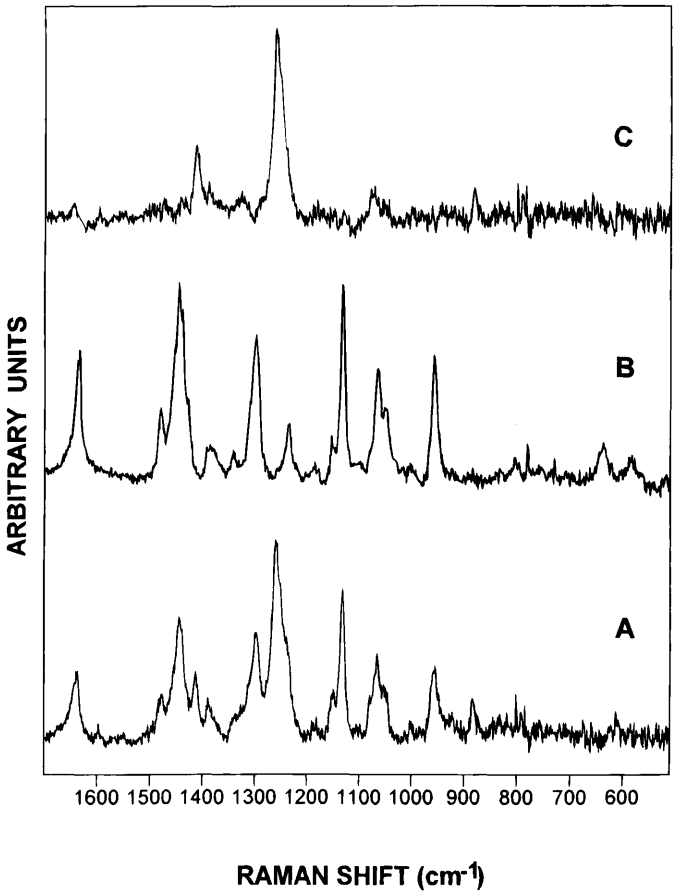

FIG. 10—*Raman microprobe spectra (with 780 nm excitation) of a blue-dyed fiber. (A) Fiber with dye; (B) Fiber only, after solvent extraction of dye; (C) Dye spectrum obtained by computer subtraction of B from A.*

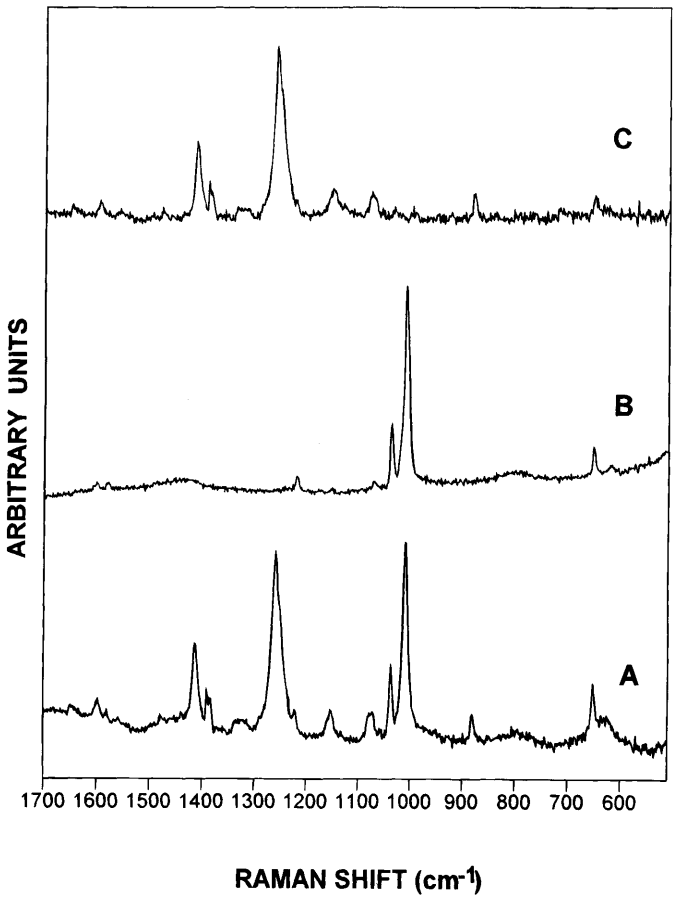

FIG. 11—*Raman microprobe spectra of blue dyestuff from fiber shown in Fig. 10. (A) HPTLC plate spotted with dye extract; (B) HPTLC plate only; (C) Spectrum of extracted dye by computer subtraction of B from A.*

Regardless of whether the dye can be identified or not, the Raman microprobe has been shown to be capable of distinguishing easily between similarly colored fibers which have different fiber structure and/or different dyes, despite the fact that the fibers may be visually identical.

Conclusions

Raman microprobe spectroscopy has been shown to be useful for the forensic characterization of fibers. No sample preparation is required and sample presentation is simple. This is a distinct advantage compared with the currently accepted method of infrared spectroscopy. Extremely small samples may be examined as a laser spot size of around 1 μm is readily achieved. High signal-to-noise spectra of synthetic fibers can be obtained in a matter of seconds, while natural fibers such as wool and cotton are weaker Raman scatterers and require measure times around 2 min. Fibers of different structure show very different Raman spectra and are easily distinguished.

Fluorescence was occasionally a problem with certain fibers, but could be avoided by leaving the sample under the laser for a few minutes, or by using exciting light of wavelength 780 nm in place of the more common 632.8 nm. The use of the 780 nm laser for all fiber work is recommended as fluorescence is much reduced but measurement time still remains typically at a few seconds.

Fibers of similar structure, but from different manufacturers, have very similar spectra but can be distinguished by careful analysis of the spectra using multivariate techniques such as PCA. Application of PCA to sets of polyester spectra and nylon-6 spectra showed that repeat measurements at different points on a single fiber were highly reproducible, and that spectra of the same fiber type from different manufacturers have distinctly different spectra.

Raman spectra of dyed fibers could also be obtained, and showed bands due to both dye and fiber. Raman spectroscopy is a sensitive technique for dyes because typical dye molecules are excellent Raman scatterers. Fibers of similar color, but a different dye compound, are shown to have quite different spectra and can be easily distinguished. Separate spectra of the fiber and the dye could be obtained by a simple extraction procedure followed by spectral subtraction of the spectrum of the dye-free fiber from that of the dyed fiber. The spectrum of the dye obtained by spectral subtraction was shown to be identical to that of the extracted dye spotted onto a TLC plate.

Acknowledgment

The authors acknowledge the assistance of Dr. Llew Rintoul in obtaining the Raman spectra.

References

1. Gaudette BD. The forensic aspects of textile fiber examination. In: Saferstein R, editor. Forensic science handbook. Vol 2. New Jersey: Prentice Hall, 1988;209–72.
2. Grieve MC. The role of fibers in forensic science examinations. J Forensic Sci 1983;28:877–87.
3. Messerschmidt RG, Harthcock MA. Infrared microspectroscopy. Theory and applications. New York: Marcel Dekker, 1988.
4. 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;36:1027–43.
5. Gal T, Ambrus I, Urszu S. Forensic analysis of textile fibers by Fourier transform infrared diamond cell technique. Acta Chim Hungarica 1991;128:919–28.
6. Tungol MW, Bartick EG, Montaser A. Forensic analysis of acrylic copolymer fibers by infrared microscopy. Appl Spectrosc 1993;47: 1655–8.
7. Hopen TJ, Schubert GD. Microscopical characterization of hydrofil nylon fiber. Microscope 1995;43:109–13.
8. Grieve MC. Another look at the classification of acrylic fibers, using FT-IR microscopy. Sci Justice 1995;35:179–90.
9. Lang PL, Katon JE, O'Keefe JF, Schiering DW. The identification of fibers by infrared and Raman microspectroscopy. Microchem J 1986;34:319–31.
10. Bouffard SP, Sommer AJ, Katon JE, Godber S. Use of molecular microspectroscopy to characterize pigment-loaded polypropylene single fibers. Appl Spectrosc 1994;48:1387–93.
11. White GW. A simple high-pressure anvil and template device for the production of infrared spectra from microfiber samples. J Forensic Sci 1992;37:620–31.
12. Pandey GC. Fourier transform infrared microscopy for the determination of the composition of copolymer fibers: acrylic fibers. Analyst 1989;114:231–2.
13. Hirschfeld T, Chase B. Appl Spectrosc 1986;40:133–7.
14. Hendra PJ, Jones C, Warne G. Fourier transform Raman spectroscopy: instrumentation and chemical applications. New Jersey: Prentice Hall, 1992.
15. Ferraro JR, Nakamoto K. Introductory Raman spectroscopy. Boston: Academic, 1994;172–8.
16. Williams KPJ, Pitt GD, Smith BJE, Whitely A, Batchelder DN, Hayward IP. Use of a rapid scanning stigmatic Raman imaging spectrograph in the industrial environment. J Raman Spectrosc 1994;25:131–8.
17. Bourgeois D, Church SP. Studies of dyestuffs by Fourier transform Raman spectroscopy. Spectrochim Acta 1990;46A:295–301.
18. Jurdana LE, Ghiggino KP, Nugent KW. Confocal laser Raman microprobe studies of keratin fibers. Textile Res J 1995;65:593–600.
19. Massart DL, Vandeginste BGM, Deming SN, Michotte Y, Kaufman L. Chemometrics: a textbook. Amsterdam, Elsevier, 1988;339–69.

20. Sharaf MA, Illman DL, Kowalski BR, Chemometrics. New York, John Wiley & Sons, 1986;179–295.
21. Hendra PJ, Maddams WF, Royaud IAM, Willis HA, Zichy V. The application of Fourier transform Raman spectroscopy to the identification and characterization of polyamides—I. Single number nylons. Spectrochim Acta 1990;46A:747–56.
22. Maddams WF, Royaud IAM. The application of Fourier transform Raman spectroscopy to the identification and characterization of polyamides—II. Double number nylons. Spectrochim Acta 1991; 47A:1327–33.
23. Rendle DF, Wiggins KG. Forensic analysis of textile fiber dyes. Rev Prog Coloration 1995;25:29–34.

Additional information and reprint requests:
A/Professor Peter Fredericks
Center for Instrumental and Developmental Chemistry
Queensland University of Technology
P.O. Box 2434
Brisbane, Queensland 4001, Australia