ISSN 1579-8410

Editors: C. Saiz-Jimenez
M.A. Rogerio-Candelera

TechnoHeritage

COALITION

Electronic Journal of the Network on Science and Technology for the Conservation of Cultural Heritage

CSIC
Consejo Superior de Investigaciones Científicas

Issue 22
July 2011

Contents

Cover Photograph:
Figure 2 of Parras *et alii*, page 9, this issue.

Edited by

CSIC Thematic Network on Cultural Heritage and Network on Science and Technology for the Conservation of Cultural Heritage

Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, Apartado de Correos 1052, 41080 Sevilla (Spain)

Correspondence to:
coalition@irnase.csic.es

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

Mercedes Barrera del Barrio[1] and Milagros Burón Alvarez[2]

Junta de Castilla y León (regional government) Centre for the Conservation and Restoration of Cultural Assets

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 area[3]. 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 1997[4]. 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 uncured leather; a raw cotton shirt and raw linen

[1]Chemist from the CCRBC of the Junta de Castilla y León.
[2]Director of the CCRBC of the Junta de Castilla y León.

[3]Studies 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.
[4]Set 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 Maria. (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 10th 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 12th 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 12th 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 14th and 15th 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.

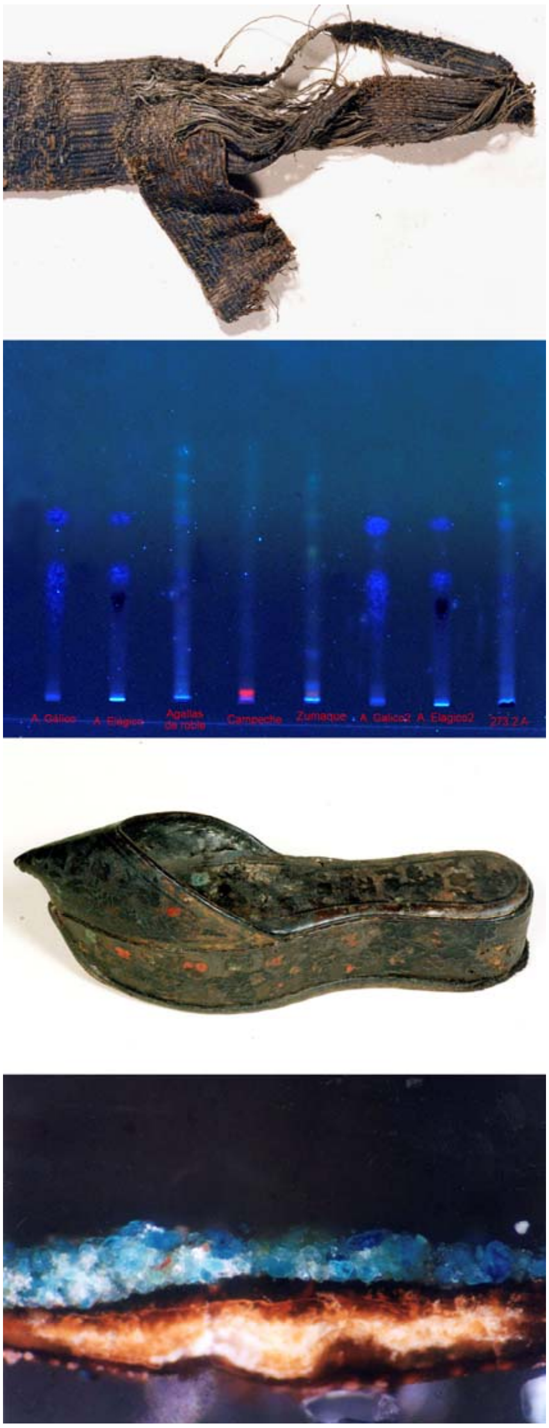

Figure 2. Teresa Petri funeral attire. TLC determination of tannin-based dye used in gallons. The acidity that connects the support produces rupture of the fibers. (above). Cross section of polychome blue clogs (below).

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

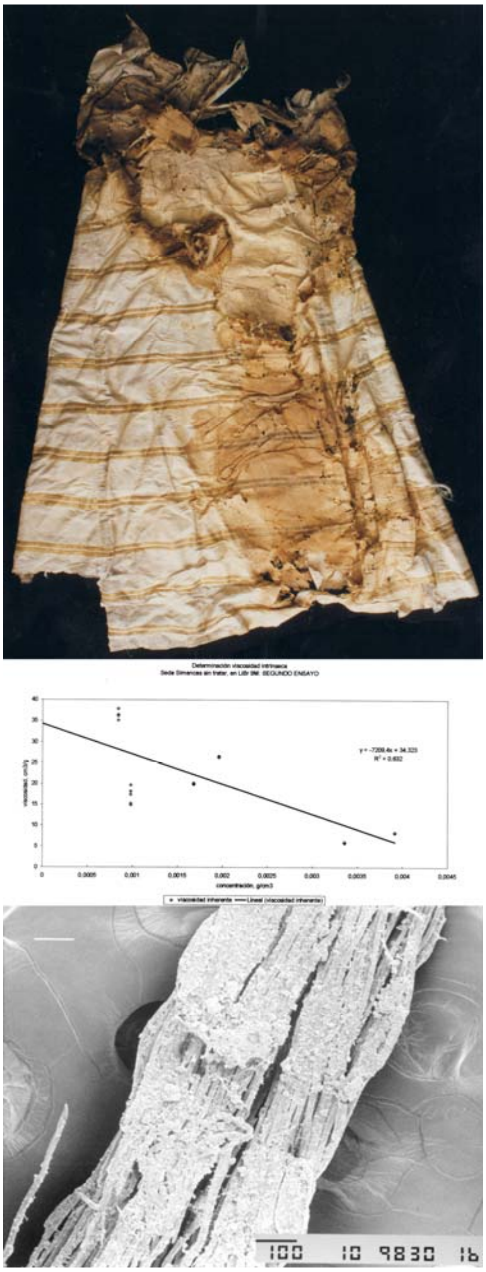

Figure 3. Identification of red color (kermes) by TLC in the shirt of the Prince García. The bleaching of the dye produces a sensitization of the silk as seen in the SEM photographs of an area without loss of color (a) over another faded (b).

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 (TCL, 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 I_{1375}/I_{2980} 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.

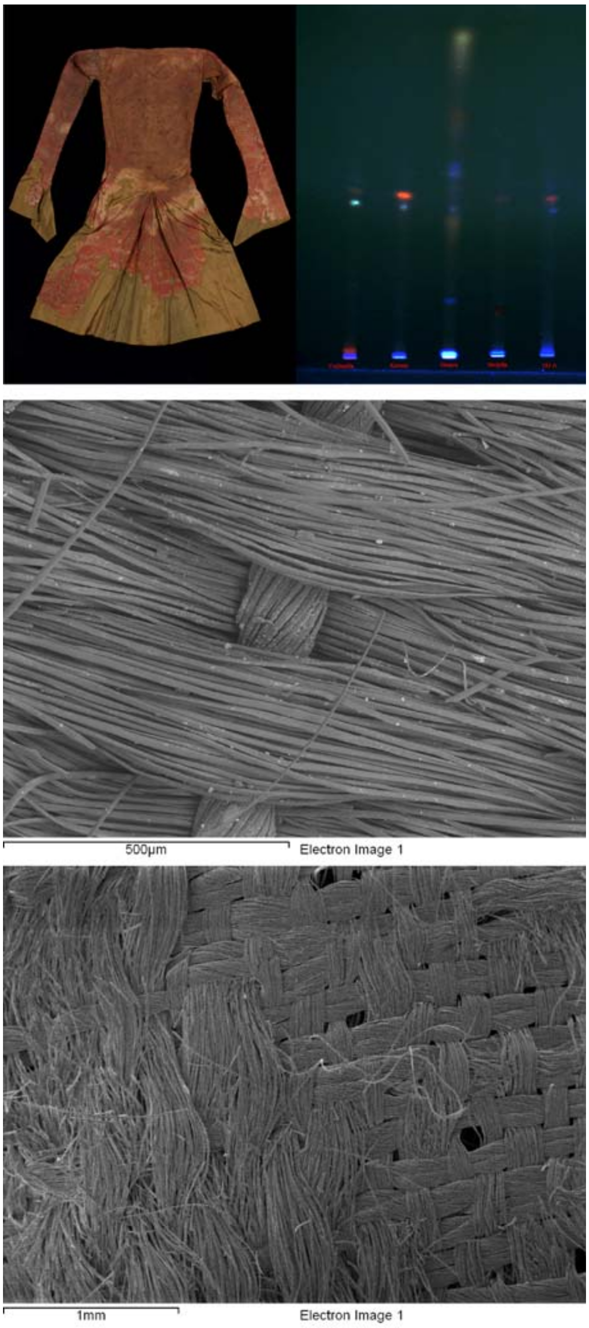

Figure 4. *Pellote* (long tunic) of the Princess Doña Maria (above). SEM observation of the silk fiber before cleaning. Calculation of the intrinsic viscosity (below).

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.

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

David Jesús Parras[1], Alberto Sánchez[2]*, Natividad Ramos[3], María Oliva Rodríguez Ariza[2], José Alfonso Tuñón[2]

[1]*Archaeological Heritage Research Group. University of Jaén, Paraje Las Lagunillas s/n 23071, Edif. C6, Jaén, Spain.*
[2] *Andalusian Centre for Iberian Archaeology, University of Jaén, Paraje Las Lagunillas s/n 23071, Edif. C6, Jaén, Spain.*
[3] *Department of Physical and Analytical Chemistry, University of Jaén, Paraje Las Lagunillas s/n 23071, Jaén, Spain.*

*Corresponding author: tel.: 34 953212132; fax 34-953212287. E-mail address: vizcaino@ujaen.es

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.

The analyses thus obtained have succeeded to identify accurately chemical markers in archeological vessels: fatty acids, sterols, acylglycerols (Evershed 2008, Colombini and Modugno 2009), wax esters (Heron et al. 1994, Regert et al. 2001) or terpenoids (Urem-Kotsou et al. 2004) revealed the occurrence of substances like vegetable oils, animal fats, milk, beeswax or coating resins (Regert 2011). In addition to the capability to identify a wide range of organic matter, GC-MS stands out for its ease of use and high sensitiveness. The latter is a major advantage, because research on contents in archaeological vessels is usually constrained by small samples and low concentrations of the compounds under study (Evershed et al. 2002).

Based on the analysis of chemical markers, this paper discusses the results obtained by GC-MS from the four ceramic vessels retrieved from tomb 121 of the Argaric settlement of Castellón Alto (Galera, Granada). The excellent state of conservation of the tomb allowed to gain access to a range of data on the burial ritual of the Argaric period. Further knowledge could be gained from the chemical data of the contents of the vessels found in the tomb as a part of the grave good.

Castellón Alto and Tomb 121

Castellón lies in the administrative term of Galera (Granada), approximately 1 km away from the town. The settlement dates back to the Argaric Culture, specifically to the mid-late Bronze period (1900-1600 b. C.) (Figure 1).

The settlement lies between two major units which are linked: one is the hill, with three natural terraces, and the neighbour eastern hillside. The bedrock of the natural terraces was artificially dug and a part of the area was flattened into several terraced plots so most of the hill could be used. The dwellings were built on the artificial terraces. A back wall was built along the rock and a front wall ran parallel to the former thus forming a quadrangle. The rooms occasionally adapted to the ground and are therefore shaped like a polygon (Rodríguez Ariza et al. 2000, Rodríguez Ariza and Guillén 2007).

Figure 1. A view of Castellón Alto in Galera (Source: Rodríguez Ariza & Guillén 2007).

Most of the rooms in the settlement house one or two tombs, so over one hundred have been recorded overall. Except for the child burials in urns, the tombs are small caves excavated in the bedrock. Most of the caves were sealed by large stone slabs or, less frequently, by wooden planks (Rodríguez Ariza 2001, Rodríguez Ariza et al. 2000, Molina et al. 2003, Rodríguez Ariza and Guillén 2007).

Tomb 121 is a small cave dug in the side of an oval-shaped terrace. It was sealed with three planks of Corsican pine (*Pinus nigra*) plastered with mud and rubble masonry. The cave was therefore safe from the outside soil and a microclimate developed which interrupted the decomposition of the organic matter, thus allowing its partial preservation (Molina et al. 2003, Rodríguez Ariza and Guillén 2007).

Inside the cave lay the remains of a man in left side prone position. The man was 1.60 m and was between 27 and 29 at the time of his death. Mummified soft tissue remains on the head and on the postcranial skeleton. It is remarkable how the hair of his head, beard and body hair in general has been preserved where skin is still present. Linen fabric and a sort of small net made with esparto rope was found around his right leg, and remains of what may be cotton can also be found (Molina et al. 2003, Rodríguez Ariza and Guillén 2007) (Figure 2).

ISSN 1579-8410
www.rtphc.csic.es/boletin.htm

The right front part of the tomb also housed remains of a child. Some of the bones were still joined. The body had been taken out from the original tomb and buried with the adult. Soft tissue could also be found on this body, as well as dark hair, presumably a head covering woven with wool, covered with leather and with remains of linen tissue.

Figure 2. A view of Tomb 121 (Source: Rodríguez Ariza & Guillén, 2007).

The funerary grave good consisted in four ceramic vessels, one of which was a cup, and also copper bracelets, silver rings, a copper dagger with remains of the scabbard leather, and a copper axe with the whole holm oax handle. Remains of the threads that held the axe to the handle were still present. The child wore a bronze bracelet on each arm and three beads as well as lamb bones (Molina et al. 2003, Rodríguez Ariza and Guillén 2007).

Experimental

Archaeological samples

Approximately 4 g of the bottom or of the base matter of the four vessels were sampled. The sampling area was a requirement to cause the least possible damage to vessels which were in outstanding condition.

The fragments of archaeological vessels selected for analysis were wrapped each in a piece of dark paper and stored in a freezer at least at -20 °C until their analysis. The fragments were then taken out of the freezer and a sample was collected, usually from the base. Any remains of soil were removed with an electric hand drill. The sample was then grinded to the appropriate size in an agate mortar. Two grams were taken for the analysis.

Extraction and derivatization

Extraction is in accordance with the procedure described in Evershed et al. (1990).Ten µL of tetratriacontane (internal standard) and 10 mL of the mixture chloroform/ methanol ($CHCl_3$:MeOH) (2:1 v/v) were added to 2 g of the ground ceramic fragment. Lipids were extracted with ultrasound for 15 minutes. The solution was centrifuged (3500 rpm, 5 minutes) eliminating the remaining ceramics and removing the supernatant where the lipids are solved. This process was repeated twice. The extract portions were combined into one for solvent evaporation under N_2 stream.

The dry extract was solved again in 500 µL of $CHCl_3$ and a 100 µL aliquot was removed and transferred to a smaller vial. This volume was evaporated to dryness under an N_2 stream. N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) with 1 % trimethylchlorosilane (TMCS) was used as derivatization agent. The derivatization reaction took place with 20 µL of this reagent at 70 °C for 30-40 minutes. When the reaction was over, the vial was cooled and the remaining derivatizing agent was evaporated under an N_2 stream. The sample was then solved again in 50 µL of cyclohexane. An amount of 1 µL of sample was injected into the chromatograph.

Gas Chromatography-Mass Spectrometry

The analyses were performed using a quadrupole type HP 5989B MS coupled to a HP 5890A serie II plus GC. Samples were introduced by on column injection into a 15 m x 0.32 mm I.D. fused silica capillary column, coated with poly(dimethylsiloxane) stationary phase with 0.1 µm film thickness. Helium was used as the carrier gas (purity 99.99%) at a flow speed of 1.0 ml/min. The GC oven temperature program was as follows: initially at 50 °C, held for 2 min; ramp to 350 °C at 10°C/min, held for 10 min.

The operating conditions were an emission current of 400 µA, an electron energy of 70 eV and an ionization source temperature with the following ramp: 0-15 minutes at 250 °C, 15-23 minutes at 300°C and 23-42 minutes at

350ºC (Parras 2008). Total ions measurements were obtained in the mass spectrometer that was scanned from m/z 50-900 at a scan rate of 2.083 s/scan. The GC-MS capillary interface was mantained at a temperature of 350 ºC.

Results

Relevant results were obtained from 2 out of the 4 samples analysed (Figure 3, Table 1). Vegetal fat, beeswax and milk fat were identified in this case.

Figure 3. A reconstruction of the vessels. Left: CA-29237, glass. Right: CA-29235 bottle.

Vessel CA-29235 (bottle). The chromatogram obtained shows two groups of compounds: one comprehends the fatty acids palmitic ($C_{16:0}$), stearic ($C_{18:0}$), oleic ($C_{18:1}$) and triacylglycerols (TAG) of oleic acid and of palmitic acid (trioleine, OOO, being the most abundant triglyceride). The amount of triacylglycerols of oleic acid is high and confirms the vegetal origin of the fat (Figure 4).

The other group of compounds belongs to the typical set of substances found in beeswax. Contemporary beeswax shows a recognizable pattern based on the occurrence of:

-Series of C_{23} to C_{33} carbon number n-alkanes displaying a unimodal distribution possessing a strong odd-over-even predominance.
-Series of C_{40}-C_{54} carbon number palmitic acid wax esters with a main constituent that contains 46 carbon atoms.
-Free fatty acids, of which lignoceric acid ($C_{24:0}$) is predominant.

In general, beeswax degradation causes a good part of the fatty acids (except for palmitic acid) to disappear, *n*-alkanes to be lost, and long chain alcohols with an even carbon number (usually from C_{24} to C_{34}, maximizing at C_{30} that are released of wax esters) to appear (Tulloch 1970, Chartes et al. 1995, Regert et al. 2001).

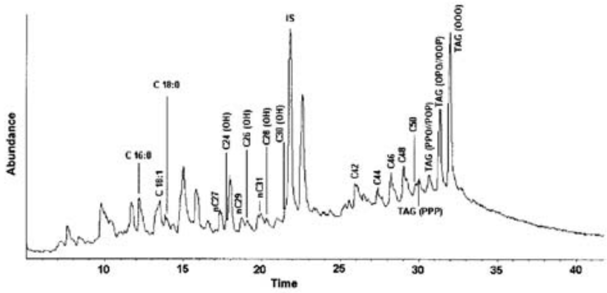

Figure 4. Sample *CA-29235.* GC-MS chromatogram of the lipid extract.

Some of these indicators, as well as others related to beeswax degradation, have been found to occur: *n*-alkanes C_{27} to C_{31} (C_{27} to a larger proportion), palmitic acid wax esters (C_{42} to C_{50}) and long chain alcohols (C_{24} to C_{30} with C_{30} as major component) resulting from hydrolysis of wax esters. Overall, these indicators confirm the occurrence of beeswax in the vessel.

The low proportion of long-chain alkanes is worthy of note. There is no evidence that the vessel was on the fire. The degradation of alkanes would thus be related either to the very dry environment of the burial site or to evaporation due to heating the beeswax before application to the inner side of the vessel (Regert et al. 2001, 2003).

Vessel CA-29237 (glass). The analysis shows peaks of fatty acids capric ($C_{10:0}$), lauric ($C_{12:0}$), myristic ($C_{14:0}$), palmitic, stearic and oleic. The former three suggest a case for milk of ruminants (Dudd and Evershed 1998) (Figure 5). Their occurrence in the milk of monogastric ruminants (humans, pigs…) is extremely low. These fatty acids are also rare in animal adipose tissues (Gunstone et al. 1994, Mirabaud et al. 2007).

A small peak occurs which has been identified as heptadecanoic acid ($C_{17:0}$), except that its proportion is comparatively smaller. Again, this fatty acid occurs in milk fat in a low proportion alongside pentadecanoic acid ($C_{15:0}$) (not found in the sample). The latter two acids may have also occurred in milk fat as ramified fatty acids *iso-* and *anteiso-* (Dudd and Evershed 1998).

The occurrence of the following group of triglycerides is also an argument in favour of a case for milk: MMP or MPM; MPP or PMP; PPP; OOP or OPO and OOO (M: myristic acid; P: palmitic acid; O: oleic acid). The occurrence of myristic acid in the triglycerides supports a case for milk fat.

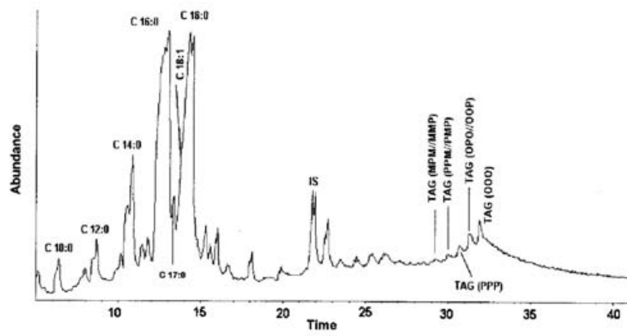

Figure 5. Sample *CA-29237*. GC-MS chromatogram of the lipid extract.

Table 1. Mass spectrometric data of the main lipidic compounds. P*: Protoned Palmitic Acid by the fission of alkyl-oxygen bond.

COMPOUNDS	MAIN PEAKS (m/z)
Fatty Acids (TMS)	
$C_{10:0}$	244 (m$^+$)-229(m$^+$-15)-145-129
$C_{12:0}$	272 (m$^+$)-257(m$^+$-15)-145-129-117
$C_{14:0}$	300 (m$^+$)-285(m$^+$-15)-145-129-117
$C_{16:0}$	328 (m$^+$)-313(m$^+$-15)-145-129-117
$C_{18:1}$	354 (m$^+$)-339(m$^+$-15)-145-129-117
$C_{18:0}$	356 (m$^+$)-341(m$^+$-15)-145-129-117
Wax Esters	
C_{42}	621(m+1)$^+$-257(P*)-239 (P$^+$)
C_{44}	649(m+1)$^+$-257(P*)-239 (P$^+$)
C_{46}	677(m+1)$^+$-257(P*)
C_{48}	705(m+1)$^+$-257(P*)
C_{50}	Detected for the retention time and the main peaks 257(P*)-239 (P$^+$)
Triacylglycerols	
MMP/MPM	523(GlyMP$^+$)-495(GlyMM$^+$)-239(P$^+$)-211(M$^+$)-129-97
PPM/PMP	551(GlyPP$^+$)-523(GlyMP$^+$)-239(P$^+$)-211(M$^+$)-129-97
PPP	551(GlyPP$^+$)-239(P$^+$)-129-97
PPO/POP	578(GlyPO$^+$)-551(GlyPP$^+$)-339(Gly O$^+$)-313(Gly P$^+$)-265(O$^+$)- 239(P$^+$)-129-97
OOP/OPO	604(GlyOO$^+$)-578(GlyPO$^+$)-339(Gly O$^+$)-313(Gly P$^+$)-265(O$^+$)-239(P$^+$)-129-98
OOO	604(GlyOO$^+$)-339(Gly O$^+$)-265(O$^+$)-129-97
PPS/PSP	579(GlyPS$^+$)-551(GlyPP$^+$)-341(GlyS$^+$)-313 (GlyP$^+$)-267(S$^+$)-239(P$^+$)-129-97
SSP/SPS	608(GlySS$^+$)-579(GlyPS$^+$)-341(GlyS$^+$)-313(GlyP$^+$)-267(S$^+$)-239(P$^+$)-129-97
SSS	608(GlySS$^+$)-341(GlyS$^+$)-267(S$^+$)-129-97

Conclusions

The results obtained from the analysis of chemical markers in the ceramic vessels of tomb 121 of Castellón Alto provide additional information on the rituals and economic activity. This information is in addition to the rest of the contextual, palynological and carpological data.

First, the highly likely occurrence of milk in vessel CA-29237 allows for putting forward some hypotheses and proposals. In general, it is assumed that the use of milk and dairy products in Europe became widespread in the 5th millennium B.C. However, the latest research by Evershed et al. (2008) based on chemical analysis proved that the milking of ruminant animals was clearly practised in the sixth and seventh millennia BC in southeastern Europe and northwestern Anatolia respectively. The chemical data of tomb support other archaeological evidence of the use of milk and dairy products in the Iberian peninsula from the 5th millennium B.C.

The presence of the infant body in the tomb is comparatively more important and also raises the question whether it is related with the presence of milk in the vessel in question. Additionally, the tomb also housed bones of a milk-producing ruminant (sheep). Use of this and other vessels before being part of the funerary dowry cannot be discarded.

Second, the occurrence of vegetal fat in the bottle (sample CA-29235) cannot be put down to a specific type of oil. Even if the state of conservation of this tomb is excellent, fatty acids go through alterations that modify their original proportion in food and therefore make it difficult to identify the type of fat accurately. In these circumstances, the palynological and carpological data available in the settlement provides further information. According to this, only wild olive trees and flax can have yielded vegetal oil. Of these, the former is rare whereas the latter is abundant (Rodríguez Ariza et al. 1996, Contreras et al. 2000).

Finally, the third element occurring in sample CA-29235 is beeswax. It can be explained in different ways according to its meaning and its timeline.

Table 2. A timeline of the use of beeswax in Eastern Andalusia-Upper Guadalquivir based on chemical markers.

Settlement	Chronology	Context
Marroquíes Bajos. Ciudad de la Justicia. Jaén	Late 3rd millennium b.C Chalcolithic	Domestic-workshop. Hut 693 (Parras 2008)
Marroquíes Bajos. Plot E.2.1, U.A.23. Jaén	Late 3rd millennium b.C Chalcolithic	Domestic (Sánchez and Cañabate 1999a)
Castellón Alto. Galera. Granada	1900-1600 b. C. Argaric Bronze	Funerary. Tomb 121
Remojadero Pescado and Huérfanos street. Jaén	IX-VIII b. C. Late Bronze	Structure built in the bedrock (Sánchez and Cañabate 1999a)
Sanctuary El Pajarillo.Huelma. Jaén	IV b. C. Iberian Culture	Storage area sanctuary (Sánchez and Cañabate 1999b)
Oppidum Puente Tablas. Jaén	IV b. C. Iberian Culture	Domestic. House 6 (Sánchez et al., 2009)

The occurrence of beeswax inside vessels since prehistory may be explained in terms of a medical use, a cosmetic, a ritual substance, protection against corrosion, paint, vessel construction, glue, coating, the occurrence of honey, or the lost wax technique (Regert et al. 2001). As the chronological and contextual frame of the materials under study allows to rule out some of the above, the most conservative approach may consider three hypotheses: as the contents of the vessel, as an inside coating, or as signalling the occurrence of honey. It cannot be said whether it cooccurred with vegetal oil and signal one and the same use where beeswax was used as internal lining, or whether the vessel may have been used for two different purposes before and after the burial.

The occurrence of beeswax completes and widens the sequence of use of this product in Eastern Andalusia thus forming a sequence where, from the point of view of chemical analysis, begins in the 3rd millennium and ends in the Iberian period (Table 2). In addition to its extensive chronological record above, beeswax occurs in a number of archaeological contexts which comprend a varied functional spectrum: a domestic area shared with a workshop of bone figurines, only one domestic area, an inhumation tomb, the storage area of a sanctuary and, again, a room for domestic purposes.

Acknowledgements

This work was supported by Andalusian Centre for Iberian Archaeology, Andalusian Government and FEDER Funds.

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Conference report

FIRST MEETING OF THE NETWORK OF SCIENCE AND TECHNOLOGY FOR THE CONSERVATION OF CULTURAL HERITAGE (TECHNOHERITAGE)

Miguel Ángel Rogerio-Candelera

Instituto de Recursos Naturales y Agrobiología de Sevilla IRNAS-CSIC, Seville, Spain

Conservation of Cultural Heritage is a multidisciplinary task involving a broad spectrum of scientific and professional institutions. To this end Spain has created a network of institutions dedicated to research and conservation of Heritage, which also involved private companies. The first meeting of the Network of Science and Technology for the Conservation of Cultural Heritage had as main objective the presentation of the different network groups and provide a forum to share experiences.

The meeting took place on 28 and 29 June in Madrid, hosted in the auditorium of IPCE, with the participation of more than a hundred scientists and professionals. The two-day program included a total of 35 communications, which have been published in an electronic book (Rogerio-Candelera and Saiz-Jimenez 2011)(Figure 1) soon to be hosted on the website Technoheritage (www.technoheritage.es).

Figure 1. Front cover of "Ciencia y Tecnología para la Conservación del Patrimonio Cultural"

The different communications included work in the areas of archaeology, architecture, physics, chemistry, biology or materials science among others, covering different issues related to the conservation of movable or immovable cultural assets, to the conservative approaches and interventions of different conservation institutions and museums, and the role of enterprises in the research/conservation system. The complete list of contributions includes: *Estructura social y territorio*, by I. Sastre et al., *Estudio de materiales y técnicas utilizados en obras de arte*, by A. Justo et al., *Materiales poliméricos y patrimonio cultural*, by M. Lazzari and A. Ledo, *Grupo de Bioingeniería y Materiales (BIO-MAT) de la Universidad Politécnica de Madrid*, by D.A. Moreno and A.M. García, *Grupo de Tecnología Mecánica y Arqueometalurgia*, by A.J. Criado et al., *ICMUV Grupo de Arqueometría*, by C. Roldán and S. Murcia-Mascarós, *Láseres y Nanotecnologías para el Patrimonio Cultural*, by M. Castillejo et al., *Rocas ornamentales: procesos fisicoquímicos*, by A.C. Íñigo et al., *Grupo de investigación en el Patrimonio Arquitectónico y Sostenibilidad (GIPAS-UAH)*, by G. Barluenga et al., *Monitorización y tratamiento de datos microclimáticos en el patrimonio cultural: IC9 Grupo de Investigación y Desarrollo Tecnológico del IVC+R*, by J. Pérez-Miralles et al., *Diagnóstico de impactos ambientales sobre el Patrimonio Cultural (Histórico, Artístico y Natural) mediante análisis in-situ, observaciones micro-espectroscópicas y modelado químico*, by J.M. Madariaga et al., *Conservación de vidrios y* *materiales cerámicos históricos y monumentales (CERVITRUM)*, by M.A. Villegas et al., *Mineralogía y Quimiometría de materiales arqueológicos*, by R. García et al., *Petrología y Geoquímica aplicadas a Patrimonio (PGPA)*, by M.P. Lapuente et al., *Ciencias de Materiales aplicadas al Patrimonio*, by M.T. Blanco-Varela et al., *Centro Andaluz de Arqueología Ibérica (CAAI)*, by A. Ruiz and A. Sánchez, *Museo Nacional del Prado, Laboratorio de Análisis, Área de Restauración*, by M.D. Gayo et al., *Ciencia y Cultura escrita: Un proyecto de investigación, formación y difusión para la conservación del patrimonio documental*, by T. Espejo, *Análisis geoambiental en medios hipogeos (MNCN y Grupo de Petrología Aplicada, UA)*, by S. Sánchez-Moral et al., *Instituto del Patrimonio cultural de España*, by A. Borraz et al., *Caracterización analítica, Documentación, Conservación y Restauración del Patrimonio*, by M. San Andrés et al., *Microbiología y Patrimonio Cultural*, by M.A. Rogerio-Candelera and C. Saiz-Jimenez, *Petrología aplicada a la conservación del Patrimonio*, by R. Fort et al., *GPAC. Grupo de Investigación en Patrimonio Construido*, by A. Azkarate, *FEMTOUSAL*, by P. Moreno et al., *Ecología microbiana y geomicrobiología: ECOGEO*, by C. Ascaso et al., *Aplicaciones de técnicas nucleares de análisis no destructivo al Patrimonio Cultural*, by M.A. Respaldiza et al., *El Centro de Conservación y Restauración de Bienes Culturales de Castilla y León*, by M. Burón, *Geomnia Natural Resources, SLNE – Artchemist*, by E. Sanz et al., *AIPA. Análisis e intervención en el patrimonio arquitectónico*, by J. Monjo et al., *MATERIAYARTE. Investigación interdisciplinar para la conservación del patrimonio a través del conocimiento material y técnico*, by M. Arjonilla et al., *SIT Grupo Empresarial*, by G. Andrade and A. Ortega, *Arqueometría y Patrimonio de la cerámica y el vidrio*, by C. Pascual et al. and *Caracterización material de obras del patrimonio cultural*, by J.F. García et al.

The next Meetings of the Network will have an international character, inviting the European and international scientific/professional communities to an active participation.

Reference

Rogerio-Candelera, M.A. and Saiz-Jimenez, C. (eds.) 2011. *Ciencia y Tecnología para la Conservación del Patrimonio Cultural*. Sevilla: Instituto de Recursos Naturales y Agrobiología de Sevilla. ISBN: 978-84-694-6137-2.

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Congress announcement

The 15th International Symposium on Biodeterioration and Biodegradation (IBBS-15) will be held in Vienna (Austria) at the University of Natural Resources and Life Sciences from 19th to 24th September 2011. The IBBS-15 Symposium is dedicated to different topics dealing with **biodeterioration and biodegradation** of organic and inorganic materials including **cultural heritage** objects, corrosion of **metals and rocks**, applied aspects of **biotechnology** such as conversion of **lignocellulose**, bioremediation of polluted **soils and water** and state of the art **techniques** to study function and **diversity of microorganisms** involved in these processes.

Topics/Sessions:

IBBS15-1 Biofilms and Biofouling.
IBBS15-2 Biogenic transformations of rock, minerals, metals and radionuclides.
IBBS15-3 Biodeterioration and bioconversion of lignin, cellulose and paper materials: biotechnological applications.
IBBS15-4 Biodeterioration of Cultural Heritage and building materials in indoor and outdoor environments: assessment and control, methods, treatments, prevention, cleaning.
IBBS15-5 Biodeterioration of miscellaneous materials: spacecraft materials, medical devices, glass, teflon, “nano” coatings.
IBBS15-6 Biodegradation of hydrocarbons and persistent pollutants: oil hydrocarbons, plastics, PAH, PCBs.
IBBS15-7 Bioremediation of contaminated soils and water, bio-filtration of industrial pollutants, development of GMOs and their use in bioremediation.
IBBS15-8 Biodiversity, ecophysiology and function of organisms involved in biodeterioration and biodegradation.
IBBS15-9 State of the art methods to study organisms and processes of BBB – genomics/proteomics.
IBBS15-10 Control of biodeterioration: new physical and chemical methods.

More information:
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