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STUDIES ON WOOLLEN THREADS FROM HISTORICAL TAPESTRIES

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Abstract:

Fourier transform (FTIR) attenuated total reflectance (ATR) and second derivative spectroscopy has been used for the first time to evaluate the state of degradation in historical woollen threads from the collections of Flemish tapestries (15th-17th centuries) in the Royal Palace, Madrid, Hampton Court Palace, and museums in Brussels. The work was performed as part of the EC-funded project 'Monitoring of Damage in Historic Tapestries', also known as the MODHT project [1]. The overall aim was to develop procedures for recognising tapestries at risk and provide analysis for informing collection care. Prior to the testing of the historical threads, model tapestries were prepared according to traditional techniques of weaving and dyeing. They were then subjected to accelerated light ageing. This paper reports on the part of the MODHT project in which ATR-FTIR was used. It was selected since it is a non-destructive method, and also because it has previously been used to study the oxidation products of cystine in wool and to provide a semi-quantitative assessment of change [2]. Evaluation was conducted on the model tapestries, and the cysteic acid peak was selected as the marker for change, as it showed a systematic change with light ageing. The same marker was used to assess the change in historical threads.

Key words:

15th-17th century woollen threads, damage assessment, keratin, ATR-FTIR

Introduction

The renowned tapestries woven in European cities from the 15th to the 17th centuries are among some of the most valuable testimonies of European cultural heritage. Their survival, however, is at risk because of ongoing degradation processes operating in the coloured wool and silk threads, combined in some cases with metal threads. As part of the EC-funded programme 'Monitoring of Damage in Historic Tapestries' (MODHT) [1], studies have been performed on the characterisation of dyes and threads in selected 15th-17th century Flemish tapestries manufactured in Brussels, Bruges, Antwerp and Arras, and are currently in Spanish, British and Belgian collections [3, 4, 5, 6, 7]. This is the first time that a comprehensive interdisciplinary study has been made using complementary analytical techniques which included chromatographic, mechanical and colour measurements [3, 4, 5], thermoanalytical [6] and X-ray analytical techniques [7]. The overall aim was to identify markers of physicochemical change. To assist with the interpretation of the results from the historical samples, model samples of wool threads were dyed with appropriate natural dye sources based on traditional dye recipes (Table 1). This paper will focus on the ATR-FTIR studies on woollen threads which were performed as part of the damage assessment of the model and the historical tapestries.

Previous studies have demonstrated that cystine residues in wool play an important part in stabilising the wool fibre's structure [2]. The chemistry of wool is dominated by S-atoms of the disulphide bonds formed between residues of amino-acid cystine. During photodegradation, the cystine residues are oxidised into cysteic acid residues (C-SO³⁻) by way of the oxidation products cystine S-monoxide and cystine S-dioxide. The formation of S-sulphonate (Bunte's salt) also occurs. The infrared frequencies of oxidised cystine species have been documented (Table 2). Second-derivative spectroscopy has also been used to resolve these peaks and measure the derivative peak areas, in particular those of the cysteic acid and Bunte's salt. In fact, FTIR attenuated total reflectance (ATR) second-derivative spectroscopy has become one of the standard methods for the semi-quantitative assessment of chemically modified textile surfaces [2, 8]. Another study used this approach to characterise the

surface composition of low-temperature plasma-treated wool fibre [9]. It was found that the presence of the functional groups which correspond to oxidised cystine residues influences the properties of the wool fibres. Their band frequencies were selected, and the absorbance values were divided by the absorbance of the Amide III frequency (at 1232 cm^{-1}) which then served as an internal standard [9]. This approach was used in the current study to assess the amount of cysteic acid which formed on light ageing in the model samples, and which was also present in the historical threads.

Experimental

Samples

The model tapestry samples were woven by our project partners at the University of Manchester for use as test samples. Altogether, 22 woollen tapestries (wool in warp and weft directions) were produced. Each was woven from yarns dyed with an authentic dye recipe translated from primary sources [3, 4]. The dyes used included madder and cochineal (red), weld and dyer's greenweed (yellow), woad (blue), mixtures of weld and woad (to give two shades of green), and the mordants oak gall, alder bark, and alum (Table 1). For dyeing black samples, iron sulphate (alone or together with copper sulphate) was added to oak galls or alder bark. The chemical basis of the dyes used are as follows: red dyes are anthraquinone-based, yellow are flavonoid dyes and mordants (oak gall and alder bark which contain tannins). These are natural substances, which have a number of free phenolic hydroxyls allowing the formation of stable crosslinks with proteins [10]. Comprehensive descriptions of the materials used for the reproduction of the traditional dyeing processes are provided elsewhere [3, 4]. Dyes and mordants which were representative of the materials used in the 15th to 17th centuries were selected. In addition, the dyes selected are known to have a differential response to light ageing in both UV and visible radiation [11]

Several hundred historical samples were taken from 17 tapestries during the project, covering a range of colours and locations. Most were taken from the reverse side, where loose threads (weft) left by the weavers enabled samples to be taken without disrupting the weave structure.

Accelerated ageing

The accelerated ageing was carried out at the Hampton Court Palace Textile Conservation Department according to standard BS EN ISO 105-B02 using an industrial light-ageing machine (Xenotest 150S) housing a xenon arc lamp with continuous spectral distribution to replicate sunlight through window glass. UV filters were used to modify the spectral distribution to that of sunlight through window glass, and IR filters were used to minimise heat gain [5]. The relative humidity was controlled to $65 \pm 2\%$, and the temperature to $20 \pm 2^\circ\text{C}$. The illuminance of the sample surface was maintained at 150,000 lux for 200, 400, 600 and 800 hrs for the undyed samples, which corresponds to 30, 60, 90 and 120 Mlux.hrs expressed in terms of received light dosage levels. Studies of the undyed samples showed that an exposure of 60 Mlux.hrs produced a measurable difference in the physical properties of the woollen tapestries. This approximates to a light exposure which may have been received by a 400-year-old tapestry. This estimation is based on archival research and current illumination levels [5]. The levels of light ageing were designed to cause damage to the fibres and so simulate the damage to historical tapestries. Given the number of dyed samples, this value was then used to age the dyed samples. In some cases, higher dosage levels of 120 Mlux.hrs were also used.

The Fourier Transform Infra-red Spectroscopy with Attenuated Total Internal Reflectance (ATR-FTIR) mode of measurement

The Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectra were recorded using a Perkin-Elmer 2000 FTIR spectrometer equipped with a TGS detector and a SensIR Technologies Durascope placed in the sample compartment. This was fitted with a diamond internal reflectance element (IRE) held at 45° to the incident beam. Under these conditions, the depth of penetration into the sample at 1050 cm^{-1} is approximately $2\ \mu\text{m}$ [8]. The spectra of the irradiated samples were recorded with the exposed side of the thread and/or fabric in contact with the IRE. Spectra within the range of 4000 to 800 cm^{-1} were collected at a resolution of 4 cm^{-1} . The FTIR data were processed using GRAMS32 AI software by Galactic®. All the spectra are the result of the co-addition of 16 scans. Reproducibility of the measurements was ensured by keeping the contact force

between samples and the diamond crystal identical, using the electronic graded scale of the Durascope. For the historical tapestries, measurements were carried out directly on the thread samples, which were less than 5 mm long. Evaluation of the accelerated light-aged model tapestries was performed by measuring the light-exposed surface of the fabric to ensure analysis of the maximum deterioration effect. Prior to analysis, all spectra were normalised at the peak height of Amide III (1232 cm^{-1}) based on previous studies on the degradation of wool [9]. The need for normalisation arises from experimental differences that may not be controllable in ATR spectra, variances in sample size and the contact between the sample and the Internal Reflective Element. The area of the relevant signal (cysteic acid) in the second-derivative spectrum was then measured and used as an index of damage.

Results and Discussion

Undyed wool, light-aged

Figure 1 shows ATR-FTIR spectra, within the region 1800 cm^{-1} to 800 cm^{-1} , of undyed wool together with light-aged wool (30, 60, 90 and 120 Mlux.hrs). In the undyed unaged wool, characteristic bands of proteins appear: (1) Amide I at 1650 cm^{-1} , which is indicative of alpha-helical structures, is mainly associated with the C=O str. vibration and is directly related to the backbone conformation; (2) Amide II at 1538 cm^{-1} corresponds to N-H bending and C-N str. vibrations; (3) Amide III at 1230 cm^{-1} corresponds to the in-phase combination of C-N stretching and N-H bending, with some contribution from C-C stretching and C=O bending vibrations. The latter is a complex band, and depends on the nature of side chains and hydrogen bonding [12]. The spectrum of undyed washed wool is also shown in Figure 1. This was from a sample which was subjected to the same boiling time as those which underwent the dyeing process (20 minutes at 80°C). It shows almost no alteration compared with the unwashed sample.

With the light-aged samples, changes can be seen in the Amide I and Amide II regions, as indicated in Figure 1. In Amide I with ageing, there is a broadening with evolution of structure at about 1670 cm^{-1} and in the region of 1720 cm^{-1} . This indicates (1) an increase in disordered structures and (2) the possible formation of fatty acids from the oxidation of lipids in wool. Fatty acids contain a carbonyl group which absorbs infrared radiation between 1715 and 1725 cm^{-1} . There is a reduction in the intensity of the Amide I band, which can be attributed to the rupture of peptide and disulphide bonds [2]. After 30 Mlux.hrs there was some absorbance decrease of the Amide II band (1538 cm^{-1}) and some broadening of the Amide III peak (to the right side of the peak), toward shorter wave numbers. The broadening could be due to the changes in H-bonding which occur upon the denaturation of keratin protein, and which affect the shape of the Amide III peak. There is also an evolution of the peak at 1170 cm^{-1} that could be attributed to formation of ester bonds in the amino-acid residues, reflecting COOC stretching [13].

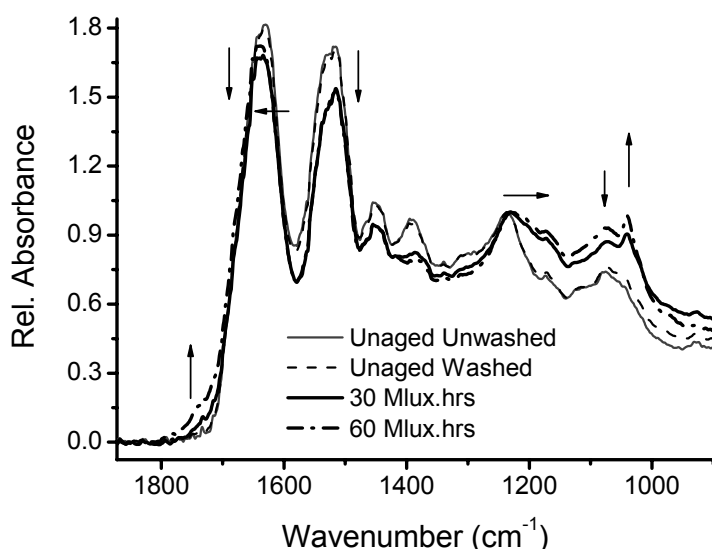


Figure 1. ATR-FTIR spectra of unaged undyed samples, together with light-aged undyed samples showing changes in the Amide I, II and III peaks and the evolution of cysteic acid at 1040 cm^{-1}

Most significant changes occur in the region $1170\text{--}1000\text{ cm}^{-1}$. Figure 2 shows the spectrum and second-derivative of undyed wool in this region. The peaks for the oxidised residues of amino-acid cystine are marked. The corresponding peak areas of the second-derivative peaks for cysteic acid and S-sulphonate (Bunte salt) were measured using GRAMS software.

The result for the light-aged undyed samples have been plotted against the light dose received (Figure 3). There is an increase in cysteic acid up to 60 Mlux.hrs, and then the rate

of change slows down. For this reason, 60 Mlux.hrs was selected for the light ageing of the model dyed samples. Some of the dyed samples were also aged at 90 and 120 Mlux.hrs to determine whether the presence of dye caused any further changes. The areas of the cystine monoxide peak decreased on exposure, as observed in other studies [2, 9]. The levels of Bunte's salt showed a slight increase with light ageing.

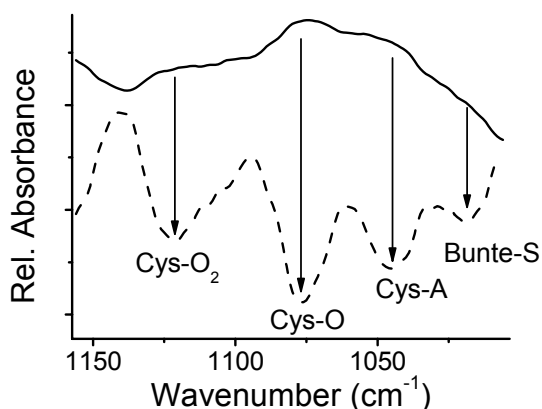


Figure 2. ATR-FTIR spectrum together with the second-derivative, also showing the location of oxidised cystine acid residues

Mlux.hrs. Given that the sulphonate absorbance band, which represents the abundance of cysteic acid, had the strongest signal increase, the area of the 1040 cm^{-1} peak (as integrated in the second derivative FTIR spectra) was chosen as a reliable marker to represent the oxidative damage of the model and historical wool samples. This will be referred to as the Cys-A index.

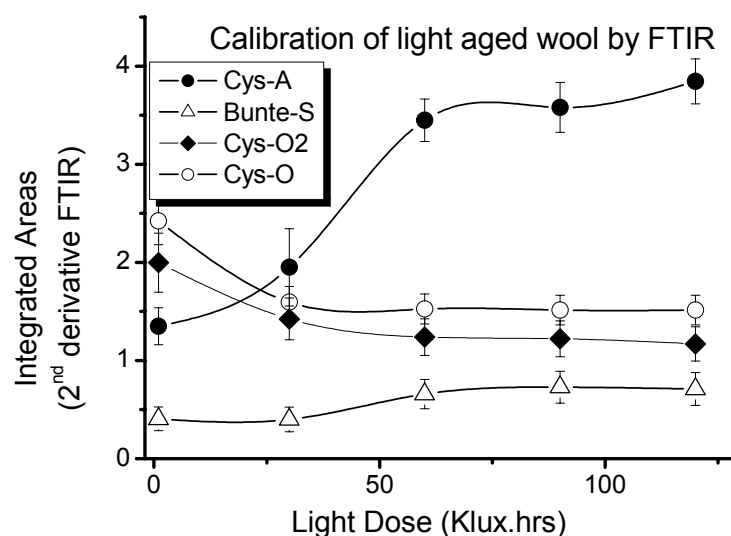


Figure 3. Area of peaks of cystine oxidation products (second-derivative spectra) against the received light dose (Mlux.hrs)

least oxidative influence to the wool as evaluated using the cysteic acid parameter was obtained by alder bark, whereas oak gall and alum had a greater effect (Figure 4). Oak gall resulted in a direct decrease of Amide I and II, a broadening of Amide III and a large increase in the cysteic acid peak. Alum had a smaller effect than oak gall with respect to the Amide I and II absorbances. However, a strong absorption peak occurred between 1200 and 980 cm^{-1} for mordanted wool using alum, obscuring the characteristic peak at 1040 cm^{-1} . Thus, the Cys-A indices of the undyed but mordanted wool-only samples were measurable only for alder bark and oak gall (Table 3).

Figure 5 below shows that mordant oak gall exhibits more damage than the most light-aged sample even before ageing. Further light ageing shows only a small increase. In comparison, alder bark shows no change in the threads, which remains true after ageing as well.

For this reason, second-derivative FTIR spectra were used to provide semi-quantification of the observable oxidative changes (Figure 3). This was carried out by integrating the corresponding peak areas. The small reduction rate shown for cystine mono- and dioxides could be attributed to their strong reactivity compared to the parent disulphides [9], and their intermediate role in the oxidation of cystine products based on the sequence disulphide \rightarrow monoxide \rightarrow dioxide \rightarrow sulphonic acid [9]. The small increase in the S-sulphonate was expected [2, 9]. The cysteic acid signal increased strongly with light, as can be observed directly on the actual FTIR spectra [2, 9]. Based on the trends, it is demonstrated that accelerated light ageing has maximum degradation effects up to a light dose of 60

Model dyed tapestries

The samples of model dyed tapestries were measured before and after accelerated light ageing (60 Mlux.hrs). Natural dyes were used to provide the following colours: red (madder, brazilwood and cochineal), blue (woad), green (weld and woad), yellow (weld, dyer's greenweed) and black (oak gall, alder bark, FeSO_4 , CuSO_4 & FeSO_4). In addition, mordants, alder bark, alum ($\text{Al}_2(\text{SO}_4)_3$), and oak gall based on traditional dyeing recipes were used (Table 1) [5].

Effect of mordants

The ATR-FTIR spectra of the mordanted samples showed that the

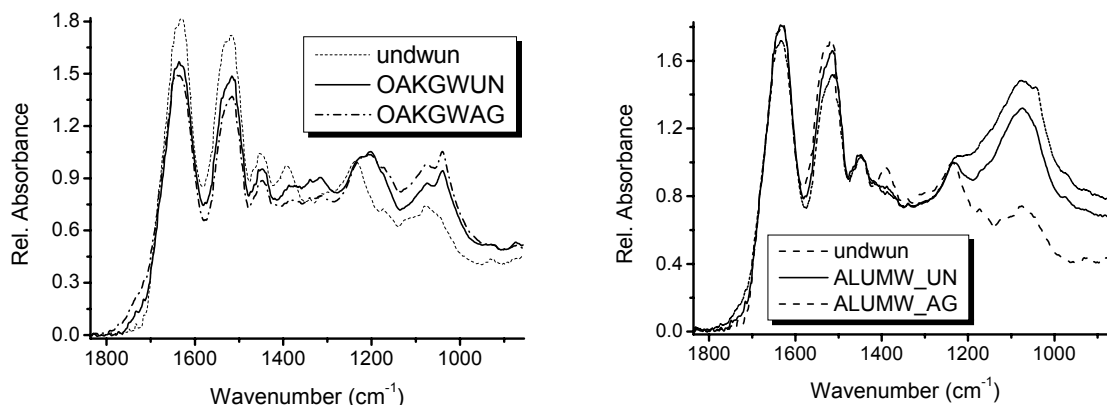


Figure 4. ATR-FTIR (region 180-800cm⁻¹) shows the influence of mordants: oak gall shows the distinctive formation of cysteic acid, whereas alum shows a significant contribution in this region which obscures the cysteic acid signal

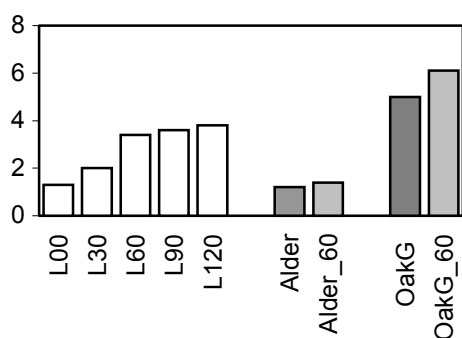


Figure 5. CyS-A index vs sample type (unaged and aged) for undyed and mordanted wool

Effect of dyes

Figure 6 shows the changes in the Cys-A indices of the model black-dyed wool samples as a function of light exposure. All values are given in Table 3. The series of the black-dyed wool samples, dyed using FeSO₄ (and FeSO₄ and CuSO₄) and oak gall were significantly influenced (BlackW1 and W2), with the Cys-A indices being 3.5 and 3.8 respectively, almost equal to the undyed wool after receiving 60Mlux.hrs light dose. Black W2, after receiving a 120 Mlux.hrs light dose, had a Cys-A index of around 7, which was almost double the value of the corresponding undyed black sample. However, black W3 and W4 samples which were mordanted using alder bark showed significantly lower values, which then increased upon light ageing.

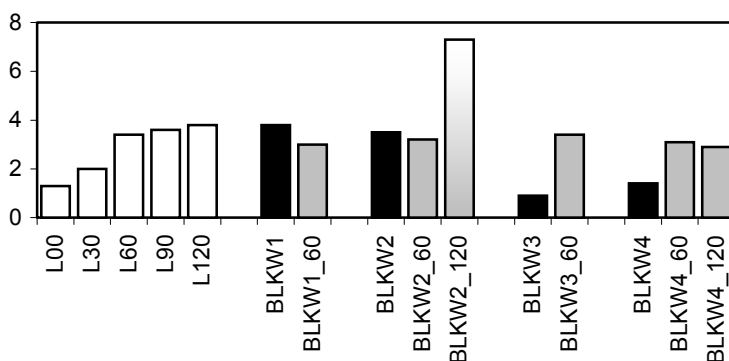


Figure 6. CyS-A index vs sample type (black dyed samples BLKW1-4)

The conditions used during the dyeing may also have a differential effect on the state of the dyed wool. To illustrate this, examples of woad, weld, and madder will be discussed. Woad dyeing was carried out according to medieval practice, in a woad vat by bacterial reduction at 45-50°C at slightly alkaline pH (pH 8.2-8.5). Weld dyeing involved first boiling with alum mordant (pH = 4) for 2 hrs, and then boiling with weld and potassium carbonate (pH = 10.2) for 1 hr.

The ATR-FTIR spectra did not show a difference in the unaged samples (Figure 7). However with light ageing, weld-dyed samples showed a significant difference (Figure 7). Weld contains the flavanoid luteolin, which exacerbates phototendering compared with undyed wool or fibres [13]. Phototendering refers to changes in the tensile strength and elasticity of the fibre.

With red madder (anthraquinone dyes), materials were boiled for 2 hrs under very acidic conditions (pH=3). In addition, oak gall mordant was used. As a result, there is a significant change in light ageing, shown by both the ATR-FTIR spectra (Figure 8) and the mechanical response to the controlled relative humidity programme, which shows that weld has a stronger response to moisture

than woad. The red W2 has quite a different response, which could be due to the crosslinking induced by oak gall mordant. This has been reported elsewhere [10].

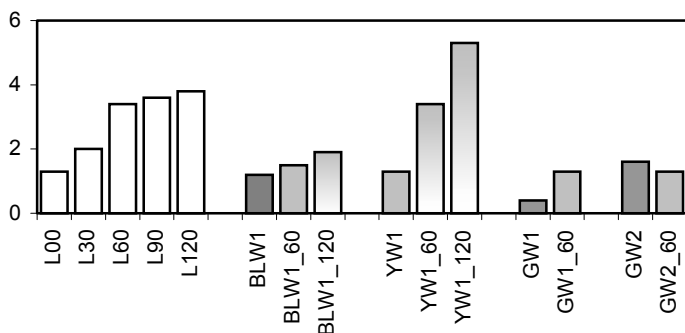


Figure 7. CyS-A index vs sample type (BLW1-woad, YW1-weld, GW1-weld and woad, GW2-woad and weld) unaged and aged (60 and 120 Mlux.hrs)

Despite the ability to provide a Cys-A index calculation in these cases using the second derivative FTIR spectra, it was decided not to compare such results with the those from samples that have a better resolved fingerprint region (in the region below 1150 cm^{-1}). An example of two different historical wool samples from Hampton Court Palace, London is demonstrated in Figure 9, where sample HRP1/10 (Group A) provides reliably better data than sample HRP3/23 (Group B), which had a distorted peak at 1040 cm^{-1} owing to the intense absorbance at wave numbers below 1200 cm^{-1} .

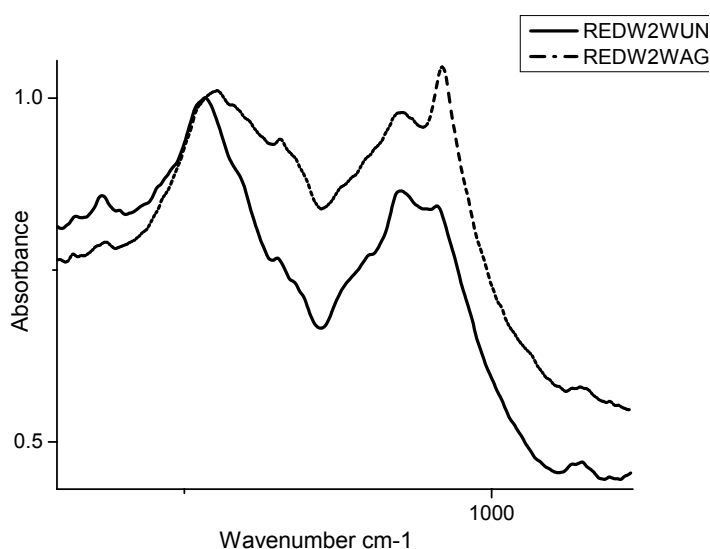


Figure 8. Red-dyed RW2 wool (madder/oak gall). Upon light ageing, significant change in Cys-A index occurs

Different photolytic reaction pathways are possible when wool keratin is irradiated. For example, (1). UVC radiation (e.g. mercury arc lamps) at 254 nm acts on the S-S bonds in wool keratin to produce cysteic acid, partially-oxidised cystine residues, and no Bunte salt at 1022 cm^{-1} . (2) Simulated sunlight UVA at 300 nm (and blue light at 420 nm) will produce cysteic acid and Bunte salt at 1022 cm^{-1} residues, but no partially-oxidised cystine derivatives [14].

Where no B-salt is observed, this could mean that threads have been exposed to differences in irradiated wavelengths. In the case of the PNM series, 17th-century practice was to take the tapestries to the river for cleaning, and then they were left to dry in the sun (with acknowledgements to C. Herrero in a private communication). In these samples, the peak corresponding to the $-\text{SO}_3^-$ absorbance band and associated with cysteic acid was measured in the second-derivative FTIR spectra. The results for wool samples from the following tapestries in the Royal Collection, Madrid, are presented in Table 4: Rafael & Tobias Vlierden, B. Van. Brussels c.1550 (PNM7), 'Atalanta hunts the wild boar', Bruges c.1620 (PNM8), and 'Wine arbors gallery', Antwerp 1660 (PNM9)

Historical tapestries

The majority of the historical samples had similar ATR/FTIR spectra to those of the accelerated light-aged samples. However, there were samples with high absorbances in the fingerprint spectral region ($< 1150\text{ cm}^{-1}$) indicated by absorbances at 1320 cm^{-1} and 1100 cm^{-1} . Based on the results shown above, there is a strong possibility of the presence of alum mordant that obscures the 1040 cm^{-1} absorbance band of $-\text{SO}_3^-$ of cysteic acid (Figure 9).

Among the selected samples in group A there were three distinct categories based on the spectral shape of the fingerprint region (Figure 10). In particular, there were cases with clear peaks characteristic of (a) cystine S-monoxide, cysteic acid and no cysteine S-sulphonate residues (B-salt), (b) less cystine S-monoxide, cysteic acid and cysteine S-sulphonate residues (B-salt), the latter resolved by second-derivative spectroscopy and (c) with cysteic acid as the major product.

These differences could be attributed to the effect of exposure to different wavelengths. The dependence of wavelength on the degradation processes has been reported elsewhere.

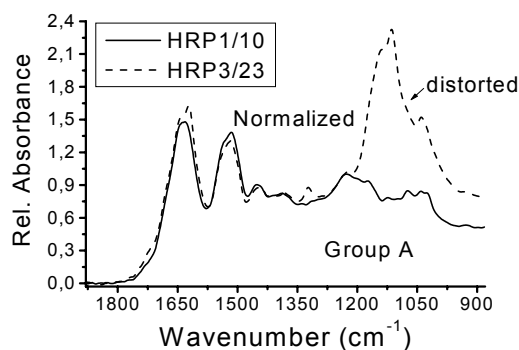


Figure 9. ATR/FTIR spectra of historical wool samples representative of 2 groups: A is suitable for evaluation of Cys-A and B is unsuitable

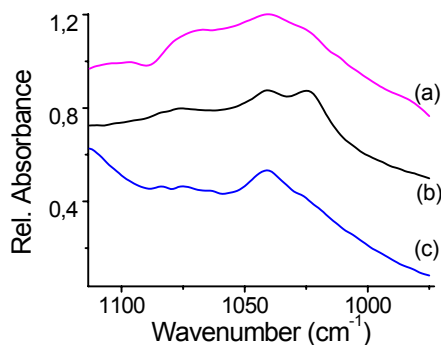


Figure 10. ATR/FTIR spectra of historical samples from Royal Palace Madrid collection (a) and Bruges, Belgium (b) where (a) PNM8/13, b: BRU1/10, and c: PNM9/18

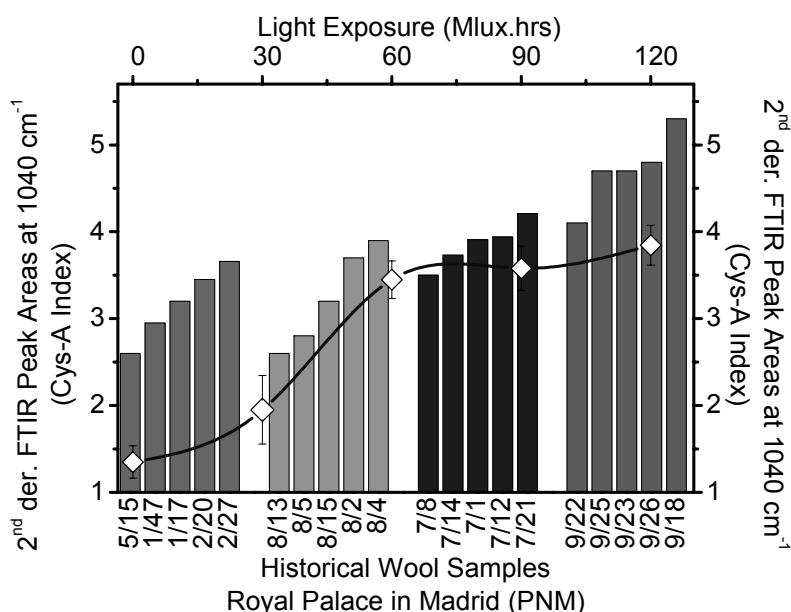


Figure 11. Cys_A index for samples from the Royal Palace collection and which represents tapestries from workshop centres in Brussels, Bruges, and Antwerp

The Cys-A indices of some of the samples fall within the category of 200 to 400 hrs accelerated-aged undyed wool samples (Figure 11). Those for PNM7 (except for PNM7/8) and PNM9 lie outside this range. The lower value for sample PNM1/47, compared to samples from PNM9, coincides with lower values as determined from amino-acid analysis (with acknowledgements to Ina vanden Berghe in a private communication). Further work is in progress to see whether a correlation can be made.

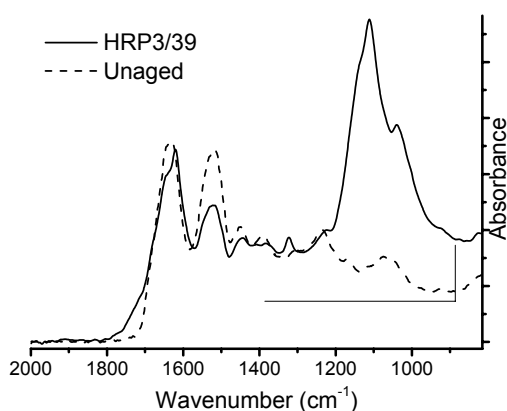


Figure 12. ATR/FTIR spectrum indicates presence of weddellite

In some cases, single fibres from the threads were tested mechanically, and the strain (%) was found to be significantly reduced for the historical samples (and higher Cys-A values) compared to modern and accelerated-aged sample. This will be discussed in detail elsewhere. An additional observation was made for the historical samples from one of the tapestries in the collection of Hampton Court Palace, London ('Triumph of Death over Chastity', Flemish 1500-1530). In Figure 12, the ATR/FTIR spectrum of brown wool (HRP3/39) is shown. The Amide 1 peak is distorted by the presence of an additional peak at 1620 cm^{-1} . This, together with the small peak at 1319 cm^{-1} , is indicative of the presence of weddellite (calcium oxalate monohydrate) (17). Additional thermoanalytical measurements on this and other samples from this tapestry are currently in progress, and will be reported elsewhere.

Conclusions

ATR-FTIR has provided a basis for assessing the damage to wool threads in model & some historical tapestries. The damage assessments have been based on levels of cysteic acid residue (Cys-A) as quantified from derivative spectroscopy. In this way, damage from the dyeing and ageing processes has been measured and located within the context of accelerated light-aged samples. Since the samples studied by ATR/FTIR were removed from the back of the tapestries, this implies that other factors such as relative humidity (which influences the tapestries' moisture content), temperature, pollutants and soiling have contributed to their degradation. Two further observations are as follows: the effect of previous treatment/cleaning, as described for some of the tapestries from the collection in the Royal Palace, Madrid, and the presence of weddellite is indicated in one of the tapestries from Hampton Court Palace. This is still being confirmed by other techniques.

Acknowledgements

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Table 1. Model wool tapestry samples

Type/Colour	Dye	Abbreviation	Mordant
Washed undyed	–	CONW	–
red	madder	RW1	alum al2(so4)3
	madder	RW2	oak gall/alum
	brazilwood	RW3	alum
	cochineal	RW4	alum
	cochineal	RW5	alum
blue	woad	BW1	–
green	weld + woad	GRW1	alum
	woad + weld	GRW2	alum
yellow	weld	YW1	alum
	dyer's greenweed	YW2	alum
mordant only	–	AlderW	alder bark
	–	AlumW	alum
	–	OakGW	oak gall

Table 2. Characteristic IR frequencies in wool

Species	Structure	Wave number (cm-1)
CO stretching, Amide I	–C=O	1635
NH deformation, Amide II	–NH	1515
NH and OCN mixed vibration, Amide III	–N–H & –N–CO	1235
Cystine dioxide	–SO ₂ –S–	1121
Cystine monoxide	–SO–S–	1071
Cysteic acid	–SO ₃ –	1040
S-sulphonate (Bunte salt)	–S–SO ₃ –	1022

Table 3. Cys-A index for model undyed and dyed wool (Black BLKW1-4, Red RW1-5, Blue BLW1 woad, Yellow YW1 weld, yellow YW2, dyer's greenweed, Green GW1 weld & woad, Green GW2 woad & weld), and upon light ageing

Light exposure (Mlux.hrs)	Calibration (undyed washed wool)	BLKW1	BLKW2	BLKW3	BLKW4	RW1	RW2	RW3	RW4	RW5
0	1.3	3.8	3.5	0.9	1.4	0.8	2.3	1.1	1.4	1.1
30	2.0	–	–	–	–	–	–	–	–	–
60	3.4	3.0	3.2	3.4	3.1	2.0	5.5	2.3	1.8	3.1
90	3.6	–	–	–	–	–	–	–	–	–
120	3.8	–	7.3	–	2.9	4.6	–	–	8.0	–
Light exposure (Mlux.hrs)	Calibration (undyed washed wool)	BLW1	YW1	YW2	GW1	GW2	Mordants			
							Alder bark	Oak gall	Alum	
0	1.3	1.2	1.3	1.8	0.4	0.8	1.2	5.0	XX	
30	2.0	–	–	–	–	–	–	–	–	
60	3.4	1.5	1.2	3.4	2.9	2.0	1.4	6.1	XX	
90	3.6	–	–	–	–	–	–	–	–	
120	3.8	1.9	5.3	1.9	–	4.6	–	–	–	

Table 4. The results for wool samples from the following tapestries in the Royal Collection, Madrid

Tapestries	Code	Colour	Dyes (3, 4)	Cys-A area
Rafael and Tobias, Vlierden, B. Van. Brussels c.1550	PNM7/1	yellow	weld	3.9
	PNM7/8	red	rubiaceae	3.5
	PNM7/12	yellow	weld	3.9
	PNM7/14	red	madder	3.7
	PNM7/21	green	dyer's greenweed, indigo	4.2
Atalanta hunts the wild boar, Bruges c.1620	PNM8/2	grey	–	3.7
	PNM8/4	brown	madder	3.9
	PNM8/5	green	weld, indigo?	2.8
	PNM8/13	black	indigoid, madder, weld	2.6
	PNM8/15	blue	indigoid, madder	3.2
	PNM9/18	brown	rubiaceae, brazilwood (tr.)	5.3
Wine arbors gallery, Antwerp, 1660 (National Palace of Madrid PNM)	PNM9/18	Brown	Rubiaceae, brazilwood (tr.)	5.3
	PNM9/22	Yellow-green	Weld	4.1
	PNM9/23	Orange	Munjeet	4.7
	PNM9/25	Green	Weld, indigo	4.7
	PNM9/26	Blue	Indigoid	4.8

▽△