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Identification of textile fiber by Raman microspectroscopy

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Abstract

Infrared microspectroscopy has been used by forensic scientists to analyze polymer. With the development of Dispersive Raman Microspectroscopy, the application of Raman to forensic analysis became more prevalent because of the complementary vibrational information to infrared. By applying both infrared and Raman microspectroscopy to forensic evidences which can reveal more molecular information from forensic evidences. Applications of these techniques in forensic laboratory have including trace evidences such as drugs, explosives, fibers, paints, pigments, inks, gunshot residues, forgeries and fakes. It has been found that infrared microspectroscopy offers a nondestructive method of fiber identification. Raman microspectroscopy is also very convenient, nondestructive and often permits any form of the sam ples with no sample preparation. This preliminary study showed that natural and manufacturered fibers can be rapidly characterized by these techniques. Raman microspectroscopy shows great potential for analysis and comparison of fiber evidences.

Keywords: Forensic sciences, Fiber analysis, Fiber identification, Raman spectroscopy, Raman microscope

Introduction

Forensic scientists prefer using nondestructive methods of analyzing fibers presented as trace evidences rather than using destructive methods. FT-IR microspectroscopy is a vibrational spectroscopic technique used for the nondestructive identification of molecular species, including synthetic fibers. Fibers can be easily classified according to their chemical structures. However, fibers thicker than about 30μm may be difficult to obtain good spectra from FT-IR microspectrometer [1]. A fiber that is too thick will produce totally absorbing spectral bands and the resulting spectrum will usually extremely difficult to interpret. Fiber samples need to be prepared by rolling flat or flattening under diamond compressing cell for infrared microscopic analysis. Raman spectroscopy has long been recognized as a valued technique in research. Raman spectroscopy is a vibrational character; it provides a convenient technique without sample preparation [1]. It can examine samples through plastic packing or in glass container with no interference. When the microscope attached to the Raman spectrometer, the sample particle size for Raman microspectroscopy can be as small as 1μm. Raman measurements are insensitive to water, which can easily be obtained spectra from aqueous samples. In the forensic laboratory, trace evidences such as drugs, explosives, fibers, paints, pigments, inks, gunshot residues, forgeries and fakes can be analyzed by Raman microspectroscopy. The samples can be performed on microscope slides or directly through glass bottles or through vials. Recently, Raman microspectroscopy has become a very useful and powerful tool; it can provide molecular structure information to complement infrared analysis of molecular identifications [1-6].

Raman microspectroscopy is continually finding new uses in studying a broad range of polymer and biological problems. Several previous researches were relevant to the use of the Raman technique in forensic science. Kalasinsky et al. [3] has been applied Raman microspectroscopy to forensic samples and pathology specimens. They used FT-Raman with 1064 nm excitation to identify the foreign materials in tissue specimen such as cholesterol and polytetrafluoroethylene in an implant case, polyethylene terephthalate and polyacrylonitrile in a pilonidalcyst, and carbenicillin in

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a skin biopsy. They showed that Raman spectra were important in identifying foreign materials in tissue and proving valuable information to the pathologist. Raman microspectroscopy also can provide an alternative for non-invasively analyzing drug crystals on banknotes. Research by Frederick et al.[8] has shown that it is possible to detect and identify single drug crystals in a heterogeneous mixture. This is particularly significant as benzocaine and lidocaine are difficult to distinguish from cocaine by mass spectrometric method. From their peak positions and intensities of the Raman spectra, it is possible to distinguish the Raman signal from each type of crystal.

The work of Keen et al. was used Raman microprobe spectroscopy to characterize synthetic fibers [2]. They found that fluorescence is a significant problem and may swamp the Raman signal. In order to avoid fluorescence by using 632.8 nm excitation, the longer wavelength light, and a 780 nm, from the semiconductor laser can be used. Fluorescence would be further reduced with a even longer wavelength such as the 1064 nm used in FT-Raman. For dispersive Raman spectroscopy, 1064 nm would not be compatible with CCD camera, 780 nm excitation does represent a useful compromise between fluorescence reducing and compatibility with the CCD camera. They had shown that Raman microprobe spectroscopy was very useful for the forensic characterization of fibers. Fibers of different structures showed very different Raman spectra and were easily distinguished. Fibers of the same polymer type from different manufactures have Raman spectra which are only slightly different but could be distinguished by the multivariate statistical technique of principal components analysis [4]. Massonnet et al. [5] studied the Raman spectroscopy of three dyed fibers: two red acrylics and one red wool using nine different laser wavelengths ranging from blue (λ = 458 nm) to near infrared (λ = 1064 nm). They showed that dyed presented in the color fibers can be detected by Raman spectroscopy. For the chosen red fibers, red lasers (λ = 633 and 685 nm) gave the poorest spectral quality whereas blue (λ = 458 nm), green (λ = 514 nm) and near infrared laser (λ = 785, 830 and 1064 nm) provided average results. Blue (λ = 488 nm) and green (λ = 532nm) gave the best quality spectra. The similar results were shown at Thomas's work. They analyze the commonly encountered black/grey and blue cotton fibers under five different laser wavelengths from two different microprobe spectrometers. For dyed fibers, the amount of background fluorescence and dyed cotton fiber are the factor in determining the overall quality of the Raman spectra. This problem was overcome by analyzing using NIR lasers. The best quality of the dyed cotton fibers spectra were obtained by using the NIR diode laser source at 785 nm and the NIR laser sources at 830 nm.

Raman microspectroscopy provides no sample preparation or little preparation to analyze fiber sample. Fibers can be taped directly to glass microscope slides or shiny side of aluminum foil covering microscope slides. Miller et al. [2] has shown that it is possible to scan through a glass coverslip and mounting medium such as Permount to obtain polymeric identification of undyed fibers. Most of the fibers can obtain Raman spectra directly from glass slide mount. No additional sample preparation was required after visual light microscopy. An exception is glass fiber on microscope mounts. Because of glass fibers will produce the same fluorescence response in Raman spectra as the glass coverslips. Therefore, glass fiber could be taped directly to glass microscope slide for Raman analysis [1]. The purpose of this article is to show both natural and manufacturered fibers can be analyzed by Raman microspectroscopy in the forensic laboratory. Raman microspectroscopy will provide a rapid, nondestructive and noncontact technique in the forensic laboratory [6-9].

Experimental

Undyed fiber samples were obtained from Testfabrics Inc. (West Pittston, PA). Fibers were taped directly to glass microscope slides for analysis. The Raman spectra were collected using a Nicolet Almega XR Dispersive Raman Spectrometer (Thermo Electron Corporation, Madison, WI, USA) equipped with 780 nm laser. The Olympus BX51 research-grade microscope and the high-precision motorized stage, combined with high-brightness lasers, create the optimal tool for micron-level analysis. The samples were analyzed using the microscope and a 50X objective was used. Spectra were collected in the range of 125 to 4000 cm^{-1}. The spectra were acquired using scan time settings of 50 s for fiber analysis. Raman data acquisition and data processing were achieved through Thermo Electron's OMNIC software.

Results and Discussion

When infrared radiation passed through a sample and was absorbed selectively at certain frequencies, it produced IR spectrum. Infrared radiation will alter the electric dipole moment of the molecule. On the other hand, Raman spectroscopy is depended on the electric polarizability of the molecule [6]. If the bond connects two identical molecules, the bonds will tend to be more active in Raman than in IR. For example, C=C bond is generally more intense in Raman than in IR spectra [9]. Raman spectroscopy measures the vibrational states of non-polar bands through the use of high intensity lasers [4-6]. Therefore, strong IR bands are related to polar functional groups, whereas non-polar functional groups give rise to strong Raman bands. This means that IR and Raman spectroscopy are complementary to each other. Figure 1 provided the differences between the IR and Raman spectra of the cotton fiber. The spectra showed that the polar group such as O-H stretching near 3300 cm^{-1} was strong in the infrared spectrum Fig 1(A), but no obvious intensity in the Raman spectrum Fig 1(B). Because O-H bonds are weakly polarisable in Raman, water is usually "invisible" in Raman spectroscopy [9]. The Raman spectrum of cotton is not dominated by O-H bands as its infrared spectrum is. An important difference to note is that the Raman spectrum has potential of a better spatial resolution than infrared spectrum. In Raman, this has fewer, sharper and less overlapped bands than in infrared spectrum. In plant fiber, cotton fiber is unique in being almost pure cellulose which consists of long chains of D-glucose units joined by β-1,4-glycosidic links [10]. Viscose rayon is the man-made fiber which is regenerated from wood cellulose. Therefore, viscose rayon is a cellulosic polymer which has identical chemical structure to the cotton fiber. The spectra in Fig 2(A) and 2(B) both showed characteristic bands from cellulose. The major features of the cotton and rayon fiber are very similar in the two spectra (Fig 2(A) and 2(B)). In Fig 2, the bands represent cellulose can be seen at 2906 cm^{-1} (CH, CH_2 stretch), 1478 cm^{-1} (H-C-H and H-O-C bend), 1379 cm^{-1}, 1334 cm^{-1} (H-C-C, H-C-O, and H-O-C bend), 1108 cm^{-1} (C-C and C-O stretch), 910 cm^{-1} (C-O-C in plane, symmetric), and 516-379 cm^{-1} (skeletal C-O-C, C-C-C, O-C-C and O-C-O bend) [10-12, 14-16]. The major difference between cotton and rayon fiber can be seen at the Raman spectrum is peak 650 cm^{-1} (C-S-C stretch). The cotton spectrum in Fig 2 (A) does not have this band. Peak at 650 cm^{-1} could be the result of incomplete regenerated the xanthate derivative back into the form of cellulose during the rayon process [13-14].

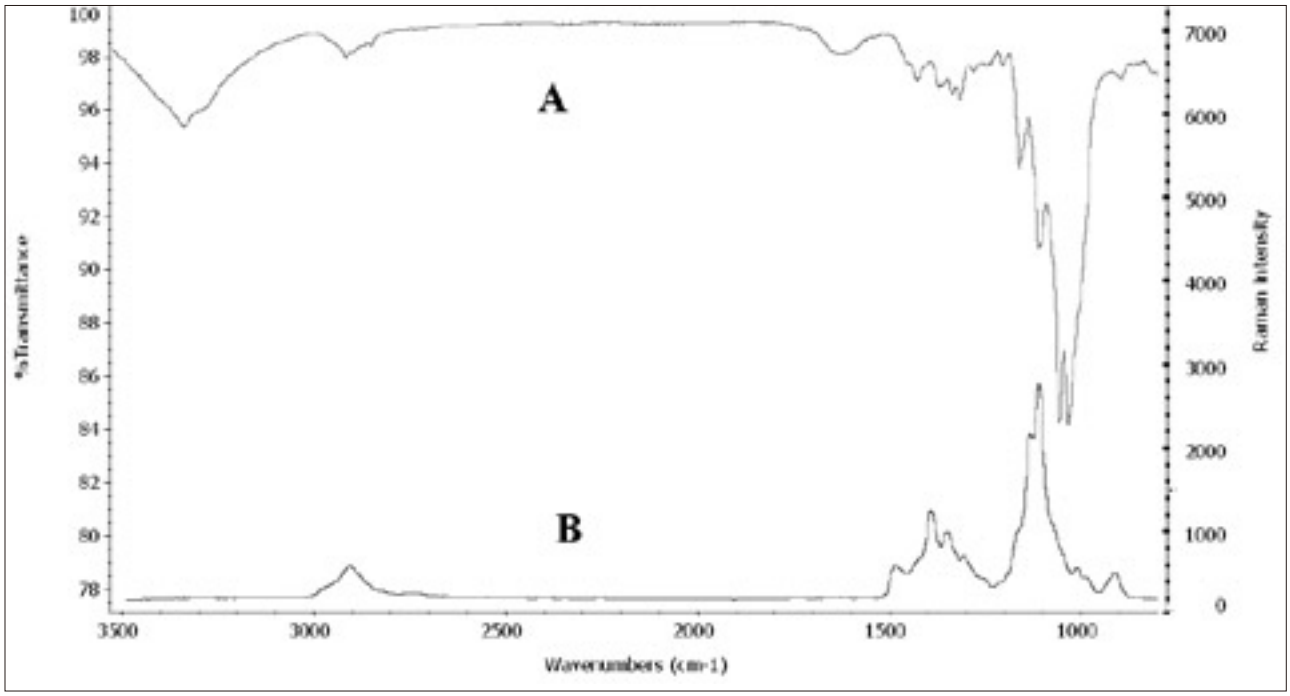

Fig 1. Spectra of a single cotton fiber: (A) Infrared spectrum; (B) Raman spectrum.

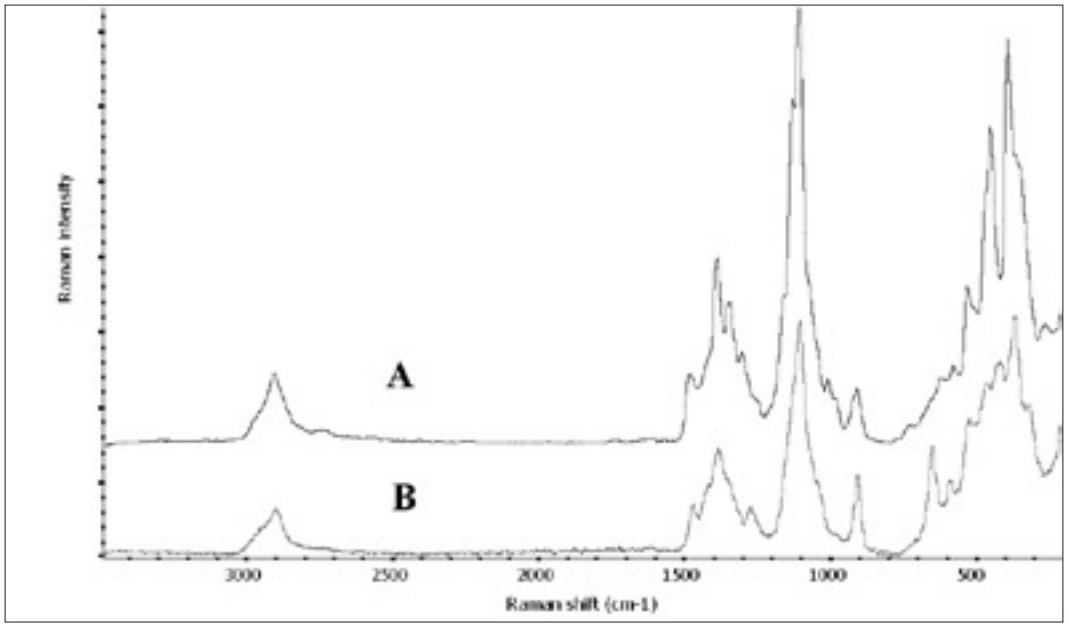

Fig 2. Comparison of Raman spectra of two cellulosic fibers; (A) cotton; (B) rayon.

In animal fibers, wool and silk are composed of the protein keratin. The only difference between wool and silk is amino acid cystine which is not present in silk but comprises some 11-12% of wool. Cystine provides the disulphide crosslinks hold the polymer chains together in wool [13]. From Fig 3, the amide I band is connected with C=O vibrations of carbonyl groups and occurs in the range of 1600-1690 cm^{-1}. The CH_2 bending occurs in 1460 cm^{-1} at both spectra. The amide III band occurs in the range of 1220-1300 cm^{-1} [17]. The position and intensity variability of amide bands is attributed to the change of conformation of the keratin molecule of wool and silk. Note the 1234 cm^{-1} and 1094 cm^{-1} had more intensity in the silk spectrum than the wool spectrum. The main difference between wool and silk is disulphide bond (S-S) [13, 18]. This is shown in Fig 3(A) at the peak 523 cm^{-1}.

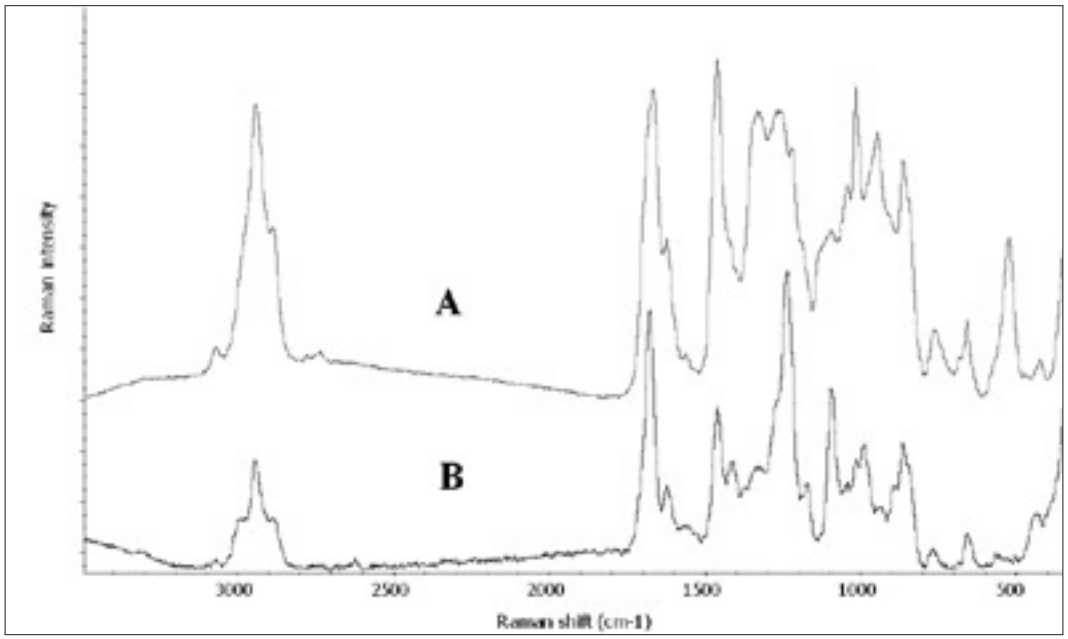

Fig 3. Comparison of Raman spectra of two animal fibers; (A) wool; (B) silk.

Polyester fibers are the most commonly fibers among the synthetic fibers. Most of the polyester fibers are polyethylene terephthalate (PET) [19]. Fig 4 is shown the comparison of IR and Raman spectra of the PET fiber, Raman spectrum has fewer and less overlapped bands than in the infrared spectrum. In Fig 4, C=O stretching was observed at both IR (1720 cm^{-1}) and Raman (1737 cm^{-1}) spectrum. The big different between IR and Raman spectra is aromatic C=C stretching at 1624cm^{-1} in the Fig 4 (B). Both IR and Raman spectra have difficulties in subgrouping polyester fibers [20]. Causin et al. [19] had suggested differentiating of the polyester fibers can be based on the evaluation of two features in the infrared spectra: the *trans-gauche* conformation and the O-H end-group content of the molecule. *Trans* conformers give rise to the bands at about 846 cm^{-1}, 973 $cm^{-1}$and 1340 cm^{-1}, while *gauche* originate the peaks at about 896 cm^{-1} and 1370 cm^{-1}. The peaks at 1370 cm^{-1} and 846 cm^{-1} were measured and ratioed. The end-group content was evaluated by ratioing the peaks at 3440 and 874 cm^{-1}. By calculating the relative standard deviation of the polyester fiber, this method can subclassify the PET fibers [19]. In Fig 4 (B), the peak at 1108 cm^{-1}, attributed to a combination of ring C-C stretching, ester C-O-stretching and ethylene glycol C-C stretching mode, which has been related to the crystallinity of PET fibers [20]. In Raman spectra, PET fibers also have similar characteristics. However, there are differences in relative intensities of bands particular near 1100 cm^{-1} and 350 cm^{-1}. Keen et al. suggested that it is possible to distinguish the polyester fibers of different manufacturers by using the multivariate statistical technique of principal components analysis [2, 21].

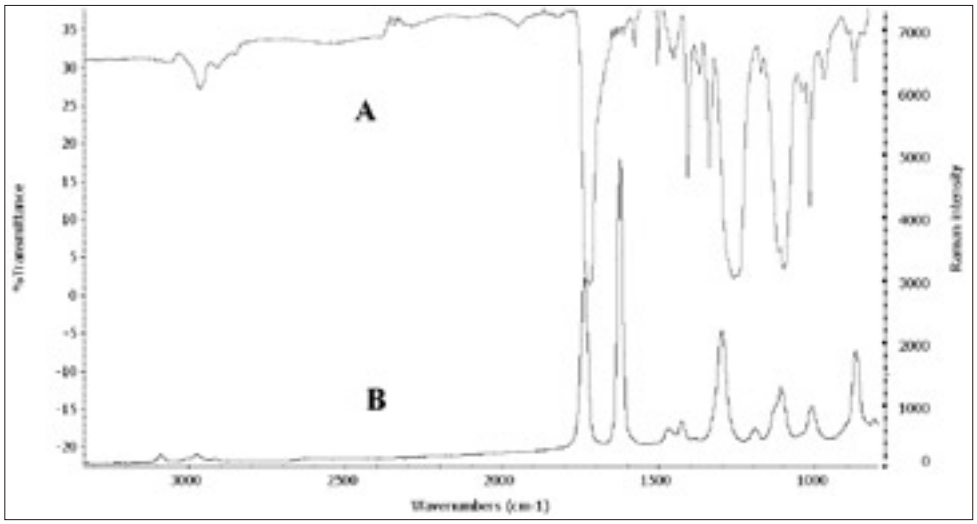

Fig 4. Spectra of a single polyester fiber; (A) Infrared spectrum; (B) Raman spectrum.

Nylon fibers are also frequently seen as evidence in forensic cases. Nylon 6,6 and nylon 6 are the most widely manufactured polyamides. The most convenient way by infrared spectra to differentiate nylon 6,6 and nylon 6 is the presence of the 935 cm^{-1} [1]. In the infrared spectra of nylon 6,6, we can find the weak crystalline band near 935 cm^{-1}. To determine the differences between the different numbered series of nylon, we can compare the small skeletal region bands (1150-1100 cm^{-1}) in their infrared spectra. Since the differences were not very obvious in the infrared spectra, it is easier to distinguish nylon fibers from Raman spectra [1]. Figure 5 shows three different series of nylon Raman spectra. The three Raman spectra show no similar bands at 3300 cm^{-1} (N-H stretch), 2853-2920 cm^{-1}(CH_2 stretching- asymmetric and symmetric), 1638 cm^{-1} (Amide I, C=O), 1440 cm^{-1} (CH_2 bending), and 1374 cm^{-1} (CH_2 wagging). The major difference between nylon 6 and others is that nylon 6 has 1281 cm^{-1} (Amide III – C-N stretch and N-H bend) (Fig 5(A)), nylon 6,6 and nylon 6,12 do not have this peak. Three spectra have CH_2 twisting at 1298 cm^{-1}, but nylon 6 is shifted to 1308 cm^{-1}. At the C-C skeletal backbone structure region between 1126 cm^{-1} and 1062 cm^{-1}, it is found that nylon 6 has two peaks but nylon 6,6, and nylon 6,12 have three peaks in this region. Peak at 1235 cm^{-1} (N-H wagging) in Fig 5 (B) is not shown in the nylon 6,12 (Fig 5 (C)), which can differentiate the Raman spectra of nylon

6,6 from the Raman spectra of nylon 6,12. In Figure 5, carefully examine the C-C-O stretch near 940 cm^{-1}, which can find that peak varied from 932 cm^{-1} for nylon 6 (Fig 5(A)), 953 cm^{-1} for nylon 6,6 (Fig 5(B)), to 948 cm^{-1} for nylon 6,12 (Fig 5 (C)). It is shown that using Raman spectra are much easier to distinguish different kinds of nylon fibers than using Infrared spectra [1-2, 22-23].

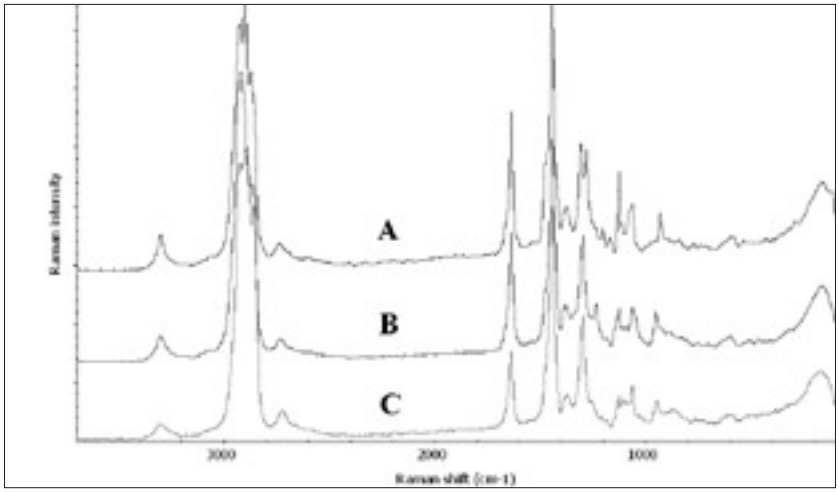

Fig. 5 Raman spectral results of nylon fibers; (A) nylon 6; (B) nylon 6,6; (C) nylon 6,12.

The other fiber usually encounter in the forensic analysis is acrylic fiber [24]. Acrylic fibers are made by the colopolymerization of acrylonitrile and other chemical monomer [13]. Acrylics of varying composition have been classified into 20 types by Grieve using infrared spectra [24]. The main difference between most acrylic and modacrylic fibers is the concentration of the polyacrylonitrile (PAN). Modacrylic fibers contain 35-85% polyacrylonitrile, while acrylic fibers contain more than 85% polyacrylonitrile [25]. Figure 6(A) is Creslan 61 acrylic fibers made from polyacrylonitrile and methylmethacrylate (MMA). Figure 6 (B) shows a particular form of modacrylic fiber that is made of polyacrylonitrile and vinylidene chloride. From both of the spectra, one important feature can represent acrylic is nitrile stretch at 2254 cm^{-1}. The variations of the band shapes are different between acrylic (Fig 6 (A)) and modacrylic fiber (Fig 6 (B)) which are located at C-H bend (1367-1320 cm^{-1}) and C-C skeletal stretch (1130-1060 cm^{-1}). It is shown that modacrylic in Figure 6 (B) has peak 465 cm^{-1} ($C=CH_2$) whereas acrylic can not find in this peak. With additional characteristic features in the acrylic Raman spectra, we can help to further discriminate subgrouping acrylic fibers.

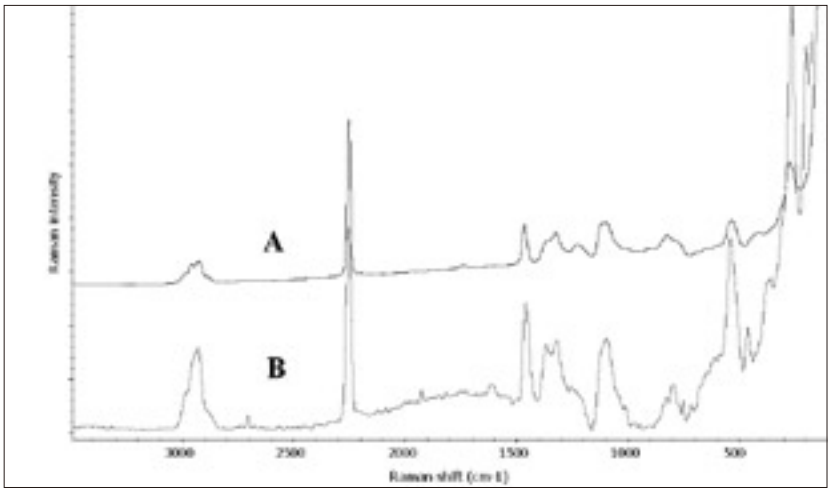

Fig 6. Raman spectral results of (A) Creslan 61 acrylic; (B) modacrylic fiber.

Conclusions

Vibrational spectroscopy has been used to analyze many evidences in forensic laboratory for a long time. FT-IR and Raman spectroscopy are complementary techniques for study of molecular vibrations and surface. Both Raman and FT-IR microspectroscopy offer information on the chemical structure of fibers. Infrared spectroscopy has reached a level of maturity in forensic applications, whereas Raman spectroscopy is just beginning to develop. Raman microspectroscopy proved to be a very sensitive technique for the small size of the evidences. It has shown to be a useful technique to analyze single fiber in the forensic laboratory. It was found that fibers with different generic class have very different Raman spectra. Fibers with the same type of the polymer from different manufacturered may have the Raman spectra with most of the similar bends. The slightly different between the Raman spectra can be distinguished by the multivariate statistical technique of principal components analysis in the further study.

Acknowledgment

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