STUDY OF COCHINEAL PRESENT IN DYED COTTON FABRICS: CHEMICAL IDENTIFICATION AND ANALYSIS OF THE CHANGES IN THE MECHANICAL PROPERTIES OF DYED SPECIMENS

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ABSTRACT: *This paper describes the use of cochineal natural dye in old cotton textiles. Cochineal-dyed cotton samples were prepared in the laboratory with the use of old materials and formulas. Firstly, the characterization of samples through chemical and mechanical tests helped establish standards for comparisons with current textiles. The identification of carminic acid and mordant agents was performed by spectrophotometric, microscopic and chromatographic techniques. Secondly, tensile tests were run in a weft direction. Stress-strained curves helped determine the stiffness and flexibility of each sample as well as their elongation and their probability of tearing under specific environmental conditions. The objective of this research is to determine the effects of dyeing and mordanting on the mechanical properties of cotton fabrics. Cochineal was used to represent natural dyes for experimental testing purposes. The mordants selected included Tin(IV) chloride, Copper sulphate, Potassium dichromate, Ferrous sulphate and Alum.*

KEYWORDS: Cotton, cochineal, carminic acid, mordant agent, tensile tests, colorimetric analysis, UV-Vis Spectrophotometry, HPLC-DAD, SEM/EDX

1. INTRODUCTION

Evidence of degradation of worn fabric can be easily determined by simple observation. Tears, holes and deformations are common signs of lack of strength and elasticity. The fabric's technical properties may include weight, density, elasticity and chemical make up, all of which may contribute to the damage caused to the material.

This study focuses on cotton, a well-known material which has widely spread across Europe since the second half of the 18th century. It was used for clothing, upholstery and decoration. It is coloured with cochineal natural dye, this being one of the most widely used and analysed natural colorants (Hofenk-de Graaff and Roelofs, 1972).

Cotton is one of the most abundant of all naturally occurring organic substrates and is widely used. It is used either alone or in conjunction with other synthetic fibres in a wide range of apparels and artistic objects. This material characteristically offers excellent physical and chemical properties in terms of water absorbency and the dye's ability and stability (Preston, 1986; Shore, 1995).

Natural dyes require chemicals in the form of metal salts to form a fixative relation between the cotton yarn and pigments, and these chemicals are known as mordants. An accurately weighed cotton sample was treated with different metal salts; only pre-mordanting with metal salts was carried out before dyeing [Becker et al., 1987).

In this study, a set of unworn cotton samples, that had been dyed with cochineal in both the presence and absence of mordants, was analysed by colorimetric analysis, UV-Vis Spectrophotometry, HPLC-DAD, SEM/EDX and tensile tests. The aim of this multi-analytical approach is to propose qualitative methods to evaluate the influence of mordant and dyestuff on the mechanical properties of cotton textiles. Since HPLC is the main analytical technique currently used to detect and identify dyes in textile works of art (Surowiec et al., 2006: 209), comparing chromatographic test results with spectroscopic and tensile test results should not only highlight the potential and limits of non-destructive spectroscopic techniques in the analytical identification of dyes in textiles, but also detect their mechanical degradation.

2. EXPERIMENT

2.1. Reagents

The chemical reagents and solutions used were: Hydrochloric acid, 37%, RS, Carlo Erba; Acetonitrile (ACN) and Methanol (MeOH), HPLC-gradient grade, Carlo Erba; Trifluoroacetic acid (TFA) 99% Panreac; Acetic acid 100% Prolabo, Ammonia, p.a., Carlo Erba ,Tin (IV) chloride, RS, Carlo Erba; Copper sulphate RS, Carlo Erba; Potassium dichromate RS, Carlo Erba; Ferrous sulphate RS, Carlo Erba; and Alum, RS, Carlo Erba. Deionised water, HPLC grade, Medica Elga (Eolia Water). HCl 3M:MeOH:H2O (2:1:1) solution and MeOH:H2O (1:1) solution.

2.2. Dyes and fabrics
The raw dye was purchased from Kremer Pigmente (Germany) (ref. 36040, Carminic acid).

A white *batista* cotton, with 46x34 yarns/cm, 0.116g/m2 supplied by Productos de Conservación, S.L, was the test fabric we used (Table 1).

2.3. Preparation of Reference Specimens
Cotton fabrics measuring 140 x 20 cm2 were coloured with the given dyestuffs under different dyeing conditions.

2.3.1. Preparing the fabric
The cotton fabric was heated at 70ºC for one hour. Afterwards, it was drained and immersed in dyeing baths.

2.3.2. Dye extraction

Cochineal dyeing Bath
Firstly, 20g of cochineal insects were powdered and soaked in 500 ml of deionised water. Then they were heated at 70ºC for one hour. The hot solution was filtered with a nylon filter, and this concentrated dyeing bath was named B1C. This solution was then diluted to 500 ml and used for dyeing. Its pH was 5.55. This dyeing bath from cochineal was named BTC.

The colour of the standard cochineal dyeing bath (BTC) was characterised by UV-vis spectrophotometry. Aliquots of 50-100 µl volumes of clear dye solution (dyeing bath) were measured using a UV-vis recording double-beam spectrophotometer. Aliquots of 50-100 µl volumes of the dyeing bath were extracted with MeOH 50%, having previously obtained the absorption spectra of these coloured solutions.

2.3.3. Dyeing procedure
Table 1 shows the outcomes of the cotton prepared by two dyeing procedures and the final pH of each stage:

Dyeing without mordant:
Soaked and unmordanted cotton was immersed in the dyeing solution (BTC) at 95ºC for one hour. After cooling the dyeing solution, the dyed cotton (C39) was rinsed in deionised water and dried under shade. One standard cotton was not dyed and kept as a control sample (C).

Dyeing with mordant:
The samples were mordanted according to two different methods. The first method involved using a chemical agent (1% acetic acid or ammonia). The second method used a mordant agent (Tin(IV) chloride 8%, Copper sulphate 8%, Potassium dichromate 8%, Ferrous sulphate 8% and Alum 15%). Mordants were dissolved in deionised water and heated to 90ºC, and then the scoured cotton was added. Stirring continued at this temperature for one hour, then dried under shade.

2.4. Instrumentation

Colorimetric analysis. Minolta CM-2600d spectrophotometer interfaced to a PC. Measurements were taken with the specula component excluded and included (SCE and SCI), using illuminator CIE D65 (6500ºK) and 10º standard observer (KONICA MINOLTA SENSING, Inc.).

UV-Vis Spectrophotometry. The spectra in the UV and visible region were measured with a HITACHI U2010 recording double-beam spectrophotometer. The work conditions were as follows: a spectral range of 200-1000 nm, a scan speed of 800 nm.min-1, a sampling interval of 1 nm, a slit width of 2 nm and a path length of 10 mm. Data were processed with UV Solutions software version 1.2. (HITACHI INSTRUMENTS, Inc.).

HPLC analysis. . HPLC analysis was carried out using a Waters 515 pump, a Waters 2996 diode-array UV detector (WATERS, Milford, MA, USA) and an injection port (Rheodyne 7725i) with a 20 µl loop (RHEODYNE, Cotati, CA, USA) with a Waters Millenium PDA workstation. The column used was 250 x 4.6 mm 5 µm, C18 Kromasil (Teknochroma).

SEM-EDX: The morphology of the cotton fabric's surface was characterised using a Jeol JSM 6300 scanning electron microscope which operates with a Link-Oxford-Isis X-ray microanalysis system. The analytical conditions were 20-kV accelerating voltage, 2×10µm 9A beam current and 15 mm as the working distance

Tensile testing
Tensile testing was conducted with the equipment donated by the *Smithsonian Museum Conservation Institute* (Washington D.C.). The equipment consists of a rectangular methacrylate box that contains several tensile testers. This box acts as a climatic chamber where relative humidity (RH) and temperature (T) can be controlled. The tensile testers are located in the upper part of the chamber whereas the light bulb and the tray are located on the lower level. A small fan circulates the air within the chamber. The fan accelerates the humidity absorption of the silica gel and creates stable and homogenous environmental conditions inside the chamber. A high precision dew point hygrometer is connected to the chamber and a small hygrometer is also located inside it. Tests were run at room temperature (23ºC) and relative humidity was controlled (45-50%).

2.5. Procedure

2.5.1. Colour measurement
The CIELab values of the dyeing were measured with a Minolta CM-2600d spectrophotometer (a sample diameter of 10 mm). One standard was used for each cotton sample, and the average was taken from among three measurements of the CIELab values L* a* b*

Name Sample	Chemical/Mordant agent, (%)	pH final		
		Chemical/Mordant bath	Mordant cotton	Mordant+Dyed cotton
C	--	7.30	--	--
C39	--	5.66	--	6.26
C35	CH_3COOH, 1%	2.76	--	3.70
C43	NH_3, 1%	10.99	--	6.76
C51	$SnCl_4$, 8%	1.67	2.26	4.96
C52	$CuSO_4$, 8%	4.02	4.41	5.30
C53	$K_2Cr_2O_7$, 8%	5.01	5.08	5.40
C48	$AlK(SO_4)_2\,12\,H_20$, 15%	2.94	3.49	4.81
C26	$FeSO_4\,7H_2$, 8%	3.64	4.54	4.77

Table 1. . Summary of the set of cotton samples

2.5.2. Chemical analysis

The analytical procedure consists of:

a. EXTRACTION OF THE CHROMOPHORES FROM THE TEXTILE MATRIX: Dyed cotton standards (C, C39, C35, C43, C51, C52, C53, C48, C26) (1-2 mg)) were hydrolysed for 10 minutes at 100ºC in an oven using 200µL HCl:MeOH:H2O (2:1:1) to cochineal.

b. CLEAN UP: The hydrolysed solution was purified on a PTFE 0.2µm filter and then dried.

c. CHEMICAL ANALYSIS:
The dried extract was then dissolved in 200 µl MeOH 50%. Aliquots of 50-100 µl volumes of the coloured phase were then analysed by UV-vis Spectrophotometry. Meanwhile, aliquots of 20 µL of the coloured extract were analysed by HPLC analysis.

c.1. UV-Vis Spectrophotometry: This coloured organic solution was measured using quartz micro cells 50 µl HELLMA in a spectrophotometer to obtain its visible spectra. The absorbance measurements were carried out in the range 300nm e 700nm.

c.2. HPLC analysis: Chromatographic separation in hydrolysate was carried out using a linear gradient system. The elution program was described in Table 2. Eluent A contained 5% ACN and 0.1% trifluoroacetic acid (TFA) in water. Eluent B contained 0.1% TFA in ACN. The flow was 1ml/min. The samples were injected into the column through a 20µl sample loop and ultraviolet absorption was recorded at 254nm.

Time (min)	Flow (mL/min)	%A	%B	Curve
0.0	1.0	90.0	10.0	Linear
5.0	1.0	90.0	10.0	Linear
35.0	1.0	10.0	90.0	Linear
40.0	1.0	10.0	90.0	Linear
45.0	1.0	90.0	10.0	Linear
55.0	1.0	90.0	10.0	Linear
Eluent A, 5% ACN and 0.1% TFA in water; Eluent B, 0.1% TFA in ACN				

Table 2. Phase programme for the gradient method

c.3. SEM/EDX analysis: in parallel with the morphological examination of cotton fabric micro samples, an elemental analysis was done by means of scanning electron microscopy combined with energy dispersive X-ray microanalysis (SEM-EDX). Samples were carbon-coated to eliminate charging effects. A qualitative analysis was done in the mapping distribution mode. The software came from Oxford-Link-Isis EDX.

2.5.3. Tensile testing

Force-strain diagrams are the result of the displacement of textile samples (mm/mm) under a constant increasing force over a given time. In this study, the force-strain diagrams provide a history of the mechanical behaviour of samples, and they help measure their breaking strength and elongation upon breaks, among others (Fuster-López et al., 2007: 115).

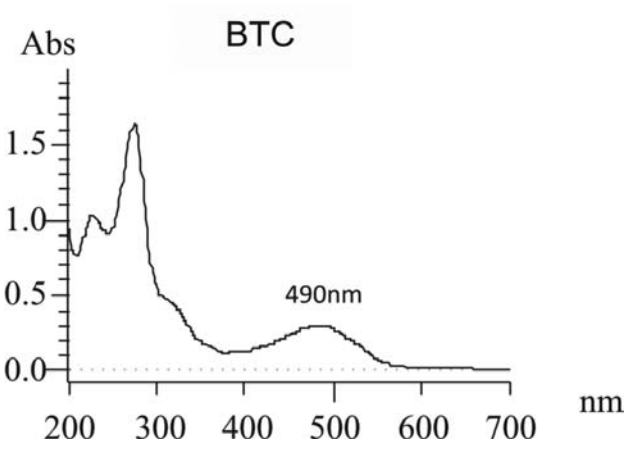

Figure 1. UV-Vis spectrum of extracted solution from dyeing bath with cochineal (BTC)

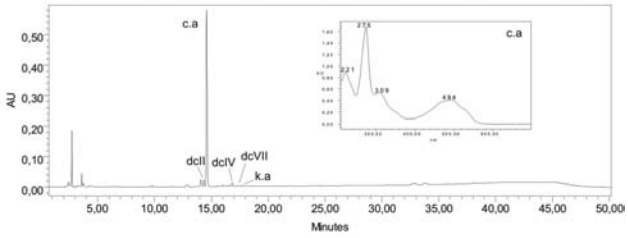

Figure 2. Chromatogram obtained for the cochineal dyeing bath solution (BTC).

The testing conditions were established according to Hacke's report (Hacke, 2006, unpublished report). Three identical samples were tested for each specimen. Samples (20 yarns) were obtained from each fabric and positioned in the tensile clamp. Additional fringed areas were retained at the edges. Measurements of the restrained cotton samples were made so that the applied force moved along the weft direction. Typically, samples measurements were: 0.61 cm (width) x 0.015 cm (thickness). A 10-cm gauge length was chosen for all the tensile tests to shorten the overall testing time (through shorter gage length) and to decrease the standard deviation (through a maximum number of yarns).

Specimens were mounted on the testing gauges and conditioned in the chamber for 24 hours at 48+/-0.5 % RH and 24+/-0.5 °C prior to testing. Then, strain increments of 0.0025 were progressively applied at 30-second intervals.

Standard Dyeing Bath	Retention time (min)	Peak	Absorption (nm)	Compound
BTC	14,34	dcII	219, 285, 433	dcII
	14,58	c.a	**221, 275, 309, 494**	**Carminic acid**
	16,84	dcIV	221, 276, 311, 492	dcIV
	17,40	dcVII	221, 276, 310, 492	dcVII
	17,76	k.a	273, 313, 491	Kermesic acid

Table 3. Chromatographic retention time (min) and absorption maxima (nm) for the solution obtained from the dyeing bath

3. RESULTS AND DISCUSSION

3.1. Spectral characterisation of natural dye from the dyeing bath

UV-Vis Spectrophotometry
The colour of a standard cochineal dyeing bath (BTC) was characterised by UV-vis spectrophotometry. An aliquot was taken of the dyeing bath and the spectrum of the extracted absorbance solution with MeOH 50% of cochineal was obtained. Figure 1 shows the UV-Vis spectrum of the extracted solution from the cochineal dyeing bath (BTC). The value of λ_{max} and the absorbance of the solution obtained by organic extraction were 490nm and 0.294Abs, respectively.

HPLC analysis
The chromatogram obtained for the extracted solution of a natural dye from a dyeing bath is shown in Figure 2 together with the UV-Vis spectra which identify the chemical species. The UV-Vis spectrum was obtained at a chromatographic peak and was considered similar to those spectra obtained by UV Spectrophotometry. The complete list of the examined dyeing bath is shown in Table 3, together with retention times under the chromatographic conditions used.

3.2. Spectral, chemical and mechanical properties of dyed cotton standards

The chromatic, chemical and mechanical effects resulting from the interactions between cochineal dye and the cotton fabric were analysed with eight cotton standards.

Cotton standard	L*	a*	b*
C	88,3 ± 0,7	2,867 ± 0,006	-11,897 ± 0,006
C39	87,75 ± 0,06	6,4 ± 0,1	-5,39 ± 0,05
C35	79,1 ± 0,4	16,4 ± 0,9	12,1 ± 0,8
C43	87,814 ± 0,008	6,11 ± 0,02	-5,23 ± 0,03
C51	82,97 ± 0,04	7,981 ± 0,007	3,972 ± 0,013
C52	70,47 ± 0,02	12,50 ± 0,04	-4,381 ± 0,013
C53	60,24 ± 0,03	15,82 ± 0,03	-8,46 ± 0,02
C48	63,7 ± 0,1	16,02 ± 0,08	-7,65 ± 0,05
C26	61,92 ± 0,06	2,96 ± 0,02	5,78 ± 0,02

Table 4. L* a* b* (CIELab) values of the cotton standards: C, undyed cotton and dyed cotton samples

Colorimetric analysis
Values L* a* b* (CIELab) of the standards of the undyed and dyed cottons presented in Table 4 show the chromatic coordinates of each sample obtained from different dyeing processes.

The shown lightness values indicate that light colours were used. The value of L*of the control cotton fabric (C) corresponds to the colour white; however, the redness (a*) and yellowness values (b*) indicate a white tone that is slightly blue in colour. For dyed cotton, all the samples contain positive values towards a* (redness). This means that they are reddish colours, ranging from the highest values among the colour samples (C35, C48, C53 and C52) to the lowest values of the samples (C51, C39, C43 and C26?. On the other hand, purplish or orange-type colours can be distinguished given that samples C53, C48, C39, C43 and C52 display a bluish component, (b* < 0) while samples C35, C26 and C51 display a yellowness component (b*> 0), respectively.

UV-Vis Spectrophotometry
After obtaining the spectrum of the colorant's absorbency from the dyed cotton, a transparent and coloured solution was obtained. For this purpose, an extraction and acid hydrolysis process was carried out with an organic solvent (MeOH 50%) of the dyed cotton. The was unable to detect the spectrophotometer values of λ_{max} max and the absorbance values of the solutions obtained because the carminic acid concentration was lower than the detection limit of the analytical instrument. This scenario indicates that natural dye is not the most suitable dye to colour this type of cellulosic textile fibre as neither the dyeing processes with chemical agents nor mordants have achieved a sufficient level of concentration to be detected.

HPLC analysis
Figure 3 shows the HPLC-PAD chromatogram obtained for the different dyed cotton samples. The time taken for one analysis was approximately 30 min.

From the chromatograms, we can observe that carminic acid had been identified in all the analysed samples as the extraction method was optimum in all the cases despite the small amount of dye in the fabric. In sample C35, which corresponds to the acid agent dyeing, we can also identify peaks dcIV and dcVII, which implies that its absorption ability is greater than the rest of the agents. While using Fe (II) as a mordant agent, as with sample C26, we were unable to identify any peak. This would indicate that the carminic acid concentration was so low that it was impossible to identify a peak.

SEM/EDX analysis
The morphology of yarns from control and mordanted cotton samples at the micrometer level is shown in Figures 4a–5a. Mordant agents were identified by SEM/EDX; X-ray energy spectrum and EDX analysis in the mapping distribution mode and are shown in Figures 4b-5b.

The elemental distribution of each mordant agent in cotton fibres was uniform, except for Sn where precise agglomerations were observed in the fibre (Figures 5b and 6).

The standardised, quantitative results obtained by means of the ZAF method indicate that both CuO and Cr2O3 and Al2O3 and FeO are found in a similar concentration, while SnO2 was of a greater concentration which could be indicative of its superficial deposits on cotton fibres. (Table 5). Its presence was also observed in each Si sample at a concentration that oscillated between 36.60-85.28% SiO2 in samples C51 and C53, respectively, whereas the cotton control (C) contained 91.75% SiO2. The presence of Si in the cotton textiles was linked to a silicone treatment carried out by same the manufacturer of the commercial fabric. Silicone as a textile finishing is conventional as it enables an enrichment and/or modification of the final quality of fabrics. It is mainly used to provide different fabric properties which include its quality to the touch, hydrophilic properties, seam durability, antistatic effects, brightness, physical state and resistance to tearing. (CEPIS/OPS, 2007.) It is also used as softeners which have proved very interesting as they achieve a soft, smooth feel together with an improvement in washing (speed) and use, as well as providing the fabric with other properties (Carrión, 2001: 11; Carrión and Serra, 1997: 61).

Sample	SiO_2	SnO_2	CuO	Cr_2O_3	Al_2O_3	FeO
C	91,75	--	--	--	--	--
C51	36,60	63,10	--	--	--	--
C52	82,34	--	9,44	--	--	--
C53	85,28	--	--	14,72	--	--
C48	63,32	--	--	--	36,44	--
C26	47,98	--	--	--	--	29,44

Table 5. Chemical composition of the studied control and mordanted cotton samples expressed as the weight % of the indicated oxides obtained by means of SEM-EDX

Tensile testing
The tests carried out clearly show that the cotton dyeing processes with cochineal, in terms of the research matter in question, significantly modify behaviour.

The following graph (Figure 7) highlights the waste generated in the cotton fabric's resistance, as well as some loss of its stretching capacity which renders the material more vulnerable to tears. This could be interpreted as an obvious weakness, so the results are more interesting from the antique fabric conservation viewpoint

However, the most interesting results were observed when both the dye and the cotton fabric sample were subjected to the mordanting process. As Figure 8 depicts, the presence of metal salts can dramatically modify the behaviour of the tested cotton samples. Those samples that did not undergo the mordanting process contained 2 N/yarn unlike the samples containing mordants which

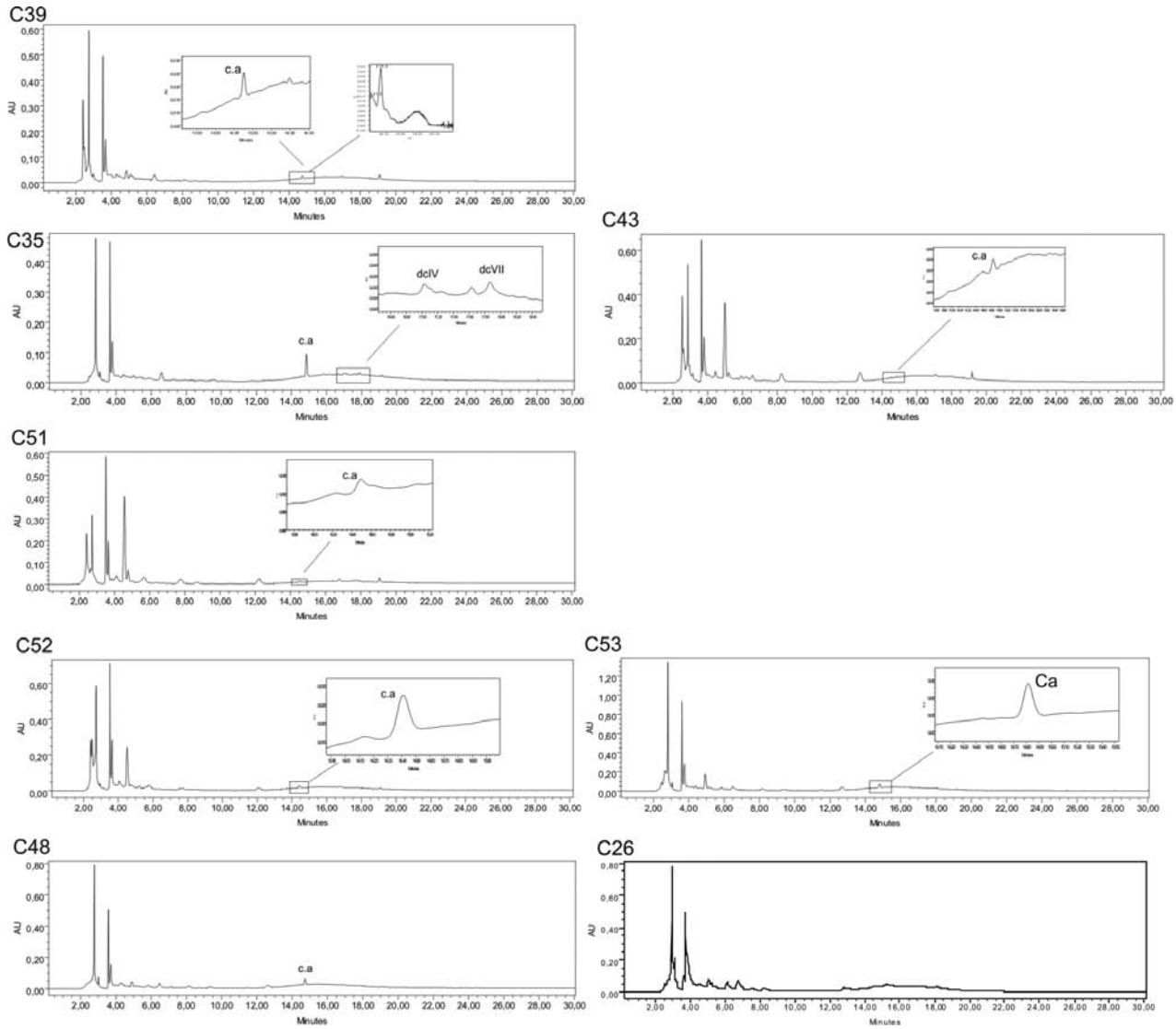

Figure 3. Chromatogram of the different dyed cottons

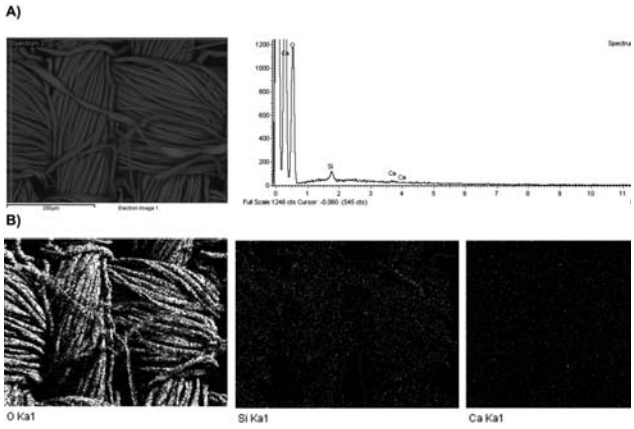

Figure 4. a) SEM backscattered electron image of the cotton control (C) and b) X-ray energy spectrum and EDX analysis in mapping distribution mode.

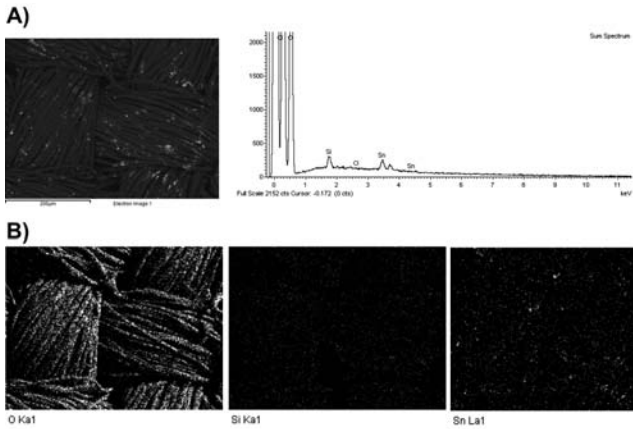

Figure 5. a) SEM backscattered electron image of the C51 sample and b) X-ray energy spectrum and EDX analysis in mapping distribution mode.

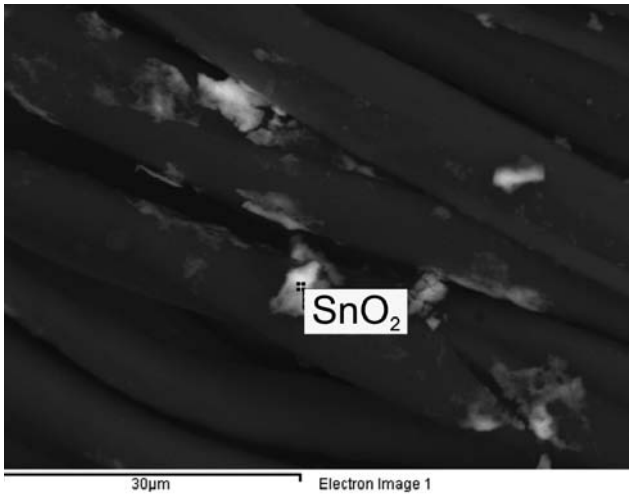

Figure 6. SEM backscattered electron image of the C51 sample. Detail 2000X.

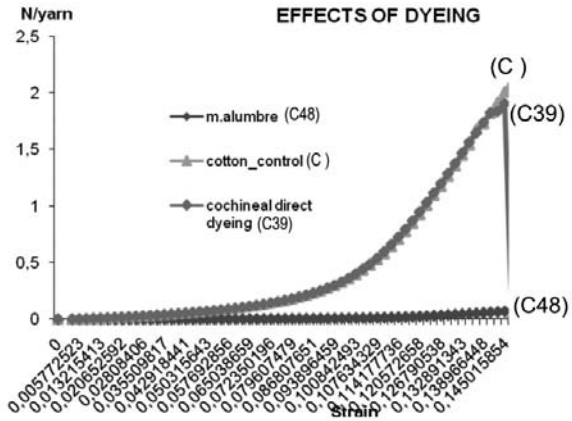

Figure 8. Correlates the force per yarn and the dimensional response of warp yarns of control cotton (C), C39 (cochineal direct dyeing, without mordant) and C48 (cochineal dyeing with alum mordant agent) (23ºC, 48% RH).

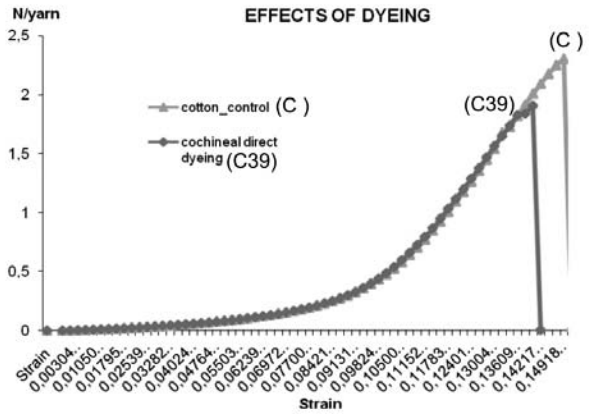

Figura 7. Correlates the force per yarn and the dimensional response of warp yarns of control cotton (C) and cochineal dyed cotton specimen (C39) (direct dyeing, without mordant) (23ºC, 48% RH).

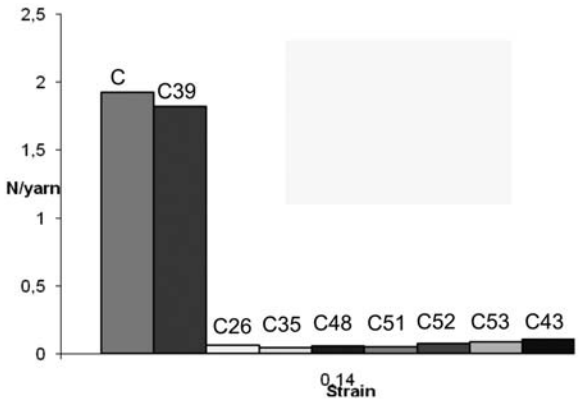

Figure 9. Correlates the force per yarn and the dimensional response of warp yarns of control cotton (C), C39 (cochineal direct dyeing, without mordant) and cochineal dyeing with mordant/chemical agents specimens (23ºC, 48% RH).

barely reached 0.5 N/yarn. In general terms and without providing details of each mordant specific effects given their chemical nature, we may obviously predict that a mordanted fabric will be much more prone to deterioration than one exclusively subject to what is known as direct staining (the absence of mordants). To date, we have been aware that the presence of metal salts not only modified the pH of the dyeing substances, but also catalysed the fabric's deterioration. This investigation enables us to know the extent of this process.

Figure 9 illustrates the different behaviours of the cotton samples (dyed and controls) in comparison with the same samples but in the presence of different mordants used for the same deformation value.

A more detailed analysis reveals special features in relation to the natural chemistry of the different mordants (Figure 10).

Therefore, the cotton samples mordanted with alum (C48) clearly show that the presence of cochineal causes certain behavioural differences. The fabric still maintains the same resistance and appears to be more rigid with less possibility of deformation due to the combined action of dyeing and mordanting, as seen in the following graph (Figure 11).
The same occurred in those samples that had been mordanted with chloride and tin (C51) (Figure 12). Their rigidity increased, but their elongation decreased. Moreover, the samples' resistance was significantly lower (0.9 N/yarn) than that of the samples mordanted with alum (C48) (0.11 N/yarn). This confirms that certain mordants can dramatically compromise the integrity of a fabric. This behaviour would be in line with the properties of both metal agents. On the one hand, the final pH of a fabric mordanted with tin is more acidic than one mordanted with alum (Table 1) (pH 2.26 versus 3.49, respectively). This fact indicates that it is easier to produce a hydrolysis process with cotton than with tin. On the other hand according to the normal redox potential (oxidizing-reducer species character), we would have the redox couple $Sn^{4+} + 2e = Sn^{2+}$ 0.15V / $Sn^{2+} + 2e = Sn$ -0.14V and the redox couple $Al^{3+} + 3e = Al$ -1.66V,; in other words, tin presents two active species. Sn4+ and Sn2+. The former is of an oxidizing character, and the latter is of a more reducing nature than the typical character of an aluminium reducer, which makes it a species that causes more damage to the chemical structure of the textile.

The following graph (Figure 13) indicates that, for the same deformation value, the strength of a cotton sample dyed with cochineal and mordanted by chloride and tin (C51) is significantly greater than that of an undyed mordanted sample.
This pattern is repeated with all the studied mordants. However, we

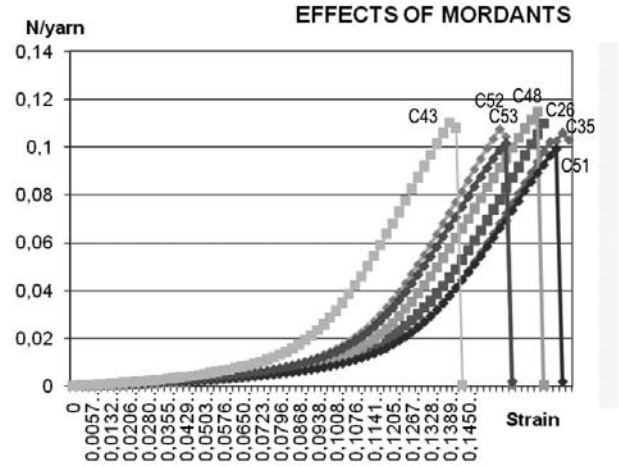

Figure 10. Correlates the force per yarn and the dimensional response of warp yarns of cochineal dyeing with mordant/chemical agent specimens (23ºC, 48% RH).

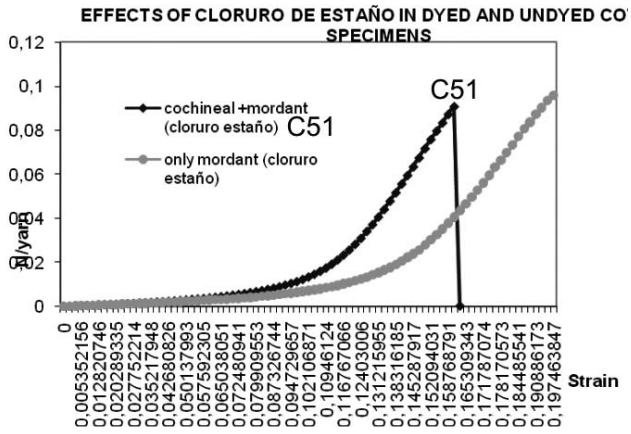

Figure 12. Correlates the force per yarn and the dimensional response of warp yarns of cochineal dyeing with tin(IV) chloride mordant agent (C51) and tin(IV) chloride mordant cotton (23ºC, 48% RH).

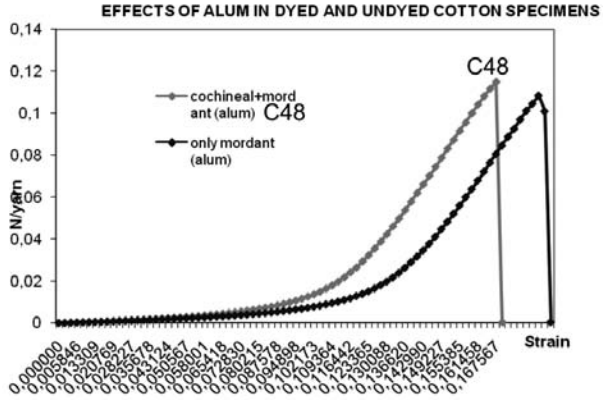

Figure 11. Correlates the force per yarn and the dimensional response of warp yarns of cochineal dyeing with alum mordant agent (C48) and alum mordant cotton (23ºC, 48% RH).

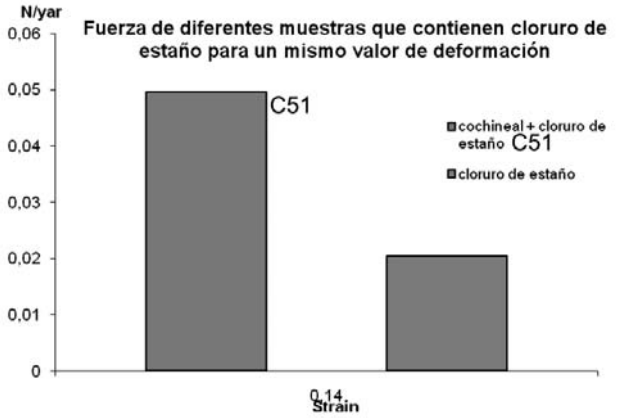

Figure 13. Correlates the force per yarn and the dimensional response of warp yarns of cochineal dyeing with tin(IV) chloride mordant agent (C51) and tin(IV) chloride mordant cotton (23ºC, 48% RH).

may conclude that the most significant differences were observed with tin-mordanted samples (C48), while iron sulphate barely induced differences when used with dyed samples (C26). This coincides with the HPLC analysis which was unable to identify the carminic acid peak, thus indicating the poor relationship between the mordant and this natural colourant on cotton fabric.

When dyeing cotton with a chemical agent, for instance, acetic acid for C35 and ammonia for C43, even though both samples still showed a similar resistance, the former displays more elongation capacity, that is, a greater capacity for deformation before tearing. Conversely, the samples containing ammonia deform less before a tear, which indicates that the more rigid samples are more likely to rip than the others mentioned before (Figure 10). In the C35 sample, the acidic agent hydrolysed the H bridges that made up the torsioned beams of the cell structure, while the basic agent did not distort the twist.

4. CONCLUSIONS

The present study indicates the importance of combining different technological advances, such as advances in analytical and mechanical tests, in the field of conservation and for restoration works with textiles. The results obtained in this study into the analytical characterisation and the study of the mechanical properties of new cotton fabrics, show differences between sample controls and the samples dyed with cochineal. The different direct dyeing and mordant dyeing methods clearly provide a distinct answer thanks to their mechanical properties. Using cochineal dye in the direct cotton dyeing process is not very effective, while the processes of dyeing with mordant agents offers a larger amount of natural dye and has, therefore, a higher dyeing success rate. However, the analyses by colorimetry, spectrophotometry and HPLC highlight that the amount of natural dye attached to the cotton fibre is less and has very light tones which are not very vivid. The SEM/EDX analysis reveals the presence of both metal mordant agents and the presence of Si in those cotton textiles bound with a type of silicone treatment, as in textile finishings or with softeners.

From the mechanical testing viewpoint however, one can establish the presence of a mordant that substantially modifies the mechanical properties of cotton fabrics, which is more demonstrative with samples that have also been dyed. It is obvious that the presence of mordants indicates that a fabric has been subject to bathing in substances that are generally acidic and that cause irreversible damage to fibres. However in terms of the ageing process of a fabric, not all the mordants have the same effect or act to the same extent.

Knowledge of this phenomenon can help us to understand why certain historical fabric samples are selectively damaged, which we may conclude is owing to the different shades present in their physical composition. Accordingly, the same sample could contain perfectly conserved parts while others have been completely worn out by both environmental factors and the characteristics of the material in question.

This research reveals that the cochineal dyeing process considerably lowers the resistance of cotton fibres due to the colourant's acidic nature (carminic acid). The presence of mordants also vastly modifies the behaviour of cotton fibres. It can be said that the dyeing process that a fabric is submitted to weakens it irreversibly. The presence of carminic acid causes fibres to fade as their resistance is affected substantially, and they progressively lose their deformation capacity before tearing. Likewise, the loss of flexibility of the cotton is also noted in most cases. It is even possible to establish special features by studying the nature of the different mordants used in the samples, for instance, in terms of the pH of the fabric after being mordanted, and the redox potential present in each kind. With cotton samples dyed with a basic chemical agent (NH3), unlike samples mordanted in the presence of an acidic chemical agent (acetic acid), we may deduce that owing to the hydrolysing action of the acidic agent, the hydrogen bonds which make up the torsioned beams in the cellulose are samples that present a greater elongation capacity. Meanwhile, the basic agent does not affect torsion, therefore more rigid samples may tear earlier.

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Versión española

TITULO: ***Estudio de la cochinilla presente en los tejidos de algodón teñidos. Identificación química y análisis de cambios inducidos en las propiedades mecánicas de las muestras teñidas.***

RESUMEN: *La presente investigación detalla el empleo de la cochinilla como tinte natural de tejidos de algodón en piezas textiles de valor histórico. A partir del volcado y optimización de recetarios y fórmulas tradicionales son elaboradas muestras de referencia mediante procesos de tinción directa y con mordientes. La fibra de algodón, el ácido carmínico presente en la cochinilla así como los mordientes son caracterizados mediante técnicas espectroscópicas (Espectrofotometría UV-Vis), cromatográficas (HPLC-DAD) y microscópicas (MO y SEM/EDX). Así mismo, han sido desarrollados ensayos de tracción en sentido trama para cada una de las muestras. A partir de las curvas esfuerzo deformación obtenidas, el estudio plantea la comparación entre el comportamiento de cada una de las muestras atendiendo a cuestiones tales como la flexibilidad y rigidez así como su capacidad de elongación y resistencia máxima en determinadas condiciones de temperatura y humedad. Los resultados obtenidos demuestran que los diversos procesos de tinción provocan diferente respuesta en las propiedades mecánicas y dimensionales del tejido tratado, observándose una gradación de comportamiento dependiendo del agente de mordentado empleado.*

PALABRAS CLAVES: *algodón, cochinilla, carminic acid, mordant agent, test de tensados, análisis colorimétrico, UV-Vis Spectrophotometry, HPLC-DAD, SEM/EDX*