HISTORICAL TEXTILES STUDIED BY THE CCRBC OF CASTILLA Y LEÓN. THE CHEMISTRY OF TEXTILE FIBRES

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The Centre for the Conservation and Restoration of Cultural Assets of Castilla y León, which falls under the remit of the Regional Ministry of Culture and Tourism of Junta de Castilla y León (regional government), which was established in 1988 in its current premises in the town of Simancas (Valladolid). Its role is to preserve and restore the heritage of Castilla y León, primarily cultural assets. It focuses on publicly-owned assets and particularly those held in centres managed by the Government of the local region, such as the archives, libraries and museums of Castilla y León, as well as all those afforded special protection as items of cultural interest or listed in the inventory of cultural heritage assets of Castilla y León.

Within this general context, one of the principal areas guiding the actions of the Centre for the Conservation and Restoration of Cultural Assets is research. Its Physics and Chemistry Laboratory carries out all the initial analysis needed to identify the various materials and evaluate the complexity of the techniques used to produce them, and to establish the suitability of the treatments needed to preserve them.

In addition, specific programmes have been developed in collaboration with other research centres and universities to advance understanding of cultural heritage assets through the use of new technologies.

In this paper, we will focus on the studies and actions carried out by the Textiles Department with the technical and instrumental support of the Laboratory and, in particular, we want to highlight the research carried out within a specific action area³. These are actions carried out on clothing belonging to various people of royal lineage in the Middle Ages and found in funeral contexts. There is a common denominator linking all of these cases, in that they are all pieces or fragments of clothing incorporating very high-quality fabrics of Hispano-Islamic origin, with extensive use of iconography (plant, animal and human themes), at times also including texts or epigraphic information.

The initial studies carried out on these holdings have been of fundamental importance in terms of finding out about the fabric composition, the technical process used to manufacture them and identifying the kind of dyes used, many of which are from regions far away from the Iberian Peninsula, such as a yellow from Persian berries and the red dye kermes.

The funeral origin of many of these fabrics was to a large extent a decisive factor in their preservation. Many of them were fragments or mutilated, which meant they had suffered a significant loss of mechanical resistance and also a lack of cohesion. They also suffered noticeable degradation through contact with exuded body fluids.

Given the singularity of these textile pieces, all the work done on them was part of a multidisciplinary study, done from an historical, artistic and technical perspective, carried out by various specialists from institutions such as the Institute of Cultural Heritage of Spain and the Valencia de Don Juan Institute.

The restoration work on the textiles began with the funeral attire of Princess Doña María, in the Royal Pantheon (funeral chapel) of the Basilica of San Isidoro in León, in 1997⁴. Doña María was the youngest daughter of King Fernando III the Holy, and died at an early age in 1235, being the last person to be buried in the Pantheon. The remains studied included the coffin; a large green silk pillow, a pellote (long tunic) in golden yellow silk with gold-entwined thread and lined with uncurled leather; a raw cotton shirt and raw linen

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³Studies carried out by Isabel Sánchez, Mercedes Barrera and Rufo Martín from the CCRBC Laboratory, with the collaboration of the Textile Institute of Terrassa and Andrés Sánchez Ledesma (Artelab). Photographies are taken by Alberto Plaza.
⁴Set of items restored by Adela Martínez Malo.
breeches. The recovery of this important funeral attire is not only significant because of the wide range of materials it contained, but also because of the way it was assembled for exhibition in order to ensure its best possible presentation and conservation, given its exceptional nature.

Figure 1. Shirt of the Princess Doña María. (above). Assessment of deterioration in cotton by spectroscopic techniques (FTIR). Oxidation (band at 1720 cm\(^{-1}\) due to the carbonyl group) and determination of the crystallinity index (0.12) (below).

Also noteworthy is the restoration work carried out between 2004-2005 on the five fragments of the jubbah (Arabian style cloak) of Prince Don Sancho García, kept at the Monastery of San Salvador de Oña (Burgos)\(^{5}\). This is a garment from the period of the Caliphate of Cordoba, made of a linen base embroidered with silk and gold-entwined thread dating from the 10\(^{th}\) Century. One of the fragments lined the inside of an ivory box. Another unique piece also came from this Monastery, the tunic of the Infante García, son of King Alfonso VII. This is a garment from the Almoravid period, dating to the 12\(^{th}\) Century, made from silk with gold-entwined thread, used for horse riding. This was a jubbah for a very young person.

Another of the collections, also including pieces of footwear, is the funeral items of the founder of the Benedictine Monastery of Santa María de Gradefes (León), Doña Teresa Petri, from the 12\(^{th}\) Century. Some of the most significant items were a funeral headpiece, hairnet or funeral casket combining two-tone threads and a silk decorative strip with thread twisted with gilded silver. The items of greatest importance, however, were without doubt some clogs in worked leather with polychromatic floral motifs and a cork sole, similar to those found in the sepulchres of the Huelgas Reales Convent in Burgos\(^{6}\). In this case, the work done also resulted with the items being restored for exhibition and preservation, in a glass display case, which allowed the various pieces to be arranged properly.

Two fabric remnants of particular interest were restored in 2008. These came from the Cathedral of Burgo de Osma (Soria)\(^{7}\). One was a fragment of Hispano-Islamic material richly embroidered in silk with a decoration of harpies and lions in polychromatic silk and gold-entwined thread, dating to the Almoravid period and said to be the shroud of St. Pedro of Osma, accompanied by a belt with an inscription in Cufic characters. The other piece is a short and very wide tunic in red silk with a series of yellow crescent moons as a decorative motif, and dated between the 14\(^{th}\) and 15\(^{th}\) Centuries, attributed to Hispano-Muslim workshops and historically said to be the bishop’s shroud, even though he had died several centuries before the garment was made.

All these objects have a value in terms of their significance that transcends that of their materials and manufacture. Maintaining them

\(^{5}\)Restored by Adela Martínez Malo.

\(^{6}\)Set of textiles restored by Adela Martínez Malo and leather footwear by Pilar Pastrana García.

\(^{7}\)Work carried out by Arantza Platero and Mónica Moreno, Alet Restauración S.L.
is essential in order to be able to preserve them, which requires constant work to prevent all forms of deterioration. Textiles are highly susceptible to all kinds of damage. In fact they are one of the most sensitive and vulnerable collections, as they are subjected to continuous attack from the environment. In unsuitable conditions they can deteriorate unusually quickly, far faster than any other assets, losing their shape, strength and colour. It is of fundamental importance to understand the chemical nature of both the original and additional materials, in order to determine how they will change. On occasions, the accumulated damage found before beginning the restoration work is irreversible and all that can be done is to try to manage the controllable parameters of the environment as much as possible, throughout the process and during subsequent exhibition.

The materials we studied are basically limited to natural fibres and historic colourants. Among the natural fibres, there are the cellulose types (cotton, linen, hemp, jute, etc.) and protein types (silk, wool, alpaca, etc.). The cellulose type fibres contain cellulose in various proportions, as well as hemicellulose, pectin, lignin, minerals, organic acids (oxalic). The most significant in percentage terms is cellulose, ß polymer -D-glucose. Cellulose has a crystalline part (rigid and hard) that is harder to dye and is resistant to ageing as well as another amorphous (flexible) part that can be dyed easily and is also more vulnerable to degradation. The crystallinity index of cotton is 70%, while that of linen is higher (close to 90%). These parameters mean it is possible to determine that a cotton fabric will deteriorate faster than a linen one in the same conditions.

Textile conservation publications identify the factors that can impact these products, such as temperature, humidity, acids, alkalis, radiation and biological deterioration. In the case of the harmful effect of humidity, if the RH (Relative Humidity) is less than 30%, the material will become rigid and even turn to dust. On the other hand, a high RH causes the fibres to swell, making them less resistant to chemical and biological agents. Cellulose is very sensitive to an acidic environment, in which acidic hydrolysis takes place. This hydrolysis is a random process in which the glycosidic bonds break down, forming very short chains. In principle, this is restricted to the amorphous part, meaning the increase in the crystalline part produces a rigid and more fragile material, which once again has the effect of turning the material to dust. Alkalis have an almost unnoticeable effect, so they cause hardly any changes to the mechanical properties of the material.

Out of all effects, the most important is light. If the amount of electromagnetic energy in the

Figure 2. Teresa Petri funeral attire. TLC determination of tannin-based dye used in gallons. The acidity that connects the support produces rupture of the fibers. (above). Cross section of polychrome blue clogs (below).
light is sufficient to break down a chemical bond, a photochemical reaction takes place. The photo-oxidation of cellulose can occur in two ways. One of these is the oxidation of the -OH (a free radical reaction mechanism) into aldehyde or ketone (chromophores), which causes changes in colour (yellowing or a browning colour), polarity and solubility. The other is the breakdown of the glycosidic bonds, reducing the degree of polymerisation and changing the mechanical properties of the material. Oxidation of the carbonyl group can even give rise to acid (carboxyl). This group is an auxochrome, which displaces absorption to a lesser wavelength (UV range) and so does not produce any colour, so if this second oxidation phase takes place, the subsequent loss of colour causes the final discoloured look of the textile. Biological deterioration is caused by the enzymes present in the microorganisms (cellulase). This causes the glycosidic bond to break down and on occasion causes oxidation, resulting from the hydrogen peroxide that some bacteria produce as they decompose. This was the main cause of the degradation in part of the funeral attire of Princess Doña María in the Royal Pantheon of San Isidoro, in particular the cotton shirt and the linen breeches.

The protein fibres, wool and silk, are made up of a series of fibroin and sericin proteins in the case of silk and keratin in wool. Although the amount of amino acids is the same, their proportions vary. This determines the structure and properties of each. In silk, the fibroin is primarily made up of amino acids with small molecular volume glycine/alanine/serine (3/2/1). Silk fibres are in the form of stretched, slightly folded sheets, with the chains held together by numerous hydrogen and Van der Waals bonds. This is why silk fibres are limited in length, because the protein chains are already fully extended. Fibroin bonds easily with water, meaning it maintains its flexibility, even at 40% RH. In water, it can swell by up to 18% over its cross section, but just 1.3% axially, meaning that washing silk in hard water can cause a dimensional change in its fibres. Silk is the most sensitive fibre to electromagnetic radiation. It contains amino acids that, through oxidation, turn into chromophore groups, absorbing light within the visible range of the spectrum and causing yellowing, brownish and pinkish colourations, etc. In the process, chromophores form. Meanwhile, free radical reactions cause the peptide bonds to break down, which in turn results in the material becoming more rigid and fragile, as well as the yellowing mentioned before. Heat causes silk to yellow more than electromagnetic radiation. In an acidic environment, hydrolysis causes the amorphous part to dissolve partially and rapidly, resulting in mechanical weakness. Alkaline hydrolysis hardly has any effect on the mechanical properties. However, silk dissolves in concentrated alkalis.

Figure 3. Identification of red color (kermes) by TLC in the shirt of the Prince García. The bleaching of the dye produces a sensitization of the silk as seen in the SEM photographs of an area without loss of color (a) over another faded (b).

The keratin in wool is made up of a long chain of amino acids, including the longest ones and
sulphur-containing ones. Keratin has a helix form, because the long protein chains have to fold in order to be stable. In high RH conditions, wool absorbs 16% to 18% of water. In RH of 100%, wool absorbs 33%. This reaction is exothermic, in other words it produces heat. When submerged in water, wool takes up to 200% of its dry weight. The fibres tend to swell horizontally (35-40%). The change in size after washing is due to the breaking and reorganisation of the secondary bonds. In general, electromagnetic radiation comprising wavelengths in the UV range causes photodeterioration, leading to yellowing and a change in mechanical properties. The sensitive amino acids with conjugated double bonds release chromophore group compounds through oxidation, and this is what causes the change in colour. Meanwhile, the disulphur bonds can reorganise, and in some cases even form sulphonic groups, which can lead to acid hydrolysis in the peptide bonds, with a consequent change to the physical properties. Heat has the same effect. The condensation reaction leads to a structure in which chromophore groups are present while the free radical reaction occurs. In both acid and base environments, a chemical reaction forms dehydroalanine (chromophore group), with the consequent colour change in the wool fibre. Another important aspect to bear in mind in the case of wool is biological deterioration.

Many of these theoretical aspects have been demonstrated in the analyses carried out on the textiles restored at the CCRBC. The diagnostic techniques commonly used were microscopes (OM, SEM), spectroscopes (FTIR, Raman), chromatographic techniques (TLC, GC, HPLC) and chemical ones (colouration test, viscosimetry). This understanding of the materials and the use of these analytical methods are the basic requirements essential for all of the actions carried out on textiles at the CCRBC.

The study of the fabric of the shirt of Princess Doña María in the Royal Pantheon of San Isidoro (León) showed a reduced crystallinity index in the cellulose, caused by the high degree of biological disturbance in the cotton material it was made from. Enzyme hydrolysis causes a breakdown in the glycosidic bond and oxidation of the alcohol groups in the cellulose. FTIR made it possible to determine the formation of C=O bonds of the carbonyl group (chromophore), with an absorption band at 1720 cm⁻¹ recorded on the spectrum. The intensity ratio I₁₃₇₅/I₂₉₈₀ provides a crystallinity index for the shirt of 0.12, a very low value compared with that expected for a cotton cellulose fibre material, which is estimated at 0.60.

Figure 4. Pellote (long tunic) of the Princess Doña María (above). SEM observation of the silk fibre before cleaning. Calculation of the intrinsic viscosity (below).

Measurements of certain parameters were carried out on certain elements of the funeral attire, such as intrinsic viscosity, colour change, the structural resistance of the fibres,
variation in the crystallinity index and Raman spectroscopy. The aim was to observe variations in these that resulted in deterioration. The effectiveness of cleaning has always been based on checking the suitability of these parameters.

The shirt of the Prince García at the Monastery of San Salvador de Oña arrived at the CCRBC in order to be adapted to a new preservation environment. Although no direct work was done on the piece, since it was recently restored, a study was carried out on the dyes used. Thin layer chromatography (TLC) identified the red dye kermes. Scanning electron microscopy techniques with X-ray analysis (SEM/EDAX) showed the fixer to be aluminium salt. A study comparing a dyed area of the shirt without any chromatic alteration with another discoloured area, using amplified SEM observation of the fibres and bonds, showed photosensitivity of the silk fabric caused by the dye in the part that had suffered colour loss.

The decorative strips of the funeral clothing of the Monastery of Gradefes displayed mechanical deterioration that is an intrinsic feature of the tannin-based colourant, which uses an iron salt as fixative. Acidity, which is accentuated in relatively unfavourable humidity conditions, caused the fibres to break.

The richness of the decoration of the fragment of the shroud of St. Pedro of Osma can be clearly seen in the materials used, thread from Cyprus and gold-silver alloy with a high gold content (53.91%), much higher than the gilded silver thread, as can be seen in the X-ray fluorescence elemental analysis.

Lastly, we should emphasize the crucial role of applied research in defining treatments and firmly establishing preservation conditions when undertaking projects involving material as sensitive as fabric at centres and institutions researching or holding such heritage.

References

**IDENTIFICATION OF FATS AND BEESWAX IN CERAMIC VESSELS OF TOMB 121 OF CASTELLÓN ALTO (GALERA, GRANADA)**

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**Introduction**

Gas Chromatography-Mass Spectrometry (GC-MS) has been used systematically for the identification of contents of archaeological vessels since the early 90s, regardless of whether the contents had been absorbed by the porous structure of the clay matrix of the vessel (Evershed et al. 1990, 1992), or remained as solid deposits (Colombini et al. 2005, Ribechini et al. 2008). This technique meant a breakthrough in archaeology, because it allows bringing together archaeological evidence, like the shape of vessels, the setting of the finding or the written sources.