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Differentiation of aged fibers by Raman spectroscopy and multivariate data analysis

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ABSTRACT

Raman spectroscopy followed by multivariate data analysis was used to analyze cotton fibers dyed using similar formulations and submitted to different aging conditions. Spectra were collected on a commercial instrument using a near-infrared laser with a 780 nm light source. Discriminant analysis allowed to correctly classify the aged fibers 100% of the time. The prediction ability of the calculated model was estimated to be 100% by the “leave-one-out” cross-validation for 3 out of the 4 series under investigation. Finally, reliability of the developed approach for the discrimination of aged vs new fibers was confirmed by the analysis of commercial polyamide and polyester textiles submitted to the same aging process.

1. Introduction

Fibers characterization is of paramount importance in forensic science and can be regarded as a preliminary step for the screening and identification of suspect materials which then might require further in-depth analyses [1]. Textile fibers can be exchanged between individuals, objects and between objects and individuals. When fragments of fibers are compared with those deriving from a specific source, information including similarity in the type of fiber found, in the color or color variation can be achieved.

Optical microscopy is a widely used method for fiber analysis: in this field, polarized light microscopy has been used to determine the generic classification of the polymer type [2], whereas IR spectroscopy proved to be very useful to further specify fiber type [3–5]. Raman spectroscopy, due to the ease of sampling can be regarded as complementary technique able to provide useful information about fiber characterization. An important advantage of this technique relies on the possibility of analyzing fibers mounted on glass slides as in the case of optical microscopy [6,7]. By contrast, there is not a full sampling compatibility between optical microscopy and IR spectroscopy due to the absorption of the support in the IR region. In this case, the need of fiber removal and cleaning prior to analysis leads to longer preparation times with a higher risk of fiber loss.

As in the case of some FTIR spectrophotometers, additional advantages rely on the miniaturization of the devices to achieve portability, thus allowing for real time analyses. This technique has been widely used in the field of cultural heritage for dating and assessing authenticity of artifacts like paintings, frescoes, manuscripts and scrolls [8–10]. More recently, attention has been paid to the use of Raman spectroscopy both for clinical applications [11,12] and to detect contaminants in drugs and food [13,14]. Being a rapid and non-destructive technique that does not require sample preparation, interesting results have been achieved in the field of forensic sciences for the analysis of varnishes, paints, narcotics, explosives [15–21] and textiles. In the latter case, the capabilities of Raman spectroscopy, sometimes coupled to multivariate data analysis have been exploited for both the discrimination of different types of fibers [6,22,23] and to characterize pigments and dyes [24–29]. As for color analysis, it has to be taken into account that usually fibers are very often dyed by using a mixture of similar reactive dyes, so identification is a challenging task. Aging is another important factor to be considered when forensic comparison among fibers is carried out. Fibers can undergo physical, photochemical, thermal, chemical and mechanical changes. Color-fading and discoloration can be of

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pivotal importance for fiber association, thus making their comparison more difficult [30–32]. To our knowledge, up till now, no studies regarding the discrimination of aged fibers have been published. In addition, taking into account that applications of chemometrics to spectra of fiber dyes has been rather limited [33–35], in this study, a chemometric approach based on multivariate data analysis was applied to Raman data in order to evaluate the possible differentiation of spectra obtained from new and aged fibers belonging to different dyed polymers.

2. Materials and methods

2.1. Samples

Red cotton textiles were stained with binary/ternary mixtures of reactive dyes, commonly used in the clothing industry by C. Sandroni & C. (Busto Arsizio, VA, Italy) dyeing plant. Three different formulations containing both fluoropyrimidine and monochlorotriazine reactive dyes were used (Table 1). Additional samples of cotton, polyester and polyamide textiles were purchased from local market (Table 2).

2.2. Aging

New dyed textiles (series A0, B0 and C0) were machine washed (20 L of water *per* kg of textile) at 90 °C for 1 h using water containing ionic (1 g/L) and non-ionic (0.5 g/L) detergents, sodium carbonate (2 g/L) and hydrogen peroxide 120 vol (1 g/L). After 4 rinsing cycles with cold water, neutralization (pH=7) was carried out by using acetic acid and a commercial cationic fabric softener.

Sunlight exposure was simulated by exposing the textiles to a sun simulator (Sun 2000 Class A, Abet Technologies, Inc., Connecticut, USA) for 12 h and 120 h, respectively. An intensity of 1 Sun was applied. Textiles aged for 12 h were then submitted to additional 5 machine home-washing cycles at 40 °C for 1 h (series A1, B1 and C1). More precisely, textiles were sun dried (real sun exposure) after each washing cycle. This procedure was applied to simulate "used" samples [31].

Textiles aged for 120 h were submitted to additional 59 machine home-washing cycles at 40 °C for 1 h (series A2, B2 and C2) in order to simulate "old" samples [31]. Again, textiles were sun dried (real sun exposure) after each washing cycle. In both cases the used washing temperature was recommended by the textile manufacturers. A schematic explanation of the aging process is depicted in Fig. 1. The photo related to the obtained series is shown in Fig. S1.

The same aging protocol was applied for the commercial textiles described in Table 2.

2.3. Raman spectroscopy

Raman spectra were collected on a DXR Raman Microscope (Thermo Scientific, Waltham, MA, USA) equipped with two excitation sources: a Nd:YVO_4 laser at 532 nm and a near-infrared (NIR) laser diode at 780 nm. A Leica DM L light microscope (Leica Microsystems, Milano, Italy) was coupled with the instrument. The Omnic 8.3 software (Thermo Scientific) was used.

Table 1
Dye formulations used to produce red cotton.

	Formulation A		Formulation B		Formulation C
Dyes	C.I. Reactive Red 243	1.5%	C.I. Reactive Red 243	1.6%	C.I. Reactive Red 158
	C.I. Reactive Orange 70	0.5%	C.I. Reactive Yellow 165	1.4%	C.I Reactive Red 123
					C.I Reactive Blue 114
Type	Fluoropyrimidine reactive dyes		Fluoropyrimidine reactive dyes		Monochlorotriazine reactive dyes

Table 2
Textile samples used in the study.

Garment	Fiber class	Color	Brand	Made in
T-shirt	Cotton	Blue	Sky	PRC
T-shirt	Cotton	Red	Navigare	Italy
Polar fleece	Polyester	Red	Decathlon	Morocco
Polar fleece	Polyester	Black	Decathlon	Morocco
Panty hose	Polyamide	Red	Oviesse	Bangladesh
Panty hose	Polyamide	Black	Oviesse	Bangladesh

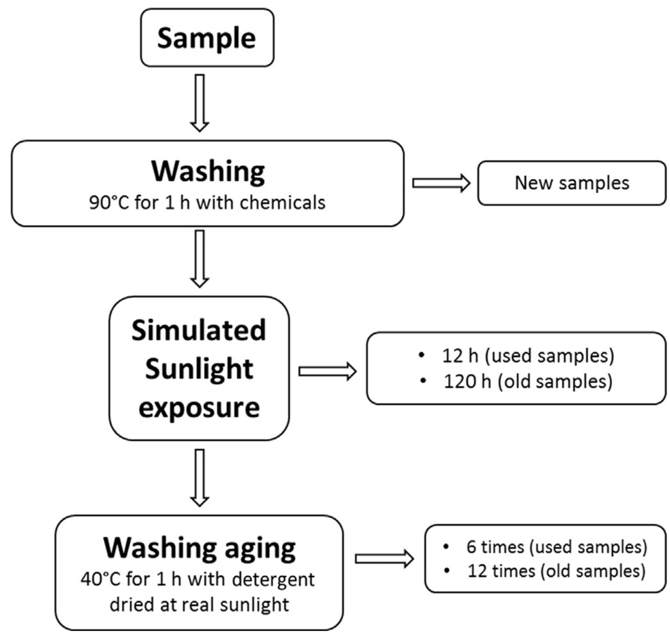

Fig. 1. Schematic representation of the aging process.

Each fiber was mounted on a microscope glass slide and fixed at the extremities using a double-sided tape.

Due to the sample size, the laser beam was focused on the single fiber by a 50x objective. Autotiming was used for data acquisition and the average spectrum was acquired for 120 s. The operating NIR laser power at the source was 6 and 15 mW for cotton and polyamide/polyester, respectively. All the spectra were acquired within a range of 300–1700 cm^{-1} in order to focus on the fiber fingerprint region.

Four fibers for any kind of dyed polymer tested, 2 replicated measurements per fiber were performed.

2.4. Data analysis

Once collected, raw Raman data were preprocessed prior to multivariate data analysis. Data preprocessing was based on the use of the Savitzky-Golay filter using a five-point smoothing window and a second order polynomial deconvolution followed by standard normal variate algorithm [36]. Finally, data were mean centered and submitted to multivariate data analysis i.e. principal component analysis (PCA) and linear discriminant analysis (LDA) [37,38].

PCA, one of the most common unsupervised patter recognition method used for data reduction, was carried out to visualize data