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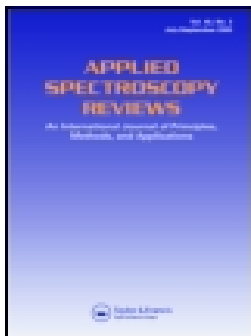
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## Spectroscopic techniques for the forensic analysis of textile fibers

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### Abstract

A review has been conducted on the application of the spectroscopic techniques to the comparative study and identification of different textile fibers. Microspectrophotometry in the ultraviolet-visible range and Raman spectroscopy are the main techniques investigated with this aim in the forensic field. UV-Vis MSP is the first recommended technique, which is principally used to study the color of the fibers. A more complete approximation focused to determine the specific color of the fibers is provided adding Raman spectroscopy to the analytical scheme. Sometimes, it also provides information about the polymeric nature of the fibers. Regarding FTIR spectroscopy, it is the recommended tool to determine the fiber nature. Raman and FTIR spectroscopy are complementary techniques and a frequent recommendation is a combination of both techniques, in order to get a comprehensive analysis of textile fibers. By other hand, new

and more informative analytical techniques are emerging to the analysis of textile fibers as traces related with criminal contacts, such as infrared chemical imaging spectroscopy and X-ray fluorescence spectroscopy.

## **Keywords**

Textile fiber; UV-Vis microspectrophotometry; Raman spectroscopy; FTIR spectroscopy; infrared chemical imaging spectroscopy; x-ray fluorescence spectroscopy; cotton; wool; polyester

## Introduction

The examination of trace elements and the assessment of its transferability are useful to demonstrate the existence of contact or to support the association between an individual and a crime scene, or between a suspect and a victim. Thus, trace evidences are interesting in all those criminal contexts involving close contact between aggressor and victim that can result in the transfer of materials [1]. The possibility of establishing a partnership based on prior contact has already been established by Edmond Locard, whose Exchange principle suggests that whenever two objects come into contact, each of them transfer part of its own material to the other object [2]. Some trace materials of interest in the context of a forensic laboratory, because of the traceability to their origin, are signs like tiny shards of paint that emerge from the body of a car after an impact, the inks used for writing or printing documents, or textile materials used in the manufacture of clothing, whose tiny fibers emerge with greater or lesser ease [3].

Forensic evaluation of textile fibers involves the comparison of individual fibers recovered from the crime scene and from an unknown source, with other fibers obtained from clothes identified and taken from an individual, who is suspected of being related with the crime scene [4, 5]. The aim of this comparative study is to determine to what extent unknown fibers collected at the crime scene during the visual inspection, are related with clothes of the suspect and establish whether or not they share the same origin. Thus, fibers are often recovered trace elements during the investigation of a wide range of crime scenes [4].

During the last years, the application of the spectroscopic techniques to the identification and discrimination of textile fibers have gradually increased. Micro-spectrophotometry in the

ultraviolet-visible range (UV-VIS MSP) and Raman and Fourier transformed infrared spectroscopy (RS and FTIR, respectively) are the main spectroscopic techniques used in the study of textile fibers. At the same time, technology continues improving and other spectroscopic techniques are emerging in this forensic area.

There are several factors that explain the increased interest of spectroscopic techniques for the examination of textile fibers. These are non-destructive techniques and require only a very small sample to develop an analysis. Moreover, these techniques involve an easy sample preparation and allow on site and quick microscopic exams in a short time [6]. Since the laser beam is around 0.8  $\mu\text{m}$ , it can be applied to the measurement of the micro-fibers present in the current market [7].

Table 1 shows the textile fibers classified according to their nature and the spectroscopic techniques used and reported in the literature published up to date. Publications cover the period from 1995 to 2015. Depending on their nature, the fibers used for textile product as clothing can be classified into two groups: natural and synthetic fibers [8]. Natural fibers are those composed of organic plants or animal tissues or containing some minerals, such as asbestos. Synthetic fibers are obtained by chemical processes of varied complexity carried out mainly in the textile industry. Each of these groups covers a wide range of materials with very different chemical structures and physicochemical characteristics. These peculiarities determine their properties when subjected to manufacturing processes used in industry for production of clothing and other textile materials of commercial interest.

Paying attention to the spectroscopic techniques used in the forensic examination of fibers and textiles, the diagram of figure 1 has been made to provide an idea of their use. As shown in

figure 1, UV-Vis MSP and Raman spectroscopy are the most widely used techniques. In fact, a similar volume of publications employing UV-Vis MSP or Raman has been reported up to date. Then, FTIR is another widely used technique. However, there are other less used spectroscopic techniques, as Infrared Chemical Imaging (ICI) and X-ray fluorescence spectroscopy (XRFS) that are emerging to analyze textile fibers.

This review aims to provide a comprehensive overview on the application of spectroscopic techniques used for the forensic analysis of fibers and textiles. Taking into account the use of the spectroscopic techniques for the examination of fibers and textiles, this work has been structured by establishing four major sections. First, we show the applications of UV-Vis MSP to the analysis of textile fibers. The sections two and three explain the uses given to Raman and FTIR spectroscopies, respectively. These both are vibrational techniques characterized by their complementarity. Finally, those works using other spectroscopic techniques are grouped.

## **Microspectrophotometry in the ultraviolet-visible range (UV-Vis MSP)**

The reviewed publications by using UV-Vis MSP to analyze textile fibers are listed in table 2, which shows the fundamental aspects of each of them. During the revision of this technique several approaches were studied, such as the differentiation of dyed fibers, the study of the fiber color variations and the importance of black dyes in textiles. Finally, some real forensics cases using this technique are also described.

### *Differentiation of dyed fibers*

Several works have confirmed the consideration of UV-Vis MSP as the most efficient analytical method for studying colored textile fibers [22]. Palmer et al [9] compared the discriminatory power of MSP in the visible and UV-Vis ranges. Measurements in the visible range provided a

discriminatory power of 0.89 between light blue cotton fibers and 0.87 between dark blue cotton fibers. However, using the UV-Vis range a discriminatory power of 0.96 for the two studied fibers was reached. Cassista et al [13] evaluated the capacity of MSP in the visible range to differentiate between green, red and blue fibers. The spectral differences were evident for most of the fibers in each group of color but, in this study, only the red fibers could be differentiated specifically from each other. The fibers that could not be distinguished were consistent with each other and attributed to a common origin.

Although today UV-Vis MSP remains the mainly used and the more discriminating spectroscopic technique available for the study of textile fibers, it has been compared with Raman spectroscopy to investigate their complementarity. Thus, Lepot et al [23] established that Raman spectroscopy was a powerful method applicable to the routine analysis of fibers and recommended its use following MSP measurements. Buzzini et al [22] also compared the selectivity of UV-Vis MSP and Raman spectroscopy for the analysis of dyed fibers of acrylic, cotton and wool. In this case, UV-Vis MSP was confirmed as the most efficient and discriminatory method for the analysis of textile fibers, whereas Raman provided a minor discrimination power and played a complementary role.

The discriminatory power of UV-Vis MSP and Raman spectroscopy were compared studying cotton fibers dyed with black/grey and blue reactive dyes, which are commonly encountered in forensic cases [1]. Finally, UV-Vis MSP was indicated as the most efficient analytical method to study the color. One of the cited investigations of Massonet et al [10] studied reactive dyes in cotton fibers and a higher potential for detecting the presence of dyes in fibers was observed for Raman spectroscopy regarding MSP traditional methods. Another more recent study of the same



group investigated reactively dyed cotton fibers with both RY145 and RB221 dyes. The differentiation between these fibers was not possible using UV-Vis MSP because both dyes showed absorbance in the range between 280-290 nm being necessary Raman spectroscopy to add the characterization of the dyes.

#### *Study of the fiber color variations*

Suzuki et al [19] investigated the color variations according to the variable dye concentrations along the surface of the garments. A small intra-variation of the transmittance intensity was observed in single woolen fibers and a relatively large inter-sample variation was observed from different areas in the same textile. These variations were related to the intensity of the spectral signals, not to maxima and minima wavelengths, nor minute shoulder bands. Other factors, such as the variations of fiber thickness and the light scattering inside the fiber, could also influence on this phenomenon. By other hand, in order to study as washing modified the coloration of clothes, Was-Gubala et al [20] proposed a kinetic model to predict the color change in fabrics and fibers treated with detergent solutions. Acrylic and polyester fibers showed similar changes of transmittance. Several factors influenced the change of color, such as the dye type, the textile composition and the type of detergent solution, the exposition time and the washing conditions of temperature and movement.

Many factors can alter the spectra corresponding to pure dyes, such as the presence of “shading colors.” These are added to the dye bath during the dyeing in order to obtain aspecific color. Thus, the use of additives during the dyeing process causes the deviation regarding the patterns of the pure dyes. Additives differ depending on the dyeing process. UV-Vis MSP was used to

classify additives into recognizable groups and to study the high degree of spectral individuality generated by their use [21, 12].

#### *Importance of black dyes in textiles*

In recent years, the occurrence of black dyes in garments has increased as consequence of its popularity as a fashion color, which results in a greater presence of the black/grey fibers in forensic examinations. With the aim of studying the evidential value of black cotton fibers, the most used dyes in their production was investigated. In this way, it was observed that the use of sulphur dyes was decreasing in favor of reactive dyes and that the discriminating power varied according to the dye class [12]. The UV-Vis spectra from sulphur dyes and from the majority of reactive and direct dyes could be easily recognized. However, the greatest difficulties were found to identify Vat dyes, due to their spectral differences. Fibers dyed with reactive dyes presented the highest detected degree of individuality. By other hand, in another work performed by Abbot et al [5], individual black dyes and mixtures of them on cotton, polyester, nylon and acrylic fibers were investigated.

Coyle et al [11] analyzed recovered fibers from tapings on car seats, being the most of them black and grey polyester fibers, whose spectra were different to the polyester fibers used in making clothes. A spectral signal associated with the carbon black pigment was observed for most of the polyester fibers recovered from car seats. Another band at 677 nm was related with a blue pigment commonly used as additive in preparing black viscose fibers. The spectrum at left in Figure 2 shows the typical UV-Vis MSP spectrum of a grey polyester clothing fiber. This presents notable differences respect to the spectrum at right in Figure 2, which is related with

fibers recovered from car seats. Interestingly, polyester fibers from clothing have a thickness lower than 15  $\mu\text{m}$ , while car seats fibers present thickness values above it.

## *Study of real forensic cases*

Houck et al [15] demonstrated the ability of UV-Vis MSP for the comparison of textile fibers in the forensic field. They performed more than two million of comparisons between fibers recovered from real forensic cases and did not observed matches between them. Thus, a low probability of finding two unrelated garments with analytically indistinguishable fibers was achieved. Other studies also supported these findings, such as the investigation of Wiggins et al [17] about the random distribution of four fiber types. The study of Suzuki et al [19] established again UV-Vis MSP as an indispensable method for the objective evaluation of color in fibers. Thus, single fibers of cotton dyed with indigo and seven indigo derivatives were clearly differentiated from each other. By other hand, Suzuki et al [16] compared the real distribution of fibers in a crime scene with the distribution obtained from the testimony of a suspect and established the existence of a strong contact between the suspect and the victim. Moreover of the fibers, other textile elements such as leather sheets have a growing interest in the forensic field, especially for the investigation of hit-and-run cases. In this sense, Sano et al [18] classified leathers by UV-Vis MSP. They evaluated the legal significance of dyed fibers from smooth surfaces of artificial leather sheets.

On the other hand, the mathematical tools for processing images helped to differentiate much closed similar fibers. Coyle et al [24] obtained very similar spectra from acrylic fibers. They applied a mathematical processing using the first derivative to get a more discriminatory analysis and attributed the observed differences to brightness variations. Wiggins et al [14] studied the

first derivative of the absorbance spectra as a tool for the forensic analysis of fibers. This procedure provided more points of comparison that facilitated the discrimination between broad and featureless spectra. However, this mathematical tool did not result in any additional discrimination when the absorbance spectra presented already a high number of comparison points. In addition, the first derivative should be applied with caution when fibers exhibit a large intra-variation in color because it could highlight the variation and provide false exclusions.

### **Raman spectroscopy**

The reviewed publications by using Raman spectroscopy to analyze textile fibers are listed in table 3, which shows the fundamental aspects of each of them. During the revision of this technique several approaches were studied, such as dyes, the analysis of natural and manufactured fibers, as well as the factors of influence on Raman measurements.

#### *Study of dyes*

The molecular structure of many dyes is characterized by non-polar bonds, thus Raman spectroscopy becomes a very good analytical technique for the efficient discrimination between the dyes used for coloring textile fibers. Most of the Raman bands from dyed fibers come from dyes; meanwhile there are only a few signals from textile polymer and these are weaker. Figure 3 shows the Raman bands obtained from a PAN fiber with and without dye. Only few bands were obtained at either excitation wavelength from undyed fibers without luster. However, spectra from strongly pigmented fibers were wholly attributed to the pigment, without bands from the matrix. Thus, the Raman sensitivity of the dyes was so big that identically dyed polymeric matrices provided the same spectral profiles [27].

On other hand, fibers without dye showed characteristic Raman bands that decreased when increasing dye concentration [32, 33]. In addition, the strong emission background observed from undyed samples was also weaker for dyed samples with RB5 as the dye uptake increased [5]. The spectra of this dye from textiles, threads and single fibers were consistent at different uptakes. Dye Raman bands dominated even at low uptake and increased in intensity at medium uptake. However, these bands decreased again at high uptake, showing an optimum concentration for observing the spectrum.

Fibers dyed with Cibacron dyes were evaluated with lasers at 514, 633 and 785 nm. The intensity of the matrix bands varied according to the dye concentration along to the range between 330 and 520  $\text{cm}^{-1}$ . Moreover, the analysis at 514 nm only allowed detecting dye bands. Using lasers at 785 nm, comparable matrix and dye bands were obtained from fibers dyed at 1.0%. However, the intensity of the matrix was clearly minor at 4.0% [3]. The differences between spectra of the same dye on different polymeric matrices are due to the dye dispersion degree in matrices and the specific interactions between them [23].

Massonnet et al [10] analyzed the RB 221 and RY 145 on textile fibers. From fibers dyed with RY145 at 5 and 0.5% only dye signals were detected, whereas a mixture of the dye and the matrix signals was observed at 0.05%. The spectra of the fibers dyed with RB221 at 0.5% was dominated by the dye bands, although only the matrix signals were identified at 0.005%. With the excitation wavelengths at 633 and 685 nm, the detection limit of RB221 was 0.05%. By other hand, the combination of several dyes at different uptakes provides specific colors. The relative intensity of each band from dyes depended on the dye concentration of the fiber. Thus, even using a constant wavelength excitation source, different spectral profiles could be obtained from

the same dye mixture, which offers evidential value for forensic analysis [8]. The RY145 bands dominated the spectra from fibers dyed with RY145 and RB221, when 458, 488 and 514 nm were employed as excitation sources. However, with lasers at 633 and 685 nm, the RB221 signals hid RY145 bands at any concentration. In this way, the limit of detection of dyes on fibers depended on their chemical nature and the wavelength excitation source [10].

The predominance of some spectral signals is explained by the resonant effect [6]. Thus, the lowest detection of RY145 was reached with laser at 458 nm, 488 nm and 514 nm. These wavelengths were closed to the maximum absorbance of the dye at 430 nm [10].

The wavelength excitation source conditioned the analytical results. Therefore, the spectra obtained at different wavelengths from a same substance were not directly comparable. The bands from yellow dyes obtained at 514.5 and 632.8 nm showed different positions to the collected from the same sample using lasers at 785 and 830 nm [6]. In another work, spectral bands registered at 514 and 633 nm from the same undyed cotton fibers were usually shifted by less than  $5\text{ cm}^{-1}$ . For analysis at 785 nm the bands were maintained in the range from 170 to  $1250\text{ cm}^{-1}$  [3]. Since different spectra are obtained from a fiber depending of the wavelength excitation used, a single NIR laser is recommended in order to facilitate a direct comparison. However, more complete discriminations between dubitable and indubitable control samples would be possible using alternative excitation wavelengths to collect several spectra [34]. Massonnet et al [28] analyzed textile fibers using nine excitation wavelengths ranged between 458 and 1064 nm. The best spectral quality was obtained at 488 and 532 nm; meanwhile the wavelength excitation sources at 633 and 685 nm provided fluorescence for all samples. This work recommended a Raman instrument with different excitation wavelength sources for the analysis of fibers, with

the aim of overcome fluorescence problems. Although several problems can hinder the Raman spectra, such as pyrolysis reactions and photochemical degradation of the sample, fluorescence is the most important problem [34]. This problem avoided obtaining spectra from car seat garments in the study of Coyle et al [11]. One variation of the Raman technique, SERRS, did not improve the fluorescence results. However, fluorescence decreased when NIR lasers were used to analyze synthetic dyed fibers [28]. Moreover, the intensity of the bands showed a marked increase and a decrease in the fluorescence signal when the laser wavelength moved from the visible to the NIR range [6].

In addition to the variation of the laser excitation wavelengths, there are other reasons that also explain the specific enhancement of some bands. Thus, Thomas et al [6] mainly observed bands from blue dyes when blue, yellow and red dyed fibers were analyzed. This was attributed to a significantly greater concentration of the blue dye. By other hand, a localized heating effect from the laser increased the intensity of the Raman bands [10]. Moreover, the type of the polymeric matrix also influenced the observed signals. Thus, the analysis of acrylic fibers by Buzzini et al [22] provided only signals about dyes; meanwhile the influence of the matrix was also detected from wool and silk fibers. Another work observed that alterations on the molecular structure of azo dyes due to different solvents and pH modifications modified their initial spectral profile [32].

#### *Analysis of natural fibers*

The differentiation between linen and jute is necessary to detect the possible adulteration of linen with jute. Edwards et al [25] found a specific band from jute samples at  $1736\text{ cm}^{-1}$  and another band for linen at  $1578\text{ cm}^{-1}$ . These bands allowed the differentiation between both textiles.

The keratin is present for both wool and silk. These materials differ only by the presence of cysteine in wool. Figure 3 shows a band at  $523\text{ cm}^{-1}$ . This band was the main difference between the Raman spectra of wool and silk in the study of Cho et al [4] using a laser at 780 nm. Other important differences were the bands at  $1234$  and  $1094\text{ cm}^{-1}$ , which were more intense for silk than for wool fibers. The position and intensity of amide bands varied according to the conformational change of the keratin molecule. Another study analyzed cotton and wool using laser excitation sources at 785 and 830 nm and also detected cellulose and keratin bands [22].

Pielesz et al [30] studied the interaction between cotton cellulose and direct dyes by two-dimensional correlation Raman spectroscopy (2D-RS). These interactions were attributed to the dyes molecules and the cellulose hydroxyl groups in the host fiber. Moreover, intermolecular interactions between the dye molecules and glycosidic groups were also observed. The natural fibers presented an irregular morphology which responded to a non-homogeneous dyeing. Thus, fabrics made with natural polymers presented low bounds intensity and the dye adsorption further reduced the bands intensity [30]. Another investigation distinguished between raw naturally colored and white cotton cellulose fibers by Fourier transform Raman spectroscopy and PCA. Moreover, it was possible to distinguish between several types of white cotton. The differences between colored and white cotton fibers appeared to be from the adsorbed water, minor structural changes and the relative difference in crystallinity [26].

An important similarity between cotton and rayon spectra was observed during an investigation about natural and synthetic fibers. The rayon fibers are man-made regenerated from wood cellulose and present an identical chemical structure to cotton, which is composed of cellulose.



The principal difference between both types of fibers was a specific band at  $650\text{ cm}^{-1}$  for rayon [4].

#### *Analysis of manufactured fibers*

Polyester is a generic term that comprises different textile materials, being PET the most commonly used for the production of synthetic fibers. Different subtypes of PET fibers have similar spectral characteristics and their differences can be seen by studying the relative intensity of bands near to  $1100$  and  $350\text{ cm}^{-1}$  [4]. During a real case, molten end colorless polyester fibers were searched in blue denim textiles. These fibers had forensic interest because of their very rare presence in blue jean fabrics. The analysis of the colorless part of these fibers confirmed PET as the polymer class [31]. By other hand, Coyle et al [11] found that most fibers used in the construction of the car seats were of black or grey thick polyester. Retrieved fibers with a higher absorption at  $677$  and  $538\text{ nm}$  provided spectra similar to the Blue Phtalocyanine and Green Phtalocyanine, respectively.

Viscose and cotton showed similar spectra due to their cellulose composition. By other hand, spectra from poly-cotton (50:50, polyester:cotton) were dominated by the stronger bands from polyester. Finally, spectra from acrylics were obscured by a very strong emission background [8].

Cho et al [4] reviewed the principal spectral differences between the most common nylon subtypes: nylon 6, nylon 6.6 and nylon 6.12. The 6 and 6.6 nylon subtypes are the most manufactured polyamides. Therefore, it is not rare that these were the most commonly present polyamides in cases of forensic interest. Miller et al [7] indicated that the differences between the nylon subtypes were more visible in Raman than in IR spectra. Figure 4 shows the Raman

spectra of three nylon subtypes. Most characteristic spectral feature for nylon 6 was the band located at  $1281\text{ cm}^{-1}$  that was not present for the other two nylon subtypes. Other important differences between the nylon subtypes was the two bands that nylon 6 presented between  $1126$  and  $1062\text{ cm}^{-1}$ , meanwhile 6.6 and 6.12 subtypes had three bands in this spectral region. Figures 4A and 4C show another specific band at  $1235\text{ cm}^{-1}$  for nylon 6.6, allowing the differentiation between the 6.6 and 6.12 subtypes. The band from the C-C-O stretch around to  $940\text{ cm}^{-1}$  presented a specific position for each subtype of nylon. This appeared at  $953\text{ cm}^{-1}$  for nylon 6.6, at  $948\text{ cm}^{-1}$  for nylon 6.12 and at  $932\text{ cm}^{-1}$  for nylon 6 [4].

Acrylic fibers are produced by copolymerization between AN and other chemical monomers. The concentration of PAN polymers constitutes the major difference between acrylic and modacrylic fibers. The first type contains between 35-85%, while the second contains more than 85% of PAN. A nitrile stretch at  $2254\text{ cm}^{-1}$  was observed by different types of acrylics and modacrylic fibers and can be an important representative spectral feature for the acrylic fibers. In the spectral region between  $1367$  and  $1060\text{ cm}^{-1}$  was assigned the signals related with a C-H bend ( $1367\text{-}1320\text{ cm}^{-1}$ ) and with a C-C skeletal stretch ( $1130\text{-}1060\text{ cm}^{-1}$ ). Another specific spectral band for modacrylic was assigned at  $465\text{ cm}^{-1}$ , which is not present for acrylics, so it can be discriminatory [4]. Buzzini et al [22] analyzed acrylics, obtaining only signals about dyes; meanwhile the influence of the matrix was also detected from wool and cotton fibers. Jochem et al [27] analyzed acrylic and cellulose-viscose fibers and the bands from the polymer matrix were more and showed higher intensity. By other hand, the differences between Saran fibers were only observed in the amount of plasticizer [7]. Abbot et al [5] analyzed fibers of cotton, viscose,

polyester, nylon and acrylic and observed a stronger emission background from undyed knitted than undyed woven samples.

Taking into account that C-C bonds of the skeletal backbone structure of many polymeric fibers present a good Raman scattering and produce characteristic bands, Miller et al [7] studied the capacity of Raman spectroscopy for identifying subclasses of polymeric matrices. For this purpose, difficulties were only found to classify acrylic and saran fibers; meanwhile the subclasses were more easily distinguishable in the Raman than in the IR spectra.

#### *Factors influencing Raman measurements*

The processes used to prepare the fiber samples affect the quality of the analytical results due to the characteristically flatness surface that the fibers present to the laser spot, as well as the small size of the dyes particles [6]. Other factors, such as the adsorbed water, the minor structural changes and the variations of the crystalline nature of the fibers also influenced the analytical results [29]. According to Massonnet et al [28] similar spectra were obtained with aluminium foils, double side adhesive tapes and glass slides. However, bands from the glass could alter the spectra when NIR lasers were used with glass cover slips. Alternatively, quartz cover slips did not interfere with NIR excitation sources. According to Miller et al [7] glass slides generated a large broad underlying fluorescence band near to  $1400\text{ cm}^{-1}$ . Zieba-Palus et al [3] also observed a signal from the glass slide causing differences in the range between  $1250$  and  $1500\text{ cm}^{-1}$ . By other hand, difficulties were also related with the use of mounting mediums because some of them present Raman activity, such as XAM<sup>TM</sup> [28]. Entellan New was proposed as the best mounting medium for the examination of textile fibers [36]. This medium provided very weak

Raman bands, so significant differences were not found between spectra from bare and mounted fibers [29].

Regarding the color, Raman scattering observed for fibers with solid amorphous or crystalline pigment particles was higher than for individual dye molecules. The enhancement of the dye signal might be due to a higher local dye density or a great number of reflections [27]. However, other study indicated that the intensity of the Raman bands was greater for the smaller dye particles [37]. In addition, dye particles presented an irregular shape that difficult the laser focusing [6]. By other hand, increasing laser irradiation time, the background emission from both not dyed and dyed cotton fibers decreased [5].

## **Fourier transform Infrared spectroscopy**

The reviewed publications by using Fourier transform Infrared spectroscopy to analyze textile fibers are listed in table 4, which shows the fundamental aspects of each of them. During the revision of this technique we studied co-monomers, solvents and additives, distribution of polymeric matrices, differentiation of polymeric classes and subclasses and the analysis of acrylics and nylon textile fibers.

### *Study of co-monomers, additives and solvents*

Co-monomers, solvents and additives are used by the textile industry in order to provide specific characteristics to the clothing. This substances and their concentration vary for each garment, so they can be used as discriminatory factors in the study of forensic samples. Their characteristic features in the infrared range allow further discrimination between the subclasses of acrylic fibers [20].

Figure 5 shows the spectrum of a PAN/MA fiber, where a band at  $1670\text{ cm}^{-1}$  is attributed to DMF. This is one of the most commonly solvents used by the textile industry [38]. Intensity of DMF band varied according to the concentration of DMF in the fiber from practically none to be similar of the carbonyl band at  $1730\text{ cm}^{-1}$ . When DMF was present in large amounts, additional signals of lower intensity were observed at  $1400$ ,  $1380$ ,  $1090$  and  $660\text{ cm}^{-1}$ . The presence of DMF in the fiber was reduced by any process involving heat and water, such as dyeing.

Other additional substances are the sodium allylsulphonate and sodium acrylamido-2-methylpropane sulphonate, whose  $\text{NaSO}_3$  groups provided a spectral band between  $1038$  and  $1042\text{ cm}^{-1}$ . This signal appeared in the spectra of all basic dyes but was absent for acid dyes. In PAN/MA fibers, the augmented intensity of the signal at  $1045\text{ cm}^{-1}$  indicated the greater affinity of these fibers by the basic dyes. By other hand, the strong signal observed at  $1730\text{ cm}^{-1}$  was associated to an ester group, that in methacrylate fibers provided other signals at  $1170$ ,  $1024$ ,  $1229$  and  $1250\text{ cm}^{-1}$ . Another remarkable signal due to the dodezylbenzenesulfonic acid was only observed for textiles with basics dyes between  $1038$  and  $1042\text{ cm}^{-1}$ . By other hand, residues of ethylene carbonate used as solution of polymerization provided spectral signals at  $1785$  and  $1805\text{ cm}^{-1}$  [38].

#### *Study of polymeric matrices distribution*

Cantrell et al [38] studied the prevalence of the different textile types in Sydney, detecting a higher prevalence of cotton in Australia; meanwhile wool was more frequent in Europe. These differences were due to several factors as the hardness of the seasons. The popularity of certain fibers, the available sources and the climate were other reasons for differences in population frequencies. These results were reached by the classificatory study of fibers using their infrared

spectra. The analytical information provided by major co-monomers, residues of solvent and thirds monomers allowed differentiating between twenty types of acrylic fibers. In this work, the 84% of the recovered fibers were natural, being cotton the most common generic type (70%). Manmade fibers represented only the 15%, being rayon the majority (51%). Grey-black cotton was the most common combination of color and generic class (33%). Blue cotton represented the second type (30%) and it was followed by grey-black wool. Grey-black and blue were the predominant colors and the 90% of the recovered fibers presented some of them [39].

#### *Differentiation of polymeric classes and subclasses*

FTIR spectroscopy is preferred for obtaining information about the polymeric matrix of textile fibers. This analytical technique was recommended for the identification of textile polymers by the American Society for Testing and Materials (ASTM) [6]. One study using IR spectroscopy at different excitation wavelengths differentiated several types of acrylic fibers; meanwhile spectral signals from dyes were very rare in dyed fibers due to the great absorption of the polymeric matrix between 1000 and 1800  $\text{cm}^{-1}$ , which masked the analytical signals from dyes. This observation highlighted the greater capacity of IR spectroscopy to studying polymeric substrates, compared with the study of dyes [27]. This specificity justified the application of spectroscopy to the identification of classes and subclasses of textile polymers. FTIR allowed the sub-classification of acrylics and saran during a study oriented to identify the polymeric nature of undyed fibers [7]. A target fiber study about the random distribution of fiber in clothing used FTIR spectroscopy in order to analyze the association between foreign fibers recovered from a victim and the garment of a suspect. This investigation concluded that finding a large number of

matches between fibers was difficult to happen by chance. Thus, it was unlikely to find fibers from two different sources on one item by chance.

#### *Analysis of acrylics and nylon textile fibers*

Acrylic fibers are composed of at least 85% of polyacrylonitrile (PAN) [40]. An investigation using FTIR spectroscopy discriminated 20 subclasses of acrylic fibers and confirmed the nitrile band near to  $2240\text{ cm}^{-1}$  as the major spectral characteristic for acrylics. Another band near to  $1730\text{ cm}^{-1}$  was related with the carbonyl groups of the co-monomers [7]. MA, VA and MMA were the most prolific types of acrylic fibers. They presented their specific signals at  $1170\text{ cm}^{-1}$ ,  $1240\text{ cm}^{-1}$  and  $1220$  and  $1130\text{ cm}^{-1}$ , respectively. By other hand, the spectral signal at  $1730\text{ cm}^{-1}$  indicated the presence of ester groups. The examined fibers had a high content in ester groups when the band at  $1730\text{ cm}^{-1}$  exceeded the band from nitrile groups [38]. The analysis of the C--O stretching spectral region between  $1100$  and  $1300\text{ cm}^{-1}$  allowed the identification of the ester type [7].

Very similar spectra were showed by the 6 and 6.6 nylon subtypes, whose major spectral bands are characteristic for polyamides. This simplified the identification of the generic classes. Thus, the band from nylon 6.6 near to  $935\text{ cm}^{-1}$  was the most convenient way to differentiate between 6 and 6.6 nylon subtypes. A carefully comparison of the bands in the region between  $1150$  and  $1000\text{ cm}^{-1}$  was necessary to differentiate the nylons subtypes [7].

Causin et al [41] developed a method for the quantitatively comparison of colorless acrylic fibers, by the study of the content of nitrile, carbonyl and C-H groups. The quantitative analysis provided data about the co-monomer nature and its relative quantity respect to the main monomer. This approximation provided a greater evidential value for forensic comparisons.

*Analysis of leather fibers and foreign materials in textiles*

The analysis of fibers from artificial leathers is increasing for investigating hit and run cases, in order to prove the relationship between a garment of the victim and the suspect automobile [18]. The artificial leathers can be of smooth surface, suede-like surface or be elaborated with polyvinyl chloride. The most superficial layer of smooth surface leather sheets was mainly composed by PU and, to a lesser extent, by a combination of polyester and rayon, meanwhile the layer base was of polyester. The presence of urethane was necessary for the identification of suede-like artificial leather sheets. By other hand, during the manufacturing of textile products, foreign materials can be introduced by error in the polymeric matrix that forms a garment. Another investigation of Siroka et al [35] applied ATR-FTIR spectroscopy in order to detect a white foreign fiber of propylene on a black textile, and a black fiber of PU on a white thread. They identified the polymeric nature of the unknown white fiber brought into a black jersey during spinning. The close contact between the fabric and the unknown fiber hampered the identification of the contaminating fiber. However, the analysis of the fiber out on the fabric provided information about it as a polypropylene fiber. Single fibers with fineness less than 16 nm could not be identified by ATR-FTIR spectroscopy.

**Emerging spectroscopic techniques**

Other techniques are emerging for the identification and comparison of textile fibers, such as those using digital imaging and data processing. These techniques facilitate a more direct report of information about fibers. The tools for sample mapping and generation of chemical images present important advantages in the forensic field, providing new visualization methods that facilitate the access to the scientific information. These techniques compare a great number of



spectra for each sample, which decreases the possibility of reach bad conclusions. At the same time, the imaging techniques provide information about the distribution of the chemical species along the sample surfaces, which facilitates the identification of its components. In order to elaborate chemical images, multiples spectra are registered using a range of interesting wavelengths.

Flynn et al [42] analyzed bi-component fibers by infrared chemical imaging (ICI), which has been proposed as a technique capable of significantly improve the standard methods applied for the analysis of textile fibers. Bi-component fibers are formed by two or more polymeric materials and present a great value as forensic evidence, due to their low frequency in the population and the specific spatial configuration of their components. The results showed the components identity and a variable success for the side-by-side configuration of the chemical regions. When one component was flattened over another the laser passed through the two components at the same time component. The two side-by-side components were clearly visible for Monvelle fibers, whose infrared chemical images were generated from the integrated spectral intensity under bands near  $1641\text{ cm}^{-1}$  (amide I in polyamide) and  $1735\text{ cm}^{-1}$  (carbonyl stretch in polyurethane). Beslon F040 and Cashmilon G4K fibers were also revealed to have a side-by-side configuration. Both were formed by PAN-MA-AA/PAN-MA.

During the study of hit-and-run cases, Sano et al [18] utilized the x-ray fluorescence spectroscopy (XRFS) to determine the inorganic contents in artificial leather fibers from black artificial leather sheets with smooth surfaces. The results showed important differences in the detected elements and characteristic X-ray intensities, even for samples with similar color. XRFS allowed the discrimination of fibers when the MSP evaluation was difficult.

## Conclusions

Today the UV-Vis MSP remains the most efficient method and the recommended analytical technique for the routine study of the textile fibers in the forensic field. It is the mainly used and the more discriminating spectroscopic technique available for the study of textile fibers, being an indispensable method for the objective evaluation of fibers color. Moreover, fibers from artificial leather were also classified by UV-Vis MSP. Within an analytical scheme, the use of the UV-Vis MSP technique for fibers and textiles is first suggested. The differences in the dye concentrations along the surface of a garment cause significant variations in the coloration and modify the intensity of the spectral signals. The additives added to the dye bath during the dyeing alter the spectra of the pure dyes.

Raman spectroscopy is become increasing studied for the forensic analysis of textile fibers, with a clear high potential to detect and identify dyes in fibers. The use of this technique is recommended following UV-Vis MSP. The special contribution of signals provided by a certain dye depends of its relative uptake and of the resonant effect. Variations in the spectra are possible as consequence of the structural changes generated by changes in the solvent or pH, adsorbed water and variations in the crystalline nature of the fibers. Raman spectroscopy was successful for the classification of undyed natural and synthetic fibers according to their polymeric composition, with the exception of acrylic and saran fibers. However, the capacity of the Raman spectroscopy to identify and discriminate polymeric matrices is relative. Moderately intense bands can be obtained from undyed fibers or with very low dye uptake. However, the intensity of these bands decreases when the dye concentration increases.

FTIR spectroscopy shows a greater capacity to study polymeric substrates compared with the study of dyes and is the recommended method for the identification of the classes and subclasses of the polymeric matrix. Co-monomers, solvents and additives can be identified by FTIR and allowed a further discrimination between the subclasses of acrylic fibers.

Regarding other promising spectroscopic approaches, infrared chemical imaging and x-ray fluorescence spectroscopy have been used for fibers analysis. Thus, ICI provides good information about bi-components fibers and their side-by-side configuration, elaborating a map on the distribution of the chemical species along the sample surface. XRFS determined the inorganic content of fibers from black color smooth surface artificial leather sheets.

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Table 1 Types of fibers analyzed using spectroscopic techniques in the reviewed studies.

Type	Material source		Denomination	Spectroscopic technique	Reference
Natural	Vegetal	Bast	Linen	FT-RS	25
			Jute	FT-RS	25
			Ramie	FT-RS	25
		Leaf	Sisal	FT-RS	25
		Seed	Cotton	UV-Vis MSP	5, 9, 10, 12, 13, 14, 15, 19, 20, 23, 31
				RS	3, 4, 5, 6, 10, 22, 23, 31
				FT-RS	21, 25, 26, 40
				SERS	5, 28
		Kapok	FT-RS	25	
		Coconut	FT-RS	25	
	Animal	Wool	UV-Vis MSP	14, 15, 16, 17, 20	
			RS	4, 22, 28	
			FTIR	17, 35	
Silk		FTIR	35		
Manuf.	Na. P.	Cellulosic	Acetate	RS	7
			FTIR	7, 39	
	Si. P.	Petroleum derivatives	Azlon	RS	7
				FTIR	7
			Polyester	SERS	5
				UV-Vis MSP	5, 11, 14, 15, 17, 20, 23, 24,
				RS	4, 11, 23, 29,
				FTIR	17, 24, 35, 39
			PET	FTIR	1
			Aliphatic polyamide (Nylon)	UV-Vis MSP	5, 14, 15,
				SERS	5, 36
				RS	4, 7, 29
FTIR	39				
Polyacrylonitril	UV-Vis MSP	27			

			e	RS	27
				FTIR	27
			Polyamide 66	FTIR	35
			No-specified polyamides	UV-Vis MSP	14, 23
				RS	23
			Modacrylic	RS	4
			Rayon	RS	7, 4
				FTIR	7, 39
			Lyocell	FTIR	35
			Aramid	RS	7
				FTIR	7
			Fluorocarbone	RS	7
				FTIR	7
			Novaloid	RS	7
				FTIR	7
			Olefin	RS	7
				FTIR	7
			Polycarbonate	RS	7
				FTIR	7
			Vinyon	RS	7
				FTIR	7
			Vinyl	RS	7
				FTIR	7, 39
			Saran	RS	7
				FTIR	7
			Spandex	RS	7
				FTIR	7
			Sulfar	RS	7
				FTIR	7
			No-specified acrylics	UV-Vis MSP	5, 15, 17, 20, 22, 28
				RS	7, 22, 28, 29
				FTIR	12, 24, 41
SERS	5, 22				
Multi-component fibers	PAN/MA	FTIR	38, 41		
	PAN/MMA	FTIR	38, 41		
		ICI	42		
	PAN/VA	FTIR	38, 41		
		ICI	42		
	PAN/SS	FTIR	35		
PAN/PVP	FTIR	38, 41			

	PAN/MVP	FTIR	38
	PAN/MA/MVP	FTIR	38
	PAN/PAN-SS	ICI	42
	PAN/MA/AA- PAN/MA	ICI	42
	PAN/MA/ Sulfonate + DMF	ICI	42
	PA/PU	ICI	42
	PU/Rayon	FTIR	18
		XRFS	18
		UV-Vis MSP	18
	PU/Polyester	Vis MSP	18
		FTIR	18
		XRFS	18
	Nylon 6.6/ No- specified polyamide	ICI	42
	PU/Nylon	UV-Vis MSP	23
		FTIR	23
		XRFS	23
	PU/Acetate/ Polyester	UV-Vis MSP	23
		FTIR	23
		XRFS	23

Manuf.: manufactured; Na. P.: natural polymer; Si. P.: synthetic polymer; FT-RS: Fourier transformed Raman spectroscopy; UV-Vis MSP: microspectrophotometry in the ultraviolet-visible range; RS: Raman spectroscopy; FTIR: Fourier transformed Infrared spectroscopy; SERS: Surface Enhanced Raman Spectroscopy; FS: Fluorescence spectroscopy; XRFS: X-ray fluorescence spectroscopy; ICI: Infrared Chemical imaging; PAN: poliacylonitrile; MA: methacrylate; MMA: methylmetacrylate; VA: vinylacetate; SS: styrene sulfonate; PVP: polyvinilpirrolidone; MVP: methylvinilpirrolidone; PU: polyuretane; DMF: dimethylformamide; PET: polyethylene terephthalate.

Table 2 Fundamental aspects (fiber type, measurement conditions and main results) for the study of the textile fibers by UV-Vis MSP.

Studied fibers	Measurement conditions	Main results	Ref.
Cotton Polyester Nylon Non-specified acrylic fibers	N.A.	Not died textiles: high diffuse reflectance and no absorption across the region at 450-500 nm. Sulphur black-1: the most strongly absorbance overall with a near-constant diffuse reflectance of 2-4% throughout 240-800 nm giving a black color. Direct Black 22: small dip in absorption at 350 nm and black color. Reactive Black 5, Vat Blue 1 (Indigo), Vat Blue 43: dip in absorption at 400-500 nm and black color. Reactive Black 5 on viscose and Disperse Blue 79:1 on polyester: dips in absorption at 350-500 nm and black color.	5
Cotton	R: 400-850 nm M: 50x Re: 5 nm	Dyed fiber spectrum with yellow and red dyes contribution to the overall color, but less than the blue dye. Vis-MSP results: Synazol gold-yellow: max. Band at 422 nm. Synazol red: max. Band at 529 and 567 nm. Sumifix Navy: max. Band at 652 nm. Moroccan Blue: max. Bands at 629 y 564 nm.	6
Cotton	N.A.	Blue cotton fibers not have little or no evidential value. Results of D.P. with Vis MSP: mid-blue garments (0.89); dark blue garments (0.87). Results of D.P. with UV-Vis MSP: both types (0.96). Forensic study without spectral discussion.	9
Cotton	Transmittance mode. R: 240-780 nm	RY145 (at 5%): signals at 290 and 430 nm. RB221 (at 5%): signals at 280, 580 and 630 nm. RY145 and RB221 LOD: 0.5%. For mixtures at 90:10 only the major dye was detected. Both dyes were detected for mixtures at 1.5-3.5% and 2.5-2.5%. Different dyes can show identical signals; therefore a good characterization needs several laser sources.	10
Cotton Wool Polyester Nylon	R:380-730 nm M: 7.1- 115x	Spectra of dyed fibers from car seats fabrics were notably different from those from clothing fibers. Doublet absorption at 516 and 555 nm and a distinctive rippled appearance. Most pigmented polyester fibers showed a	11

		typical band spectral trace associated with carbon black pigment or with an additional absorption at approximately 677 nm. Spectral differences among grey pigmented three distinct bands at approximately 568, 606 and 677 nm, a doublet at 528 and 583 nm and a mixture of the previous two with dominant absorptions at 583 and 677 nm. The last was the one identified in pigmented fibers from car seat fabric samples.	
Cotton	R: 240-760 nm M: x 40	Discriminating power to sulphur dyes: 0.13 Reactive dyes: 0.93 Information below 400nm is important for making distinctions and is critical in the case of direct dyes. Reactive dye: active in the UV-region below 300 nm. Vinyl sulphone dyes (Reactive Black 5) show two peaks in the lower UV range and four peaks between 350-500 nm. Manufacturing processes and additives provide slight differences. Monochlorotriazine dyes (Reactive Black 8) show a single large peak in the UV-region. Mixture of Reactive Black 5 and Reactive Orange 72: two peaks in the lower UV range and three peaks between 350-500nm. Greenish-blue grey fibers: slight differences between 400-530 nm. Dispersing, solubilizing and anti-foaming agents or optical brighteners cause differences in the UV-region. Yellow or light brown dispersing agents: absorption band between 380-480 nm. Direct dyes: major transmission peak below 400 nm. Dyes in a mixture may interact resulting in a totally unpredictable mixture curve absorption curve.	12
Cotton	R: 400-700 nm M: 200x	Spectral differences between red, green and blue cotton fibers were clear in most of the samples from each color group. Forensic study without spectral discussion.	13
Cotton Wool Polyester Nylon Non- specified acrylic fibers	R: 250-710 nm T: 50 y120 ms	The first derivative provided additional points of comparison facilitating the discrimination of spectra featureless. Clear intra-sample color variations were highlighted with the first derivative. Forensic study without spectral discussion.	14

Cotton Wool Polyester Nylon Non- specified acrylic fibers	R: 300-800 nm	No fibers were found with the same analytical properties after the inter-comparison of fibers from twenty unrelated cases. Forensic study without spectral discussion.	15
Wool	N.A.	By comparing the distribution and number of target fibers collected in the simulation experiments and the investigation, the reliability of the suspect's confession was not considered to be reliable, as a stronger contact with the victim was demonstrated by our simulations. Target fiber: dark yellowish-green woolen of the garment that the suspect wore when he entered the crime scene. The fiber intelligence was highly significant to explain the suspect's behavior at the crime scene. Forensic study without spectral discussion.	16
Wool Polyester Non-specified acrylic fibers	R: 390-710 nm A: 400x	Finding a large number of fibers that match a control is unlikely to happen by chance. Forensic study without spectral discussion.	17
Polyurethane/ Polyester	R: 400-700 nm A: 200x	Smooth surface artificial leather sheets were classified as a function of their color. It was possible to differentiate between samples with similar color and difficult discrimination. Forensic study without spectral discussion.	18
Cotton Wool	R: 240-760 nm	Small intra-variation of the transmittance intensity in woolen fibers. Large variation for different areas in the same textile attributed to the dye concentration and not to maxima and minima wavelengths or minute shoulder bands. Differentiation between cotton fibers dyed with indigo and seven indigo derivatives. Forensic study without spectral discussion.	19
Cotton Wool Polyester Non-specified acrylic fibers	R: 380-700 nm Ac: 10	Elaboration of a new mathematical model on the color change of fibers treated with detergent solutions. Several factors influence the color change: the type of fiber and dye; the finishing process; the exposition time and the surfactant type. Forensic study without spectral discussion.	20
Cotton	R: 240-760 nm M: 40x	Discriminating power variation to the dye class from 0.13 for sulphur dyes to 0.93 for reactive dyes. Information below 400 nm is important	21

		for the dye class differentiation and is critical in the case of direct dyes. Spectral variations are produced by: usage of shading colors, uptake of the color components, additives present in dyes or added during the dyeing. The additives used differ as a function of the dyeing process employed. In the range below 400 nm there is much spectral information.	
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R: recorded spectral region; T: acquisition time; Ac: n<sup>o</sup> of accumulations; M: magnification microscope; N.A: not available; ATR: attenuated total reflectance; UV: ultraviolet; RB 5: reactive blue 5; SB 1: sulphur black 1; RY 145: reactive yellow 145; RB 221: reactive blue 221; LOD: limit of detection; MSP: micro-spectrophotometry; CM: comparison microscopy; FLM: fluorescence light microscopy. Other abbreviations as defined in table 1.

Table 3 Fundamental aspects (fiber type, measurement conditions and main results) for the study of the textile fibers by Raman spectroscopy.

Studied fiber	Measurement conditions	Main results	Ref.
Cotton	E: 514, 633, 785 nm R: 150-2500 $\text{cm}^{-1}$ T: 10 s Ac: 5 A:100x Rs: 4 $\text{cm}^{-1}$	E. 514 nm: only detection of cotton bands. E. 633 nm in 1.0% dyed fibers: bands from dye and one low intensity band from cotton. E. 633 nm in 4% dyed fibers: no bands from cotton. E. 785 nm: band from glass slide analyzing fibers dyed with bi-functional reactivities placed on a microscope slide. Fibers dyed at 1.0%: comparable intensities between the highest bands from cotton and the highest bands from dye. Fibers dyed at 4%: minor intensity for cotton. Intensity varied according to the dye concentration in the range from 330-520 $\text{cm}^{-1}$ .	3
Cotton Silk Polyester Nylon Modacrylic PAN/MMA	E: 780 nm R: 125-4000 $\text{cm}^{-1}$ T: 50 s A: 50x	Raman spectra presented a better spatial resolution than infrared spectra. Viscose rayon showed a specific C-S-C stretching at 650 $\text{cm}^{-1}$ which was the major difference with cotton. The disulphide bond (S-S) of wool provided a band at 523 $\text{cm}^{-1}$ that can differentiate wool and silk. Differences in relative intensities were observed near 1100 and 350 $\text{cm}^{-1}$ for the different types of polyester fibers. The specific band at 1281 $\text{cm}^{-1}$ for nylon 6 was the major difference respect to nylon 6.6 and nylon 6.12. The band at 1298 $\text{cm}^{-1}$ for nylon 6 and nylon 6.12 was shifted to 1308 $\text{cm}^{-1}$ for nylon 6. Nylon 6.6 and nylon 6.12 had three bands between 1126-1062 $\text{cm}^{-1}$ , while nylon 6 only presented one. Nylon 6.6 had a band at 1235 $\text{cm}^{-1}$ that allowed differentiating it respect to nylon 6. C-C-O stretching near 940 $\text{cm}^{-1}$ appeared at 932 $\text{cm}^{-1}$ for nylon 6, at 350 $\text{cm}^{-1}$ for nylon 6.6 and 948 $\text{cm}^{-1}$ for nylon 6.12. Acrylic and modacrylic present C-H bend bands at 1367-1320 $\text{cm}^{-1}$ and C-C skeletal stretch at 1130-1060 $\text{cm}^{-1}$ . Modacrylic showed a specific band at 465 $\text{cm}^{-1}$ .	4
Cotton	E: 514.5, 632.8, 685, 785, 830 nm R: 2100-400 $\text{cm}^{-1}$	Ex. 632.8 nm: good results for the major dye component with little acquisition time and no spectral degradation. Ex. 514.5 nm: fluorescence completely masks any signal from undyed cotton	6



	LP: 1.125, 2.25, 4.5, 14, 17, 300 mW Ac: 10. A: 50x T: 10-120 s Rs: 8 cm <sup>-1</sup> and 1.5-2.5 cm <sup>-1</sup>	fiber. Fluorescence came from cotton. Only some bands were observed between 1700-1000 cm <sup>-1</sup> from Moroccan Blue dyed cotton fiber. The band at 1400 cm <sup>-1</sup> disappeared and band shape at 1300 cm <sup>-1</sup> changed when moving from visible to NIR lasers. Ex. at 785 and 830 nm provided excellent spectra for dyes and dyed fiber.	
Acetate, Polyester Nylon Modacrylic Rayon, Aramide Fluorocarbone Novaloid, Vinyon, Saran	E: 785 nm LP: 300 mW M: 50x R: 200-2400 cm <sup>-1</sup> T: 120 s	Glass slide provides a large broad underlying band near of 1400 cm <sup>-1</sup> . Aluminum foil to back the fiber eliminated the fluorescence of glass. Signal-to-noise ratio was generally lower for fibers mounted in Permout, than those measured on aluminum foil slide. Nitrile stretch of acrylic fibers is observable near 2240 cm <sup>-1</sup> but the C-O stretches do not appear.	7
Cotton	E: 458, 488, 514, 633, 685 and 785 nm R: 200-2000 cm <sup>-1</sup> M: 20-100x	Major bands for RY145: 1610, 1410 and 1140 cm <sup>-1</sup> . Major bands for cotton: 1380, 1340, 1130, 1090, 460 and 360 cm <sup>-1</sup> . Major bands for RB221: 1600, 1500, 1370, 1340, 1050, 900 cm <sup>-1</sup> . Ex. at 458, 488, 514: only cotton bands at RB221 concentrations of 5%; mixture of signals from cotton and RB221 at 0.5% (RB221 is dominant), at 0.05% (cotton is dominant); at 0.005% only cotton signals were detected Ex. At 633 nm: only RB221 bands at 5 and 0.5%. RB221 are dominant at 0.05 and 0.005%. Ex. At 685 and 785 nm: only RB221 at 5%. Mixture of signals from dye and cotton at 0.5%; only cotton bands at 0.05 and 0.005%.	10
Cotton Wool Polyester Nylon	E: 532, 780 nm R: 1600-200 cm <sup>-1</sup>	Fibers with a dominant absorption at 677 nm or at 583 nm produced Raman spectra similar to Blue Phthalocyanine or Green Phthalocyanine. No useful spectra could be obtained from fibers with a doublet at 516 and 555 nm due to the fluorescence.	11
Acrylic Cotton Wool	E: 514.5, 632.8, 785, 830 nm M: 50x, 100x R: 2000-200 cm <sup>-1</sup> T: 10 s	E. 633 nm: no signal from acrylic. E. 514 nm: no signal from red fibers. E. 785 and 830 nm: cotton and wool signals. Raman analysis is recommended after UV-Vis MSP.	22
Polyester Nylon Non-specified acrylics	E: 514.5 nm R: 1000-1700 cm <sup>-1</sup> <b>Dyed textiles:</b> LP: 20 mW T:	Cotton without dye: bands attributed to the cellulose component and a strong background emission. This was higher from the knitted than the woven sample. Weaker cellulose Raman bands	23

	30 min <b>Undyed textiles:</b> LP: 50 mW y 10 mW T: 20 min <b>Threads and fibers:</b> Re: 5 $\text{cm}^{-1}$ LP: 4 mW T: 20-30 min M: 20x Ac: 4-6	were observed with increasing dye uptake. Textiles without dye were white and gave no absorption bands across the 450-800 nm. An increasing in the irradiation of dyed and not dyed cotton time causes a decrease in the background emission. Dye did not photo-degrade significantly during the experiment. Raman spectrum was consistent across different molecular environments.	
Flax, jute Ramie Cotton Sisal, kapok Coconut, coir	E: 1064 nm LP < 50 mWA: 40x or 100x	Jute: 1736 $\text{cm}^{-1}$ (medium-weak intensity) Stretching band near 1062 $\text{cm}^{-1}$ : measurement of the unsaturation extent. Flax and ramie: no detectable scattering in this region. Flax: 1758 $\text{cm}^{-1}$ (medium intensity)	25
Cotton	FT E: 1064 nm LP: 400 mW R: 3600-200 $\text{cm}^{-1}$ Rs: 4 $\text{cm}^{-1}$ Ac: 256	Region 1600-1800 $\text{cm}^{-1}$ : FT-Raman spectra were very similar and reflected a common composition for cellulose. C-C ring asymmetric stretching at 1160 $\text{cm}^{-1}$ . C-O-C glycoside link symmetric stretching at 1122 $\text{cm}^{-1}$ . C-O-C glycoside link asymmetric stretching at 1096 $\text{cm}^{-1}$ . Bands at 1605, 1625 and 1720 $\text{cm}^{-1}$ ; only observed for green and brown cottons. In PCA, two similarly groups were identified for cotton dyed with dyes 3 and 4, and for cotton dyed with dyes 7 and 8. Bands from azo groups: 1300-1400 $\text{cm}^{-1}$ . Bands from at naphthalene 1600 $\text{cm}^{-1}$ . New bands were attributed to interactions cotton cellulose - dyes: 1416, 1510--1512 and 1564 $\text{cm}^{-1}$ (dye 3); 1416, 1514 and 1566 $\text{cm}^{-1}$ (dye 4); 1416 and 1554 $\text{cm}^{-1}$ (dye 7).	26
Polyacrylnitrile	E: 514.5, 632.8 nm LP: 8-12 mW T: 10-90 s Rs: 1.5- 2.5 $\text{cm}^{-1}$ M:50x	Main pigment component from a coloration mixture was identified by Raman. Acrylic fibers showed low intensity bands in the spectral fingerprint region from 400 to 1700 $\text{cm}^{-1}$ . Fibers of Dolan 37 type give not good spectra due to the great fluorescence of Yellow 3 dye. Carbon black spectrum presented two overlapping broad bands at 1370 and 1600 $\text{cm}^{-1}$ . Excitation at 524 nm presented considerable fluorescence problems. Yellow three presented great fluorescence preventing the analysis of the Dolan 37 fiber.	27
Wool PAN/MA	E: 458, 488, 514, 532, 633, 685, 785, 830,	Ex. at 633 and 785 nm: fluorescence. Some bands suffered a modification of their relative intensities between 514 and 830 nm. Ex. 633 nm: poorest	28

	1064 nm R: 200-3500 $\text{cm}^{-1}$ M: 10x-100x	results for the tested dyes due to fluorescence problems. Ex. 488, 532, 785, 830 and 1064 nm: more than 50% good spectra for the tested dyes. Ex. 685, 458 and 514 nm: less than 50% good spectra for the tested dyes. Ex. 633 and 685 nm: no response for the red fiber samples. Ex. 514, 785, 830 and 1064 nm: less than 50% of good spectra for the tested dyes. Red wool analyzed at 532 nm: the fiber spectrum corresponded to the main dye component. The two other were not detected. Red acrylic fibers with an identical dominant dye compound gave very similar Raman response after analyzing with different laser wavelengths. Ex. 785 and 830 nm allowed differentiating these two red acrylic samples. Fluorescence problems for red wool fiber excited with: 514, 633, 685, 785 and 830 nm. For <i>in situ</i> analysis of dyes, the dilution procedure reduces fluorescence problems. Ex. 1064 nm: bands for the acrylic fibers were almost all generated by the PAN. SERRS techniques did not report amelioration of the Raman spectra for the three red fiber samples.	
Polyester Nylon Non-specified acrylics	E: 532nm M: 60x LP: 10 mW R: 100-3380 $\text{cm}^{-1}$ T: 30 s Ac: 5	Bands about 1605, 1625 and 1720 $\text{cm}^{-1}$ were identified through the analysis of green and brown cotton fibers. The <i>in situ</i> analysis of textile fibers mounted in EntellanNew did not need further sample preparation. Bare fibers and these embedded in Entellan New were statistically indistinguishable, when their variance was studied by ANOVA.	29
Cotton	FT E: 1064 nm Rs: 4 $\text{cm}^{-1}$ R: 950-1650 $\text{cm}^{-1}$	Synchronic map: two distinct auto-bands at 1100 and 1125 $\text{cm}^{-1}$ attributed to the interaction of dyes with COC groups or CC rings in cotton. Pairs of negative cross bands at: 1125 and 1300 $\text{cm}^{-1}$ , 1300 and 1125 $\text{cm}^{-1}$ , 1100 and 1300 $\text{cm}^{-1}$ and finally, 1300 and 1100 $\text{cm}^{-1}$ . Signals from Azo groups in direct dyes: 1400-1300 $\text{cm}^{-1}$ . Signals from naphthalene groups in direct dyes: 1600 $\text{cm}^{-1}$ .	30
Polyester	E: 514.5, 785 nm LP: 0.5, 100 mW M: 50x, 100x	Excitations lasers at 514 and 785 nm detected indigo spectrum in blue molten ends of fibers. Spectra from color-less part did not provide additional information. Raman results were less discriminant than these obtained by Vis MSP.	32

		Nature of fiber polymer was identified as polyethylene terephthalate without FTIR.	
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E: laser excitation; SR: spectral resolution; LP: laser power; PCA: principal component analysis;

Other abbreviations as defined in tables1 and 2.

Table 4 Fundamental aspects (fiber type, measurement conditions and main results) for the study of the textile fibers by FTIR spectroscopy.

Studied fibers	Measurement conditions	Main results	Ref.
PET	R: 500-4000 $\text{cm}^{-1}$	PET fibers differences are more frequently located at the fiber core. Study without spectral discussion.	1
Cotton	E: 785 nm Rs: 4 $\text{cm}^{-1}$ Ac: 256	Bands with consistency shape: 170-1250 $\text{cm}^{-1}$ . Differences in the range 1250-1500 $\text{cm}^{-1}$ , caused by a signal originated from glass slide.	3
PU/Rayon PU/Polyester	ATR mode Ac: 64 Rs: 4 $\text{cm}^{-1}$ R: 650-4000 $\text{cm}^{-1}$	Component clarification by FTIR was useful for the identification of smooth artificial leather sheets. The extra-fine fibers from suede-like artificial leather sheets were classified by FTIR spectroscopy. Forensic study without spectral discussion.	18
Wool Polyester Non-specified acrylics	N.A.	Tapings from clothes no related with a crime show similar results to those from crime relates. Forensic study without spectral discussion.	24
Polyacrylonitrile	Transmission mode. R: 580-4000 $\text{cm}^{-1}$ Rs: 4 $\text{cm}^{-1}$ Ac: 50	IR showed more signals that Raman for dyed and non-lustered <i>Danufil</i> and Dolan fibers. Region 400-1700 $\text{cm}^{-1}$ : low intensity signals for acrylic and more intense for viscose. The strong matrix absorption in 1000-1800 $\text{cm}^{-1}$ hindered the dye signals.	27
Lyocell Silk Polyester Polyamida 66 Wool	ATR mode R: 400-4000 $\text{cm}^{-1}$ A: 32 Rs: 4 $\text{cm}^{-1}$	Band at 2363 $\text{cm}^{-1}$ , attributed to $\text{CO}_2$ . Band at 1595 $\text{cm}^{-1}$ , assigned to CO stretching vibrations and justified to a product of bleaching. Polyamide 66: NH stretching and bending vibrations, C = O stretching vibration, $\text{CH}_2$ asymmetric and symmetric stretching vibrations and aliphatic $\text{CH}_2$ bending. Polyester: stretching bends for C = O and C-O. Wool fiber: C = O stretching and N-H bending vibrations.	36
Polyacrylonitrile PAN/MA	Transmission mode. M: 15x Rs: 4 $\text{cm}^{-1}$	DMF: 1670 $\text{cm}^{-1}$ (Main band). DMF: 1400, 1380, 1090 and 660 $\text{cm}^{-1}$ (Secondary)	39

PAN/MMA PAN/VA PAN/MVP PAN/MA/MVP	Ac: 512 R: 4000-650 cm <sup>-1</sup>	bands). The region 1100-1300 cm <sup>-1</sup> allowed identifying the ester type. MA: 1170 cm <sup>-1</sup> (Main band). MA: 1204, 1229 and 1250 cm <sup>-1</sup> (Secondary bands). VA: 1240 cm <sup>-1</sup> (strong C-O stretching). MMA: 1220-1130 cm <sup>-1</sup> (C-O stretching). NaSO <sub>3</sub> : 1038-1042 cm <sup>-1</sup> . PAN/MA fibers of type Dolan U have an extra affinity for basic dyes increasing the band at 1045 cm <sup>-1</sup> .	
Cotton Wool Silk Acetate Polyester Nylon	Transmission mode.	Fibers recovered from cinema seats: N° fibers per textile seat: 53.000 N° fibers per vinyl seat: 750 Fiber type: 84% natural, 8% manmade (cotton, 70%, and rayon, 51%). Acrylic: 5%. Polyester: 3%. The most common dyeing: grey-black and blue. The season, the climate and the textile available sources condition the frequency of the materials. Forensic study without spectral discussion.	40
PAN/MA PAN/MMA PAN/VA PAN/SS PAN/PVP	Transmission mode. R: 4000-650 cm <sup>-1</sup> Rs: 4 cm <sup>-1</sup> Ac: 8	Band of nitrile group: 2240 cm <sup>-1</sup> . Band of carbonyl group: 1730 cm <sup>-1</sup> . Band of C-H group: 1370 cm <sup>-1</sup> Most reproducible data was obtained by rationing: A <sub>1730/2240</sub> ; A <sub>1730/1370</sub> . Ranges of integration: carbonyl band (1760-1700 cm <sup>-1</sup> ); nitrile signal (2264-2220 cm <sup>-1</sup> ); C-H band (1390-1340 cm <sup>-1</sup> ). Relative standard deviation (RSD): 1% (for repetitive analysis on the same location); 3% (along the length of the same single fiber).	41

SS: styrene sulphonate; PU: polyuretane. Other abbreviations as in the tables 1, 2 and 3.

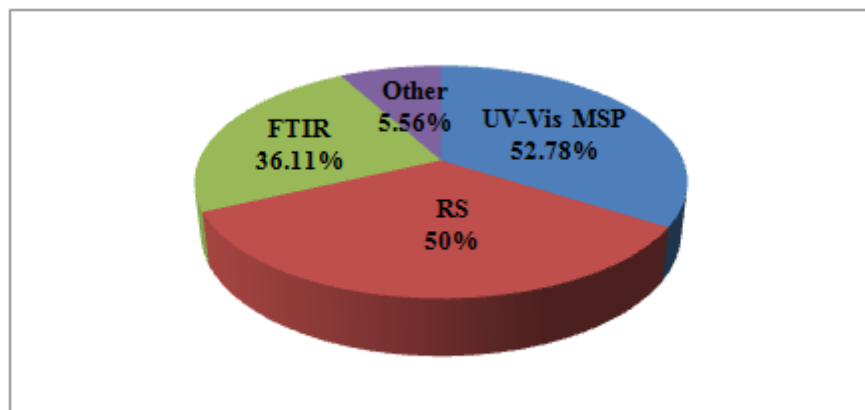


Figure 1. Graphic representation of the volume of publications classified according to the spectroscopic technique used. Other abbreviations as defined in table 1.

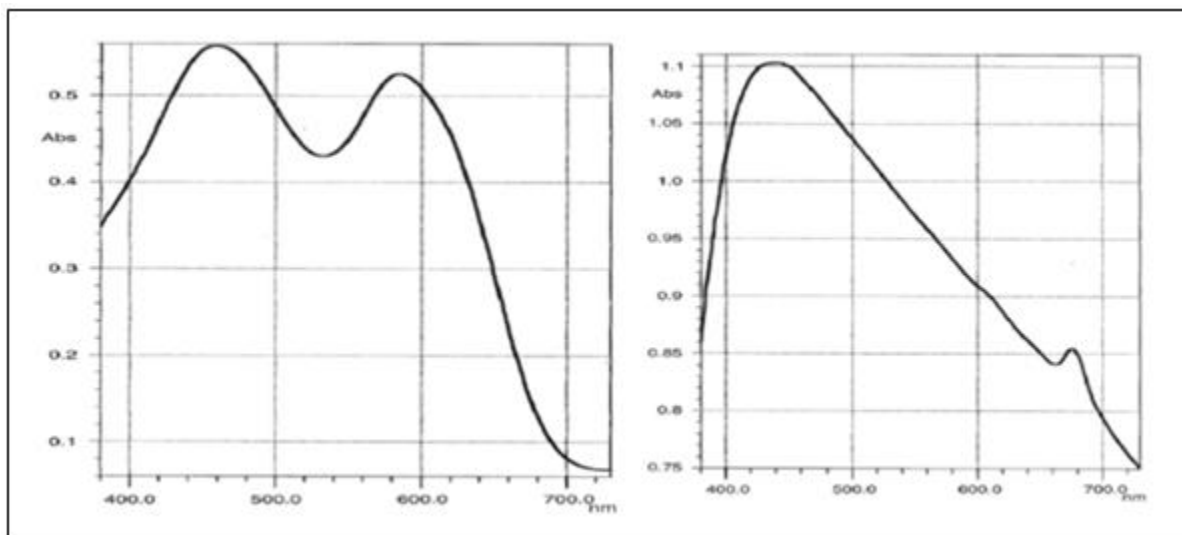


Figure 2. UV-Vis MSP spectra of a grey polyester clothing fiber (left) and polyester fiber dyed with carbon black and blue pigment. Taken from [11] with permission of Elsevier.



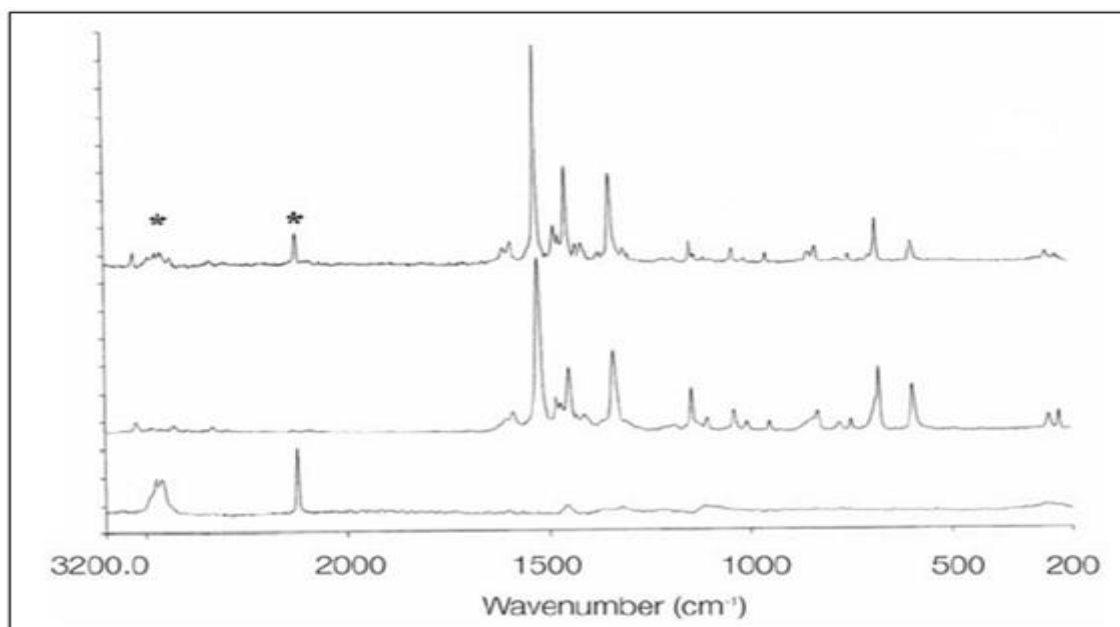


Figure 3. Raman spectra of a blue dyed PAN fiber, the used blue dye and the undyed fiber (from top to bottom) using an excitation wavelength at 514 nm. Taken from [27] with permission of Elsevier.

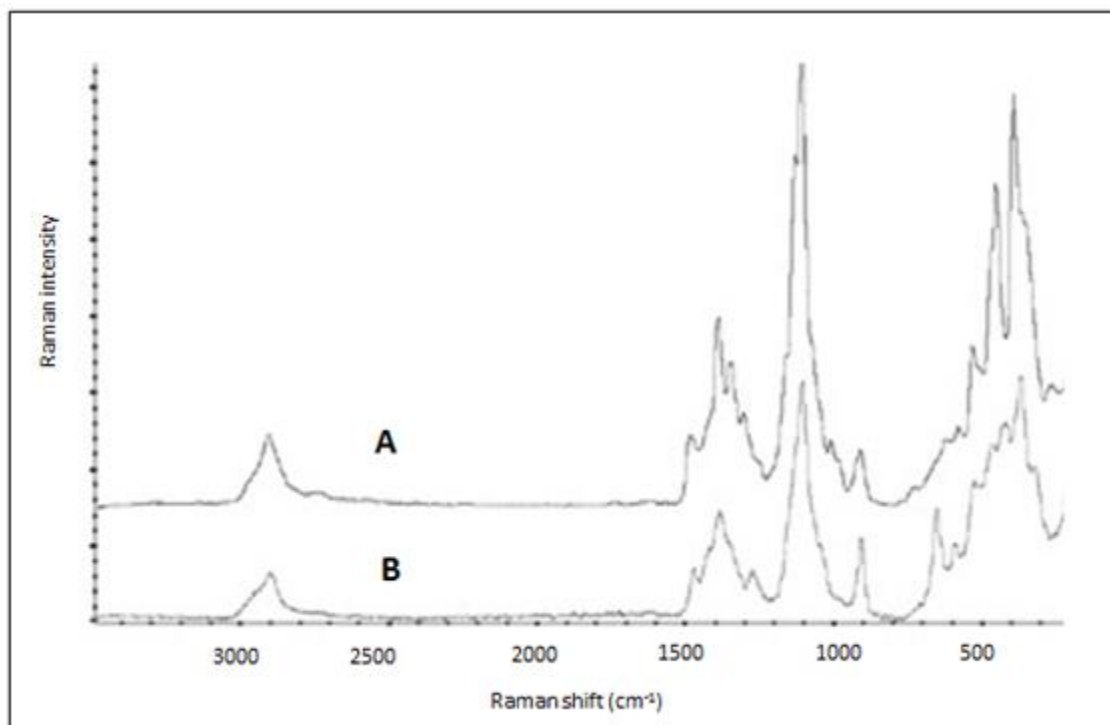


Figure 4. Comparison of Raman spectra of two animal fibers: wool (A) and silk (B). Taken from [4] with permission of Department of Forensic Science, Central Police University, Taiwan (Republic of China).

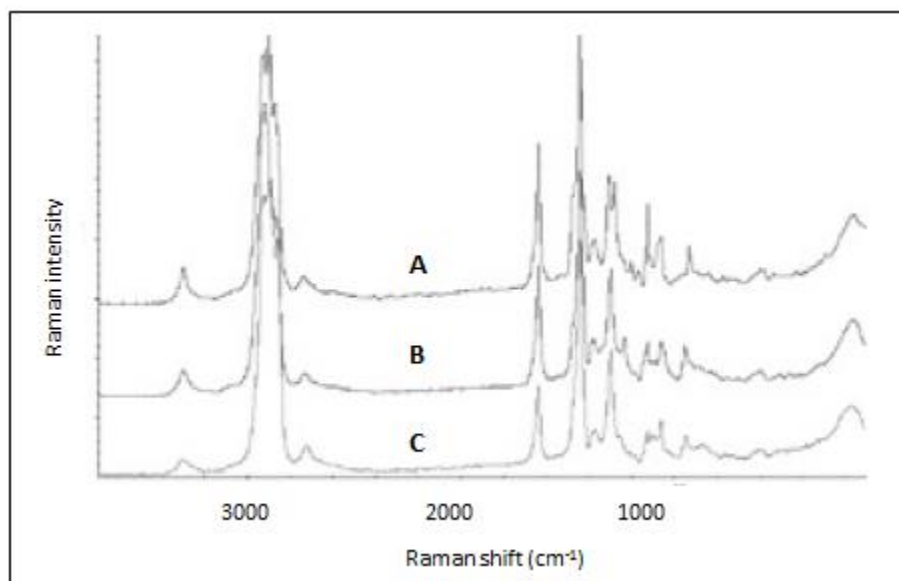


Figure 5. Raman spectra obtained from nylon 6 (A), nylon 6.6 (B) and nylon 6.12 (C). Taken from [4] with permission of Department of Forensic Science, Central Police University, Taiwan (Republic of China).

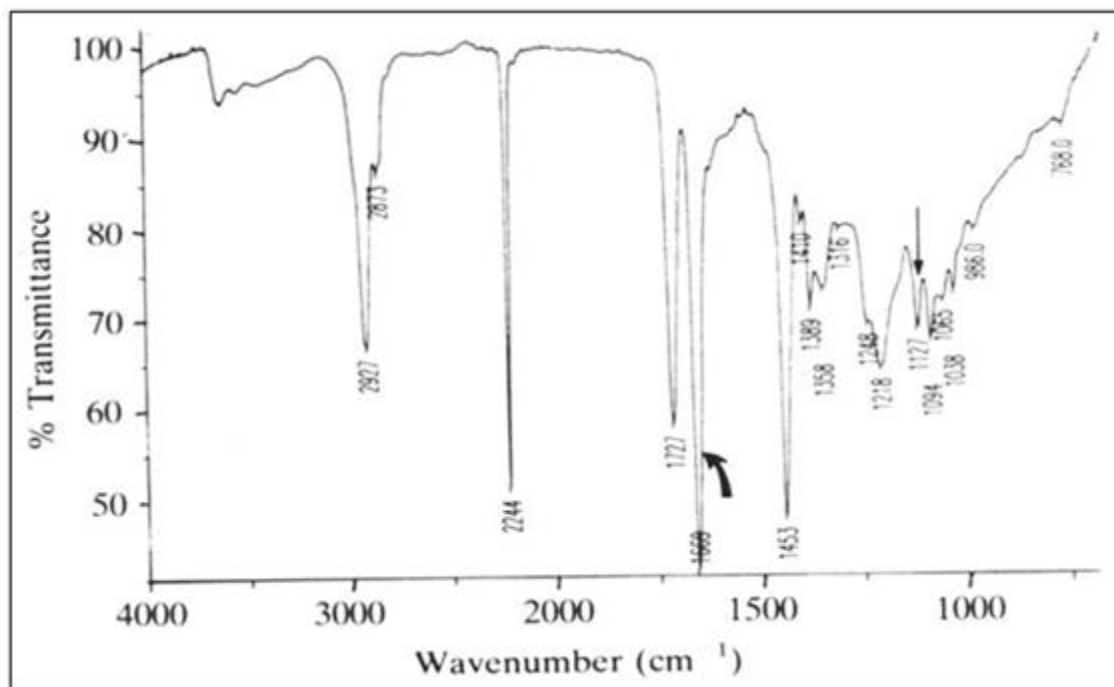


Figure 6. Observation of the DMF band at  $1669\text{ cm}^{-1}$  in the FTIR spectrum of a PAN/MMA fiber. Taken from [38] with permission of Elsevier.