

The analysis of colored acrylic, cotton, and wool fibers using Raman spectroscopy

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ABSTRACT

There has been a resurgence in Raman spectroscopy for its application in forensic science. This method allows for the measurement of the inelastic scattering of light due to the vibrational modes of a molecule when irradiated by an intense monochromatic source such as a laser. The Raman technique presents advantages such as its non-destructive nature, its fast analysis time, and the possibility of performing microscopic *in situ* analyses. In its forensic application, it is a versatile technique that covers a wide spectrum of samples such as drugs of abuse, trace evidence, and inks.

Its potential was also demonstrated for the analysis of textile fibers. Raman spectroscopy allows for the detection of dyes used in the coloration of such samples. In this study, 180 samples were randomly collected: 60 acrylics (20 blue, 20 red, and 20 black), 60 cotton (20 blue, 20 red, and 20 black), and 60 wool samples (20 blue, 20 red, and 20 black). The Raman instrument was equipped with four laser excitation sources: argon ion laser at 514 nm, helium-neon at 633 nm, and two near infrared (NIR) diode array lasers at 785 and 830 nm. The importance of using different laser wavelengths was also emphasized in the forensic Raman analysis of fibers. Several aspects were investigated according to the best analytical conditions for every type/color fiber combination; particular attention was placed on the discriminating power of the technique. Based on the results from the Raman analysis, it was possible to obtain different classes of fibers according to the general shape of spectra, more particularly on the basis of additional bands. Raman spectroscopy was not considered as an isolated technique but rather as a step in the conventional analytical scheme for textile fibers. Thus, in order to optimize the analytical sequence, it was determined at which stage Raman spectroscopy should be integrated and under which conditions. For this purpose, the collected samples were also analyzed by light microscopy (bright field, double polarization, and fluorescence), UV-Vis microspectrophotometry (MSP), and thin layer chromatography (TLC).

This approach allowed for the determination of which situation requires Raman spectroscopy to be used in conjunction with the conventional methods for fiber dye analysis.

INTRODUCTION

Raman spectroscopy is becoming a method of increasing interest in forensic science. It involves the detection of the inelastic scattering of light depending on the vibrational modes of molecular non-polar bonds. Instruments characterized by a high sensitivity and coupled to light microscopes supply a high potential for the micrometric and *in situ* analysis of many types of materials of forensic interest. The analysis of textile fibers constitutes a clear example. In this field several studies have been carried out (e.g. Bourgeois and Church, 1990; Bouffard *et al.*, 1994; Keen *et al.*, 1998; Miller and Bartick, 2001; Jochem and Lehnert, 2002; Massonnet *et al.*, 2004, Thomas *et al.*, 2005, Massonnet *et al.*, 2005a and b; Massonnet *et al.*, 2007). The usefulness of this technique for the forensic analysis of fibers mainly focuses on the detection of dyes.

In this study the most common fiber types and colors were considered, meaning blue, red and black wool, cotton and acrylics. The purpose of this project was the following:

1. The detection of dyes. This stage was undertaken to confirm the ability of the technique of detecting fiber dyes, but above all to determine the influence of the different available parameters (i.e. the choice of the laser source) and the occurrence of the fluorescence.
2. The discriminating power. The selectivity of the Raman technique was tested on fiber samples of the same color and type and then compared to the results obtained with the conventional techniques (light microscopy, UV-Vis microspectrophotometry and thin layer chromatography).
3. Integration in the analytical sequence. The useful location of the Raman technique is evaluated for the considered classes, mainly based on discrimination properties.

MATERIALS AND METHODS

Samples

In this study, 180 samples were randomly collected: 60 acrylics (20 blue, 20 red, and 20 black), 60 cotton (20 blue, 20 red, and 20 black), and 60 wool samples (20 blue, 20 red, and 20 black).

Raman spectroscopy

A Renishaw System RM 1000 spectrometer fitted with a Leica DM L research microscope was used. Four excitation sources were available: argon ion laser at 514.5 nm, helium-neon laser at 632.8 nm and two near infrared (NIR) semiconductor lasers at 785 nm and 830 nm. For the focalization on the samples, the 50x and 100x objectives were used allowing a 1-3 microns laser spot size. A Peltier-cooled charge coupled device (CCD) camera was used as the detector. The spectrometer worked with a 1200 line/mm grating as the dispersive element. Measurement times were generally 10 seconds and the spectra were collected in the spectral region of 2000-200 cm^{-1} . GRAMS/32 (Galactic Industries Corporation) software was used for the display and management of data.

Single fibers were directly exposed to the laser and were fixed on an aluminum foil deposited on a glass slide. At least three fibers (two spectra per fiber) per sample were analyzed in order to check the reproducibility of the results.

RESULTS

1. The detection and identification of dyes

It was observed that no particular laser has an advantage or a better affinity with a given combination of fiber type and color. Some lasers resulted actually proved inefficient for some classes as shown in Table 1. For example, the red Helium-Neon laser (633 nm) did not obtain any informative spectra for acrylic fibers and the Argon ion laser (514 nm) was inefficient for red fibers of the three considered types.

	<i>Blue Acrylic</i>			<i>Black Acrylic</i>			<i>Red Acrylic</i>		
	<i>v</i>	<i>f</i>	<i>x</i>	<i>v</i>	<i>f</i>	<i>x</i>	<i>v</i>	<i>f</i>	<i>x</i>
514	13	4	3	6	0	14	9	1	10
633	0	0	20	0	0	20	0	0	20
785	0	17	3	1	12	7	6	7	7
830	10	9	1	4	14	2	13	6	1

	<i>Blue Cotton</i>			<i>Black Cotton</i>			<i>Red Cotton</i>		
	<i>v</i>	<i>f</i>	<i>x</i>	<i>v</i>	<i>f</i>	<i>x</i>	<i>v</i>	<i>f</i>	<i>x</i>
514	2	8	10	4	13	3	0	0	20
633	2	11	7	2	15	3	0	1	19
785	9	4	7	10	7	3	8	8	4
830	10	3	7	10	2	8	14	4	2

	<i>Blue Wool</i>			<i>Black Wool</i>			<i>Red Wool</i>		
	<i>v</i>	<i>f</i>	<i>x</i>	<i>v</i>	<i>f</i>	<i>x</i>	<i>v</i>	<i>f</i>	<i>x</i>
514	8	4	8	14	4	2	2	1	17
633	10	2	8	12	3	5	0	2	18
785	5	0	15	15	3	2	16	0	4
830	5	2	13	9	6	5	15	0	5

Table 1-Samples repartition (20 for each class) according to the quality of the spectra obtained for each class and according to the four available laser sources. *v*: informative spectra; *f*: informative spectra influenced by fluorescence; *x*: non informative spectra.

Concerning the detection of dyes, for acrylics, the spectral information obtained was not attributed to the polymeric fiber type. The substrate did not influence on the spectra of colored fibers. The detected information provides data on the dyes impregnated in the fibers, and not related to the polymer.

For cotton and wool, the influence of the substrate was only observed for red cotton and wool fibers and using near infrared laser sources at 785 nm and 830 nm. Some Raman bands attributed to cellulose for cotton, and keratin for wool were detected. Examples are

shown in Figure 1. It was regularly observed that Raman spectra supplies information on the fiber dye content. Some examples are shown in Figure 2.

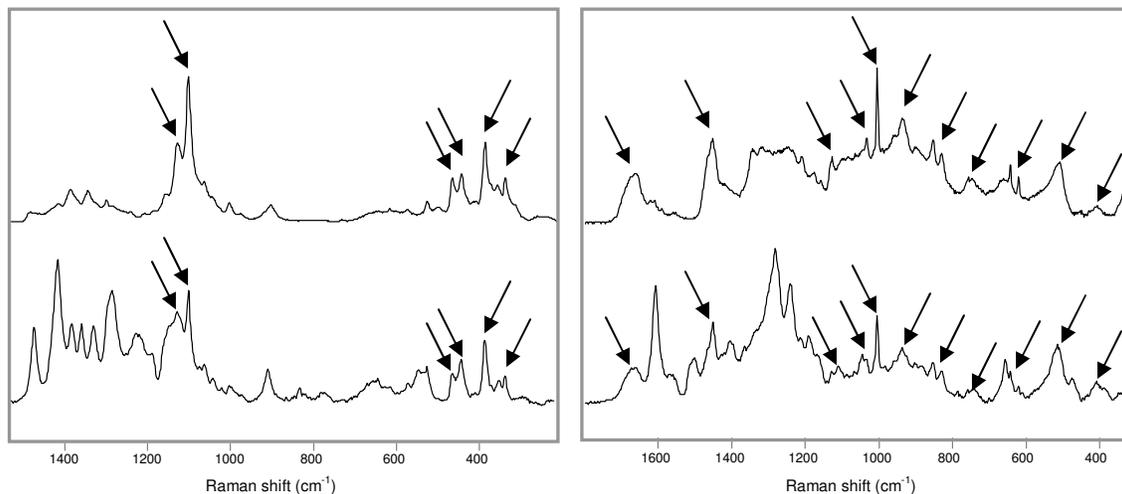


Figure 1 –Example of influence of the substrate. Left: comparison of Raman spectra of an undyed (top) and a red colored cotton fiber (bottom). Right: comparison of Raman spectra of an undyed (top) and a red colored wool fiber (bottom). Arrows indicate the bands attributed to the substrate. Laser source: 830 nm.

2. Selectivity of the method – discriminating power

In order to evaluate the selectivity of the Raman technique, the discriminating power (DP) was used as an indicator for the comparison of the obtained results as well as for the comparison with the other classical technique for fiber examination (light microscopy, UV-Vis MSP and TLC). The formula for non correlated attributes of Smalldon and Moffat (1973) was used:

$$PD = 1 - \frac{2M}{[N(N-1)]}$$

where M is the number of undifferentiated pairs

and N is the total number of samples.

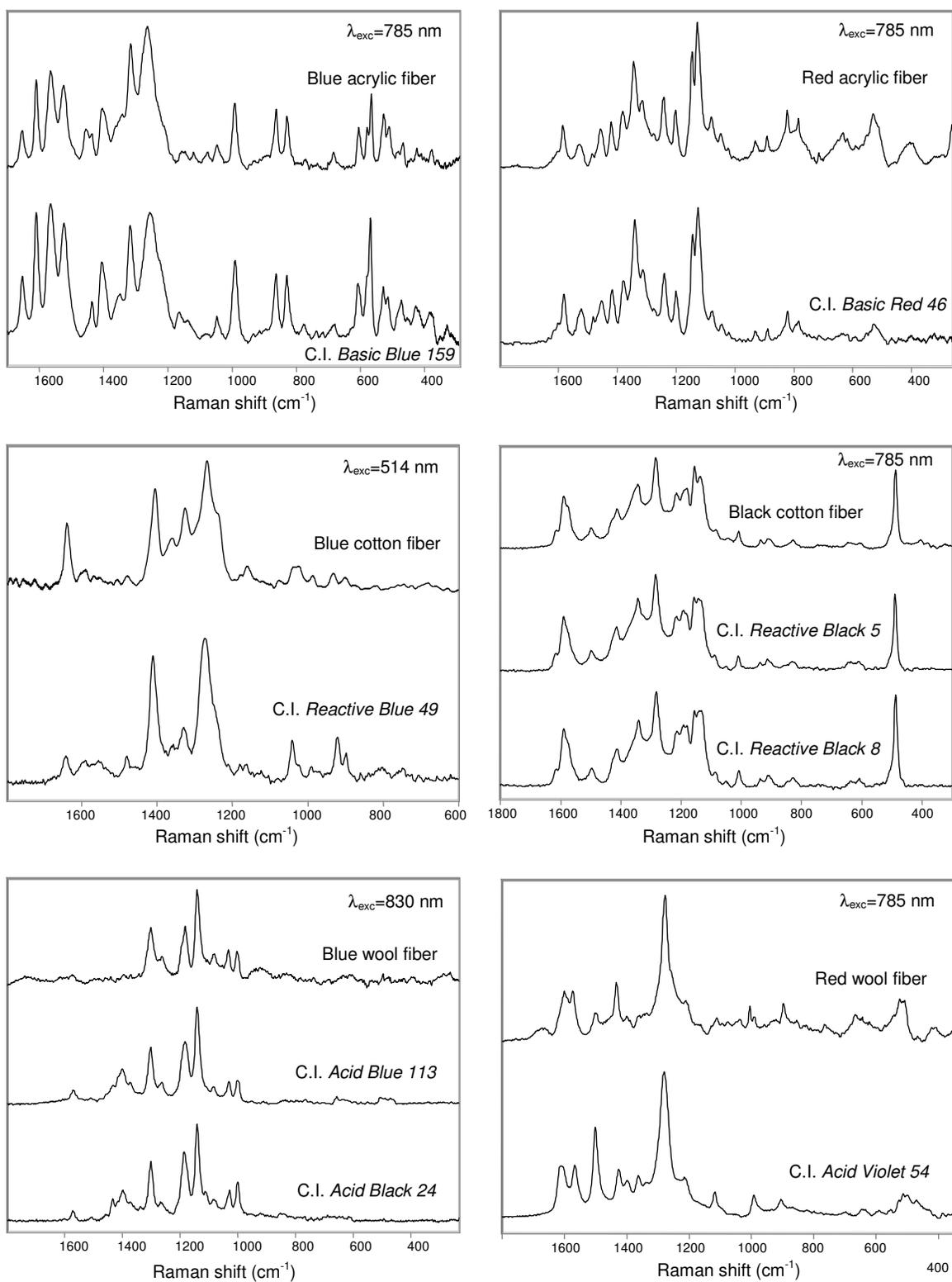


Figure 2 – Examples of comparisons of Raman spectra of colored fibers and reference dyes.

For every class, groups were subdivided according to the configuration of bands characterizing the Raman spectra. The number of undifferentiated pairs was observed.

The results are reported in Table 2.

N=20	Raman				Microscopy	MSP	TLC
	514 nm	633 nm	785 nm	830 nm			
Blue A.	0.69 (59)	-	0.78 (42)	0.84 (31)	0.98 (4)	0.98 (4)	0.91 (17)
Black A.	0.52 (91)	-	0.69 (59)	0.73 (52)	0.87 (25)	0.80 (38)	0.84 (31)
Red A.	0.53 (90)	-	0.69 (58)	0.73 (52)	0.96 (7)	0.92 (15)	0.75 (47)
Blue C.	0.70 (57)	0.60 (76)	0.65 (67)	0.65 (67)	0.94 (12)	0.93 (13)	0.56 (107)
Black C.	0.69 (59)	0.58 (79)	0.58 (79)	0.50 (94)	0.82 (34)	0.86 (26)	0.66 (65)
Red C.	-	-	0.49 (97)	0.52 (92)	0.38 (118)	0.58 (79)	0.10 (171)
Blue W.	0.72 (53)	0.71 (55)	0.44 (107)	0.58 (80)	0.94 (12)	0.98 (3)	0.89 (20)
Black W.	0.82 (35)	0.82 (35)	0.80 (37)	0.80 (38)	0.62 (72)	0.91 (17)	0.94 (21)
Red W.	0.27 (139)	0.20 (153)	0.94 (12)	0.93 (13)	0.88 (23)	0.98 (3)	0.83 (32)

Table 2 – Discriminating power calculated values for the analytical techniques of Raman (4 lasers), light microscopy examination, UV-Vis microspectrophotometry and thin-layer chromatography for the nine selected fiber classes (20 samples per class). In bracket: the number of undifferentiated pairs (N).

Light microscopy and MSP resulted to be the most discriminative methods. Raman spectroscopy allowed for the observation of less discrimination than the other techniques. However, further discriminations were observed by the combination of several laser wavelengths.

3. Integration in the analytical sequence

It was found that the location of Raman spectroscopy in the analytical sequence is highly recommended after UV-Vis microspectrophotometry. A small number of further discriminations were obtained with the Raman technique, but above all the additional contribution of Raman spectroscopy is the possibility of identifying the main dyes.

Even if TLC resulted in more discriminations than the Raman technique, this latter could also be applied for two main reasons. The first is that the Raman method, being non

destructive, must be applied before the TLC dye extraction. Secondly, it was observed that despite high DP values, the chromatographic technique did not allow a large number of additional differentiations than those already observed using MSP.

DISCUSSION

For the fiber dye analysis Raman spectroscopy plays a complementary role that allows for identifying the main dye used for the impregnation of the fiber. In some cases it allowed for further discriminations after MSP. In fact, the choice between TLC and Raman after MSP could depend on different factors like destructivity, successful dye extraction from the fiber, or speed of analysis.

In terms of discrimination, Raman spectroscopy was affected by two main factors: the first was fluorescence and the second the fact that some spectra configurations occur frequently and thus the variation in a given set of 20 samples was low.

UV-Vis microspectrophotometry confirmed once again to be the most efficient method for fiber analysis. Light microscopy is efficient too; even if different colors were easily differentiated, in several doubtful situations it was difficult to discriminate between pairs. Such comparisons sometimes carry the risk of being affected by subjective perception. MSP played an important role to alleviate this problem. Concerning the analytical sequence it can be noted that MSP was also more discriminating than light microscopy, suggesting the potential to use it first.

Thin-layer chromatography allowed good discriminations. Examinations were undertaken on abundant amounts of fibers and thus the problem of sensitivity was not addressed. In real cases, however, this problem is real for the analysis of individual fibers. In this study

TLC was applied only for non reactive dye types and this explains the lower discriminating power values particularly for cotton and some wool samples.

CONCLUSION

For a successful fiber dye Raman analysis, the possibility of combining several laser wavelengths is a fundamental option. This technique allows for identifying the main dyes used for the impregnation of the fiber. In term of discriminations, it only plays a complementary role compared to UV-Vis microspectrophotometry.

Given the potential of Raman spectroscopy for identification purposes, the realization of an extended spectral library of reference dyes is an ambitious but useful aim for an operational perspective.

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