

Color study of historic silks

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Abstract: The chemical characterization of silk textiles of historic value may be necessary to achieve a better understanding of the production processes applied, to evaluate their preservation, to detect manipulations or forgeries, and to value the combination of tradition and innovation in contemporary manufacturing techniques. The main objective of this work was to study four historical silks from the Garín collection, all of them from the 20th century, although with 19th century designs. To this end, non-invasive spectroscopic and microscopy techniques were applied in order to obtain information on the dyes used during their production and their link with those used in the silk industry in previous centuries, and to ascertain their state of conservation. Moreover, the images in LM, SEM and CM are contributing to the development of a 3D virtual loom that will favor more accessible and inclusive museography in museums specialized in the silk sector. Both the study of dyes and silk fibers and their virtual reproduction through artificial intelligence programs applied to the study of cultural heritage, by specialists from the Robotics Institute of the Universitat de València, has been developed in the framework of the SILKNOW project (https://silknow.eu/).

Keywords: silks, colour, diffuse reflectance spectroscopy, natural dyes, Fourier transformed infrared - attenuated total reflectance (FTIR-ATR), microscopic image by LM, LMi and SEM image, SILKNOW

Estudio del color de sedas históricas

Resumen: La caraterización química de sedas de valor histórico puede resultar necesaria para alcanzar un conocimiento más preciso del proceso de producción aplicado, para evaluar su estado de conservación, para detectar posibles manipulaciones o falsificaciones, y para valorar la combinación de tradición e innovación en técnicas de manufactura contemporánea. El principal objetivo de este trabajo fue estudiar cuatro sedas históricas procedentes de la colección Garín, todas ellas de cronología del siglo XX, aunque con diseños del siglo XIX. Para ello se aplicaron técnicas no invasivas espectroscópicas y de microscopía, a fin de obtener información relativa a los tintes utilizados durante su producción y su vinculación con los empleados en la industria sedera en siglos precedentes, y conocer su estado de conservación. Las imágenes microscópicas, además, están contribuyendo al desarrollo de un telar virtual en 3D que favorecerá museografías más accesibles e inclusivas en museos especializados en el sector sedero. Tanto el estudio de las tintas, como el de las fibras sederas y su reproducción virtual a través de programas de inteligencia artifical aplicadas al estudio del patrimonio cultural, a cargo de los especialistas del Instituto de Robótica de la Universitat de València, se ha desarrollado en el marco del proyecto SILKNOW (https://silknow.eu/).

Palabras clave: seda, color, espectroscopía de reflectancia difusa, colorantes naturales, espectroscopía infrarroja con transformada de Fourier - reflectancia total atenuada (FTIR-ATR), imagen microscópica por LM, LMi y SEM, SILKNOW

Introduction

Chemical analysis of silk textiles of historic and artistic value is needed in a variety of contexts, mainly to get an insight into the materials and techniques used for their production (Han *et al.* 2017; Tamburini 2019), to assess the preservation state of ancient pieces (Ahmed & Darwish 2012), and to detect manipulations or forgeries (Moini & Rollman 2017). In this respect, UV-Vis reflectance diffuse

spectroscopy is increasingly used for the characterization of the components responsible for the colour of the samples in replacement of liquid chromatography (HPLC) with diode array (DAD) and/or with mass spectrometry (MS), which are considered the reference techniques (Gulmini *et al.* 2013; Kramell *et al.* 2019; Shaid *et al.* 2019; Tamburini 2019). Likewise, the microscopic study of silk tissues also provides relevant information in historical studies (Hacke 2008; Gaitan et al. 2019), analyzes focused on conservation and restoration processes (Kaplan et al. 1994; Miller & Reagan 1989), and 3D research oriented to new paradigms in inclusive, accessible and multisensory museography and dissemination (Kim et al. 2019). Focusing on diffuse reflectance spectroscopy, the popularity of this technique can be explained by the facts that the instrumens are easy to useand the samples can be processed without a previous tretament. As a result, to use and the technique is suitable for on-site tests. In the analysis of valuable samples, reflectance diffuse spectroscopy is very atractive due to its non-invasive character. Even though the amount of sample required to obtain solutions amenable for modern HPLC instruments is very low, reflectance spectroscopy is a better option for the analysis of irreplaceable textile samples. The spectral information provided by diffuse reflectance spectroscopy is related to the electronic transitions of the dyeing molecules and, thus, to the dyestuff and materials used in the dyeing processes, as well as to the fibre substrates (Gulmini et al. 2013). Several works have been carried out during the past few years that report the application of reflectance spectroscopy to the characterization of the coloured species of textiles of different eras and cultures (Verhecken et al. 2014; Barbache et al. 2018; de Ferri et al. 2018; Tamburini et al. 2019a and 2019b; Tamburini & Dyer 2019; Ding et al. 2021) and, indeed, to the study of other valuable objects such as paints and manuscripts (Fonseca et al. 2019; Pottier et al. 2019).

Despite the progresses made during the past decade, the combination of diffuse reflectance spectroscopy with other non-invasive techniques that provide complementary information is still necessary to obtain complementary information that can be used for a better characterization of the colorants of textiles. Examples of such techniques are FTIR-ATR, scanning electron microscopy with energy-dispersive X-ray detection (SEM-EDX) or fluorescence spectroscopy (Barbache *et al.* 2018; Shahid *et al.* 2019; Petroviciu *et al.* 2019; al-Sharairi *et al.* 2020).

The main goal of this work was to study four historical silk samples from 19th century collections by different noninvasive spectroscopic techniques and by microscopy, in order to get a better characterization of the samples regarding to their production and preservation, without altering the sample. Non-invasive spectroscopy techniques, namely reflectance diffuse spectroscopy and FTIR-ATR, have been used to establish the chemical composistion of the compounds responsible for the colors observed, and therefore, potential sources of dystuffs used in the elaboration processes. Likewise, the microscopy studies developed in this research fulfilled two purposes (a) to verify the state of conservation of century-old silk fabrics, whose manufacture has been based on the combination of traditional and innovative techniques implemented in La Fábrica Garín, a national and international reference in the contemporary silk sector; and to obtain high-resolution images that will

provide information to experts in artificial intelligence (Institute of Robotics of the Universitat de València) who are currently working on the recreation of a virtual loom for museographic purposes.

Instruments and procedures

Spectrophotometric measurements on different points of the silk samples were carried out using a Cary 60 Fiber Optic UV-Vis spectrophotometer (Agilent Technologies, Waldbronn, Germany), fitted with a remote fiber optic diffuse reflectance accessory from Harrick Scientific Products (Mulgrave, Victoria, Australia). Data were recorded and processed using a Cary WinUV software (Agilent Technologies). The spectra were measured in the 250-750 nm range in diffuse reflectance mode.

Infrared characterization of the samples was carried out with a Cary 630 FTIR-ATR spectrophotometer from Agilent Technologies (Böblingen, Germany). Spectra were recorded in the frequency range of 4000-600 cm-1 at a resolution of 4 cm-1. For data collection and processing, MicroLab FTIR and ResolutionPro softwares (Agilent Technologies) were used, respectively.

Optical microscopy of the silks was carried out using a Microscope LEICA EZ4 ocul 10x. For image processing, the LAS EZ (Leica Aplication Suite) program has been used. For its part, Leica DMI 3000 research inverted microscope (LMi), with long-lasting phase fluorescence and contrast with 2000-hour halide illuminator and fiber optic transmission. Filters for Dapi, Fluorescein and Rodamina has been used to complete the information obtained by optical microscopy. The objectives used have been 10x, 20x, 40x and 63x. Image acquisition system with high resolution and high sensitivity digital camera has been employed.

Scanning Electron Microscope-X-Ray Microanalysis of the silks was carried out using a Hitachi S4800 Field Emission Cannon Sweep electron microscope (FEG) with a resolution of 1.4nm to 1kV. This unit has a backscattered detector, RX Bruker detector, transmitted detector. In addition, it has the QUANTAX 400 program to do microanalysis and has five motorized axles

Four silk samples were tested. Sample S1 was a red silk fabric with different reddish and yellow embroidered ornaments. Samples S2 and S3 were dark and pale pink fabrics, respectively, with different reddish ornaments, while sample S4 was a brownish textile with ornaments of different hues, mainly dark red and yellow. Images of some of the areas tested throughout the study are shown below [figure 1A]. For sample S1, images of the fabric (area S1a; see figure 1c) and a yellow embroidered (area S1b) are shown, whereas for samples S2-S4 the images correspond to the grounds. The FTIR-ATR spectra of the tested areas were also recorded [Figure 1B].





Figure 1.- a-b (left image).). Images taken from: (A) the grounds of samples S1(S1a)-S4 and a yellow embroidery on sample S1 (S1b); (B) registration of the FTIR-ATR spectrum of area S1b. Figure 1c (right image). Figures 4 and 5. Optical microscope (LM) images of the red zone of the analyzed silk textile. The LM does not show the signs of deterioration that will be visible with the study of these silk fibers by Inverted Optical Microscope (LMi) and Scanning Electron Microscopy (SEM)

Results

The microscopic images obtained by LM, LMi and SEM show (a) the continuity and smooth surface that are characteristic of silk fibers [Figure 2] and (b) the irregularities that are due to the original manufacturing process and different causes of deterioration [Figures 3, 4, 5]. In this last sense, Mikolaychuk and Pinyagina (1997) point out that in silk fiber there are irregularities since it is constituted the cocoon, which grow during embroidery (as a result of the handling and abrasion of the threads as they pass through the fabric), and mainly with aging, due to abrasion and the action of agents of chemical and photochemical deterioration. The deterioration of the silk fabrics studied is even patented in those areas in which the fibers are contained by the metallic wraps. Also, here it is possible to identify surface discontinuities and gaps between fibrils. In areas without metallic wrapping, these fibers have also experienced notable breakage and detachment. In the development of the virtual 3D loom in which the specialists of the Robotics Institute of the Universitat de València are working through artificial intelligence programs, the information provided by these images will be considered not only at the level of fiber structure silk, but also its deterioration over time. In this way, this virtual 3D loom (currently in progress) will transfer tactile information that allows learning in line with the materiality of the silk, but also with regard to their degradation processes over time and other factors.

Moreover, this groundbreaking Loom acts as a digital memory of silk heritage as it preserves historical weaving techniques which most of them are only known by artisans who have kept alive this ancestral know-how. It conserves and documents several weaving techniques thanks to



Figures 2 & 3.- Figure 2 (left image). SEM image of the silk tissue studied. Note the continuity and smooth surface characteristic of the sea fibers. The image shows signs of deterioration, more visible in figures 3, 4 and 5. Figure 3 (right image). Figure 3 (left image). SEM image of the metallic wraps that surround the silk fibers in these historical fabrics, which show signs of deterioration (fraying and tears) despite the metallic covering.



Figures 4 & 5.- Inverted optical microscope (LMI) images of the analyzed tissue in its red (left image) and yellow areas (right image). The signs of fraying and breaks in the silk fibers are visible, as a consequence of the natural aging of these silk textiles

its 3D visualization, which allows understanding the interlacement between wefts and warps by applying the necessary restrictions for each technique. Therefore, the Virtual Loom shows those techniques as they are in real life. For this, the catalog of microscopic images that we developed in the Laboratory of Analysis and Diagnostics of works of art of the Universitat de València, such as those presented in this contribution, has been of vital importance. Finally, the Silknow's Virtual Loom also enables traditional industries to reduce costs by letting them select colours and techniques with just a click, and it encourages designers to create fabrics from historical silk models. Besides, this tool allows the creation of new designs applied to sustainable and recycled materials in 3D printing.

The reflectance spectra were recorded at different positions of the samples tested. The obtained spectra were studied in order to allocate absorbance maxima and other relevant spectral features that could be related to the composition of the colorants used for dyeing the silks. First, the spectra registered at points of different colours of the same sample, namely red, yellow and brown coloured zones of sample S4, were investigated [Figure 6]. The spectra recorded on the reddish zone showed an intense and well-defined band with a maximum at 273 nm. A large and intense band was also observed in the 500-600 nm region, with a maximum located at 532 nm; a shoulder was observed in this band at 568 nm. Absorption bands in this region are characteristic of compounds with red tones. Between those major bands, a wide and weakly structured band was observed. Absorption bands within this wavelength interval are characteristic of colorant with yellow chromophores.

A band similar to that found at 273 nm for the reddish area was also found for the other two areas tested, more specifically at 274 nm and at 272 nm in the spectra recorded from the brown ground and yellow ornament, respectively. The spectra registered in the yellow-coloured area, showed two significant bands at 341 and 429 nm (shoulder), and a minor band at 660 nm. Finally, the brown area (ground) of sample S4 showed bands characteristics of yellow colorants (at 367 and 432 nm), although their intensities were lower



Figures 6.- Spectra registered for red, yellow and brown areas of sample S4.



than those observed for the yellow and red areas of this sample. A low intensity shoulder located around 536 nm was observed, which suggested that a small proportion of a red colorant was used in the dyeing process of the fabric. A minor band at 667 nm (purple hue) was also found in this area.

Next, the spectra collected for samples of similar hues were compared in order to establish possible similarities and differences regarding the colorants used to prepare them. Red areas, grounds or ornaments, of the four tested samples were selected for the study [Figure 7]. All spectra show a similar shape, with a characteristic band around 273 nm, a wide band in the region of red colorants (around 500-600 nm), and high absorbances between the above bands. The presence of weakly structured bands from 300 to nearly 650 nm is a common feature of red colorants (Barbache *et al.*, 2018). Despite the high absorbances measured, which were >1 in most part of the tested wavelength interval, different maxima and shoulders could be distinguished in some of

the registers. It is interesting to note the shift towards longer wavelengths observed for the band corresponding to the red chromophores for the sample S3, indicating a purple hue.

The spectra recorded on pink coloured grounds of samples S2 and S3 were also evaluated [Figure 8]. The spectral shapes of the two samples were rather similar, although in this case the absorbance values measured were much lower for sample S3 (pale pink fabric). The highest absorbances in both spectra correspond to the band located around 272 nm. Both samples presented significant absorbances in the region of yellow and red chromophores. The main difference between the two registers is due to the bands corresponding to the red colorants, which were much higher for the dark pink sample. In this region, two maxima allocated at 527 and 558 nm were observed for the dark pink fabric (S2), and at and 520 and 553 nm for the pale pink fabric (S3). The registers also showed minor bands around 664 nm and 656 nm for S2 and S3, respectively.



Figures 7.- Spectra obtained for red areas of samples S1-S4.



Figures 8.- Spectra obtained for pink areas of samples S2 and S3.

Finally, the spectra recorded for two yellowish ornaments of sample S1 were analysed [Figure 9].

One of the registers was obtained from the area marked as S1b in figure 1, while the other area tested corresponds to the area denoted as S1c. Besides the common band around 274 nm, both spectra showed significant absorbances around 350 nm, corresponding to the yellow chromophores, as well as in the zone of red colorants (around 500-550 nm), especially in that corresponding to S1b.

The most relevant information derived from the spectra of figures 6-9 were summarized in Table 1, which was then used to stablish general patterns and differences regarding the colorants used to prepare the four silks studied. As it can be deduced from this table, most of the absorption bands found for the areas and silks tested belong to one of these four spectral regions: (i) 272-276 nm, (ii) 325-435, (iii) 500-568 nm, and (iv) 644-667 nm. The specific spectral details of each region, as well as the possible colorants responsible for such bands are addressed below.



Figures 9.- Spectra obtained for two yellow areas of sample S1.

The first region corresponds to the band centred around 272-276 nm. All samples and areas tested showed a single, well-defined, and intense band in this region. Moreover, this band presented a shape almost identical in all the samples. The above observations suggested that this band was due to the intrinsic components of silk, probably to the amino acids of fibroin. This is in agreement with the results reported by different authors that have shown that

the main amino acids of fibroin absorb UV radiation of this part of the electromagnetic spectra (Millington 2012). The intensity of this band varied slightly even between different areas of the same silk, as it can be observed for samples S4 and S1 [Figure 6 and Figure 9, respectively], which can be explained by the differences between the raw silks and the materials used during the production of the textiles.

Sample	Spot	Absorption bands (nm)									
S1	Red	276				397		521		556	
	Yellow ornament b	273	340)			425	52	0		644
	Yellow ornament c	273			370		435		535		664
S2	Dark pink	272		354	366		427	5	27	558	664
	Reddish ornament	272			3	85	405		530		
S3	Pale pink	273	339	355				520		553	656
	Reddish ornament	276			365			500		553	
S4	Red	273	330		365				532	568	
	Dark red ornament	273	325		37	9		505		563	
	Brown	274			367		432		536		6
	Yellow	272	341				429				66

 Table 1.- Absorption bands found for the analysed points of the tested samples.



Within the interval 325-435 nm most of the spectra recorded showed significant absorbances. Bands in the 320-380 nm interval with maxima around 365 nm are generally attributed to flavonoid colorants, more specifically to $\pi \rightarrow \pi^*$ transitions of the carbonyl groups in flavonoid structures (Gulmini et al. 2013). Historically, weld and old fustic were used as the main sources of flavonoid colorants in Europe, being luteolin and apigenin (hydroxy flavones) the main ingredients in these dyestuff (Gulmini et al. 2013). Lutein and apigenin exhibit absortion maxima at 336 nm and 348 nm, respectively (Petroviciu et al. 2019). However, in dyed textiles important shifts may occur depending on the metallic cations used as mordants, and variation in the spectra shape can be observed even for samples that have undergone similar dyeing processes (Gulmini et al. 2013). In the present study, bands compatible with flavonoid colorants could be seen in areas where the absorbances due to red chromophores were low to moderate. This is the case of the pink fabrics and most of the areas of sample S4. The presence of bands in the 400-500 nm may be also due to the presence of carote-noids, although within this interval the absorption bands of the tested silks were less significant.

As regards the 500-568 nm interval, most of the tested silks and areas exhibited intense bands. In fact, because of the high absorbances in this region, the precise allocation of maxima was not possible in some the spectra recorded. For most of the samples with lower absorbances in this region, two subbands could be clearly distinguished, which is characteristic of anthraquinone dyes. These two bands are due to $n \rightarrow \pi^*$ tran-sitions of the carbonyl groups in the anthraquinone core; additional bands between 350 and 450 nm due to $\pi \rightarrow \pi^*$ are also characteristic of these compounds (Fonseca et al. 2019). The later band would be overlapped with the band corresponding to the yellow flavonoids. The main sources of anthraquinonic dyes are some vegetal species such as madder, which contains alizarin and purpurin and minor amounts of other coloured compounds, and dyes obtained for animal sources like cochineal insects, which contain carminic acid as the main colorant. The position of the two sub-bands can be related to the origin of the dye. Two sub-bands around 510-515 nm and 540-545 nm are characteristic of colorants of vegetal origin, whereas subbands at 520-525 and 550-565 nm are indicative of the presence of dyes of animal origin (Fonseca et al. 2019). According to the values obtained throughout the study [Table 1], most of the subbands observed are compatible with the presence of dyestuff of animal origin, most probably cochineal-type. Even though the two sub-bands in this region suggested a common source of dyes, small differences in the respective two maxima were seen between the samples, which could be explained by the employment of different mordants during the silk production. For example, in sample S3 the band on this region showed a colour shift of about 20-60 nm towards higher wavelengths (violet hue) [Figure 7]. Similar shifts have been described for dark pink-red textiles (Barbache et al. 2018). This shift can be due to the

employment of a specific mordants (de Ferri *et al.* 2018) and/or to the employment of an alkaline media during the dyeing process. Basic media in the dyeing bath produce darker hues, whereas acidic pHs lead to orange tones (Barbache *et al.* 2018). A specific treatment under acidic media would explain the shift of the first subband towards shorter wavelengths in the red ornaments of samples S3 and S4.

Interestingly, the spectrum of the brown area of sample S4 showed a single band with a maximum at 536 nm. This suggests the employment of a colorant of different origin, probably tannins from a vegetal source (de Ferri *et al.* 2018; Tamburini and Dyer 2019). The shifting of this band towards higher wavelengths is also compatible with the presence of dyes of botanical origin such as madder. A band centred about 530 nm is also characteristic of red-ochre tones due to employment of safflower (Verhecken *et al.* 2014; Petroviciu *et al.* 2019; Tamburini *et al.* 2019a). Although cochineal colorants were massively used in Europe in replacement of other red dyestuff since the 16th, the employment of mixtures of dyestuff was a common practice during the next centuries (Gulmini *et al.* 2013; de Ferri *et al.* 2018).

Finally, some of the samples presented a single band in the 644-667 nm region. However, the intensity of such band was much lower than those found for the yellow and red chromophores. This band can be due to the presence of old fustic among the ingredients used during the dyeing process. Old fustic was typically used to produce yellowish tones, which is in agreement with the fact that this band was present in the three yellow areas studied, as well as in the brown zone of sample S4 (Giulmini *et al.* 2013).

The above results indicate that cochineal dyes were predominantly used to produce the red and pinkish silks. As regards the areas with red tones, the differences observed in the spectra suggests the application of different dyeing conditions (mordants and pHs) during the dyeing processes, and/or the employment of minor amounts of other dyestuffs. Intermediate absorbances due to yellow and red chromophores were found in the spectra recorded for the pink fabrics, which are indicative of the employment of mixtures of red (cochineal) and yellow dyestuff. The results obtained along the study suggest a predominance of flavonoids as yel-low colorants, but diffuse reflectance is not considered adequate for the unambiguous identification of the source of yellow dyestuffs (de Ferri et al. 2018). An additional difficulty was that, as the yellow areas corresponded to embroideries, superimposed signals of the ground and the yellow threads were observed when the coverage of the fabric was not complete. The brown colour of sample S4 could be achieved through the combination of vegetal dyes containing flavonoids and tannins.

The studied silks were also analysed by FTIR-ATR for comparative purposes. The spectra recorded for the



Figures 10.- IR spectra obtained for the grounds of samples S1-S4.

grounds of the four silks tested are depicted in figure 10. All the samples showed the bands characteristic of the peptide bonds of fibroin at 1618-1625, 1510 and 1439-1443 cm⁻¹, known as amide I, amide II and amide III, respectively, with a relative intensity indicative of good preservation of the samples (Ahmed & Darwish 2012; Boulet-Audet *et al.* 2015; Badillo-Sánchez *et al.* 2019).

Most of the characteristic bands of natural organic colorants present similar vibrational spectral patterns. This may be indicative of strong intermolecular bonding between the silk substrates and the colorants (Al-Sharairi et al. 2020). However, a careful revision of minor bands in the spectra of figure 10 revealed differences that could be related to the identity of their dyes. This is the case of the band at around 894 cm⁻¹ that can be observed in some of the registers of figure 10. According to the literature, carminic acid (the main component of cochineal dyes) presents, among many others, a band at 894 cm⁻¹ due to the wagging vibration of -OH groups (Koperska et al. 2011). As it can be observed in the figure, this band was present in the registers corresponding to the red-pink areas of samples S1 (894 cm⁻¹), S2 and S3 (both at 892 cm⁻¹ ¹), which also showed characteristic subbands of cochineal dyes in diffuse reflectance spectra (see Table 1). In contrast, the intensity of such band was negligible in the brown area of sample S4. No specific bands due neither to flavonoid nor to other compounds with yellow chromophores were observed in the FTIR-ATR registers.

Conclusions

Reflectance diffuse spectroscopy has been applied to study different areas of four historical silks, more specifically areas of yellow, pink, red and brown hues. The spectra collected have been examined systematically for spectral features that could be related to the composition of the colorants used in the dyeing processes. Four spectral regions have been set for the investigation of the silks, one of them related to silk itself (around 272-276 nm). For the silks tested throughout our study, the region with higher discrimination power corresponed to the red colour (500-550 nm). The bands observed in this region allowed the identification of cochineal-type dyestuff in the samples, although important shifts were observed even for areas of similar colour, which can be explained by differences in the dyeing conditions (mordants, pHs). Those results were further con-firmed with the spectra obtained by FTIR-ATR spectroscopy. The bands observed in the spectral region corresponding to the yellowish (325-435 nm) and purplish tones (644-667 nm) were compatible with different natural dyestuffs, although they did could not be attributed to any specific dyeing matter. Finally, the identified colors belong to silk fibers that have experienced the first signs of deterioration due to natural aging. Rips and frays are visible through Inverted Optical Microscopy (LMi) and Scanning Electron Microscopy (SEM) images. These same images in the LMi, SEM and LM are currently used for the development of new multisensory museographies and accessible through the Virtual Loom in 3D that has been commented on in the previous sections. The purpose of this tool is also related to the conservation of the memory and practice of a heritage of a tangible and intangible nature, as well as the need to lower costs for current artisans in specific phases of the manufacturing process, by having all this information in digital format.

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