

THE USE OF NEAR INFRARED SPECTROSCOPY AS A DIAGNOSTIC TOOL FOR HISTORIC SILK ARTEFACTS

SCIENTIFIC PAPER

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As a prestigious and expensive textile, silk is found in many historic artefacts of cultural importance. However, as silk ages it becomes increasingly fragile and thus prone to damage through handling, display or even conservation treatment; these problems are exacerbated by some of the processing methods traditionally applied to such materials. Therefore, in order to minimise the danger to these objects, it is vital to have a good understanding of the physical state of the silk component. It is shown that near infrared spectroscopy, in combination with multivariate analysis, provides a method of assessing the stresses within a silk artefact, thereby highlighting areas at particular risk and allowing informed decisions to be made as to the potential dangers of intervention. As near infrared spectroscopy may readily be used with a fibre optic probe, these analyses can be performed in situ, rapidly and in a non-invasive manner, thus allowing assessment to be carried out in collections and displays without requiring samples to be taken, limiting the disturbance to artefacts. Therefore, the technique provides a valuable tool to gain a practical understanding of the condition of silk artefacts, and a means of informing conservation, display and storage strategies.

1 Introduction

For thousands of years, silk has been regarded as one of the most prestigious and valuable of textiles and so is found in many objects of cultural and historic significance, including garments, upholstery, tapestries and banners. However, silk is prone to deterioration through a variety of mechanisms, and as it ages it becomes increasingly fragile, and thus susceptible to further damage through use and handling. Furthermore, many of the processing techniques traditionally applied to silk fabrics, including dyeing, weighting with metallic salts and bleaching, may also have deleterious effects and lead to the weakening of the material. Therefore, silk artefacts pose particular problems in terms of their conservation, and these problems are exacerbated when then requirements to display or store these objects

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within collections are considered. Silk itself is a proteinaceous fibre, derived from the cocoon of the domesticated silkworm, *Bombyx mori*; in its natural state, the fibre consists of two continuous fibroin filaments bound together with a second protein, sericin.¹⁻⁶ Fibroin is largely composed of a hexapeptide motif (-Gly-Ala-Gly-Ala-Gly-Ser-), and is highly crystalline with extensive anti-parallel E-sheet structures forming crystallites aligned parallel to the fibre axis; these features give silk its characteristic strength, lustre and resilience. Sericin, on the other hand, is principally amorphous, and is frequently removed during commercial production by a process known as 'degumming' (as is the case with the silk considered in this study).

Many textiles are best appreciated when displayed in the manner originally intended, with tapestries and banners, for example, allowed to hang, and clothing exhibited on mannequins which mimic the form of the original wearer. Unfortunately displaying objects in the manner can introduce damaging stresses which may lead to future problems. As a result, it is of value to a conservator or curator to be able to assess the physical forces at work within an object, as this will allow informed decisions on the most suitable means display and support. A means of monitoring these physical conditions will also help to highlight those objects at most immediate risk of mechanical damage, permitting appropriate interventions to be made.

Examples of these kinds of assessments on objects made from a variety of materials include the work on the fore topsail of the *HMS Victory* (Nelson's flagship at the Battle of Trafalgar, 1804) and the Ensign used by Shackleton on his last expedition to the Antarctic in 1922. The *Victory* sail was principally composed of linen, bound with hemp rope; although one of the original plans had been to display it hanging from a mast as it would once have been seen aboard ship, physical analyses revealed that it would not have withstood these conditions without undergoing permanent deformations, so the final decision was to display it flat.⁷ The Shackleton Ensign was constructed from silk, and was deteriorated to the point at which it was incapable of maintaining its own structure, so consolidation with silk crepe-line net and a suitable adhesive was required both to preserve the artefact in its original form and to allow it to be exhibited. In many other objects the deleterious effects of physical stresses can readily be seen, leading to stretching, deformation, tearing and ultimately failure, with the resultant loss of form, function and history.

The assessment of these objects was carried out either through mechanical testing of individual fibres, followed by correlation to bulk properties through the use of surrogates (as with the *Victory* sail), or through appraisal by observation and handling based on experience (in the case of Shackleton Ensign). With objects where ethical or aesthetic considerations make it impossible to take samples, and it is not easily possible to examine the object in sufficient detail, due to its size, lack of time, insufficient access or limited experience of the materials, another approach may be of advantage. It would be of use to have a means of assessing the physical stresses in an object by a technique that was non-sampling, non-invasive, rapid and capable of being carried out *in situ*.

Near infrared (NIR) spectroscopy potentially fulfils these requirements.⁸ It may be used with a conventional fibre optic probe, rather than the more brittle calcogenide probes required for work in the mid infrared region. This allows spectra to readily be recorded on site, thus permitting the item to be left in its display or storage conditions with minimal interference. Spectra can typically be recorded within a few tens of seconds, permitting multiple locations on a single object to be rapidly monitored and making the assessment of a collection a viable proposition. Finally, and perhaps most importantly, the use of multivariate analysis (MVA) techniques potentially allows the spectra to be correlated with physical parameters, providing a suitable model has previously been generated using known materials under measured conditions. The aim of the research presented here has, therefore, been to assess the suitability of NIR spectroscopy, in combination with multivariate analysis, to indirectly measure the physical stresses found within silk artefacts. This technique has been used successfully within the heritage community to look at the condition monitoring of silk,⁹ paper,^{10,11} and wood,^{12,13} and the identification of synthetic textile material.¹⁴

Multivariate analysis (MVA) is used to reduce large data sets, containing many variables, to a smaller set of components in order to monitor trends or highlight any co-dependant variables not readily seen in the raw data set.^{15,16} MVA uses matrix algebra to study and find correlations across a multi-dimensional, multi-variable space. The initial data matrix is known as the X matrix and is made up of n rows and p columns. In the case of NIR spectra, n is the number of recorded spectra and p the number of variables, corresponding to spectral data points. This larger matrix is reduced to smaller matrices and places the samples onto a new coordinate system which describes

the variance in the data, commonly known as components (PC).

For NIR spectroscopic data, the number of variables can be anywhere in the region of 2,000-12,000. This corresponds to the number of recorded data points across the spectral region for each sample, and is dependent on the spectral resolution. The use of multivariate calibrations allows spectroscopic changes to be monitored, which relate to changes in the sample sets. This is a particularly useful application when studying near infrared spectra. NIR spectra are derived from overtone and combination molecular vibrations, which cause the spectra to be characteristically complicated with many overlapping bands. The low visual resolution of the spectra inhibits ready monitoring of wavenumber shifts and changes in absorbencies, as such variations may be related to a change in one or more factors.

To apply these techniques, a series of silk samples were subjected to known loads and NIR spectra recorded; correlations between the spectral data and the load were then drawn via MVA. Initially specimens from which the weft yarns had been removed (thus yielding simpler and more easily modelled data) were assessed to investigate the potential of the technique. When this proved promising, data were recorded from samples in which the weave structure was left intact, and this was employed to construct a more comprehensive model of the silk behaviour. Finally, surrogate samples designed to mimic the types of structure commonly encountered in textile artefacts were assessed using the model, to determine that it responded in the appropriate manner and adequately described the properties of the silk.

2 Materials and Methods

2.1 Loading and Spectroscopy

To establish the initial model, samples were prepared from habutae (plain weave) silk, measuring 10 × 80 mm (weft and warp directions, respectively); for the first set of samples, the weft yarns were removed from the central section, whilst these were left in place for the second set.

The samples were subjected to a loading regime with an Instron '5544' mechanical tester. Using a 50 mm initial gauge length and a rate of extension of 5 mm/min, each specimen was stretched in 1 mm steps, then allowed to relax for 5 min after which a spectrum was recorded and the load on the sample measured (Figure 1). Near infrared spectra were acquired using a PerkinElmer Spectrum One NTS Fourier transform spectrome-

ter with an *Axiom* fibre optic probe attachment. The probe head contains a fibre optic bundle to the rear of the rod, which has an acceptance angle of plus or minus 12.7 degrees. Therefore, the probe will detect specular as well as diffuse reflectance as long as the normal to the surface falls within this range of angles. However, the centre of the optical field of view is inclined at approximately 18 degrees from the probe axis reducing the amount of specular reflectance reaching the optical fibres. This sampling depths are in the region of a few millimetres, therefore a Spectralon® reflector was placed behind the silk to lower interference.

The spectral range was 4,000-10,000 cm⁻¹, with a resolution of 8 cm⁻¹ and 50 accumulations.

The samples were subjected to this progressive loading to breaking point, and a total of 15 separate calibration specimens and 9 validation samples were assessed, over five different days to minimise systematic bias to the data due to particular conditions of temperature or humidity. During the course of the experiments temperature and relative humidity fluctuations averaged 21 ± 1 °C and 50% ± 4% RH, respectively. For each sample there were approximately five spectra recorded, depending on the point of rupture for each individual specimen.

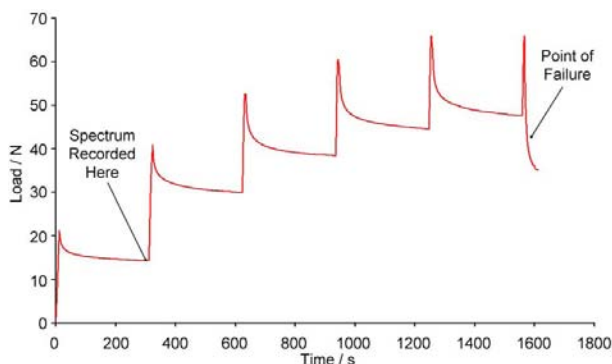


Figure 1: Loading regime for the silk samples.

2.2 Multivariate Analysis

The software used for the multivariate analysis was Camo Technologies Inc The Unscrambler® version 9.7. The technique applied during this work was the Partial Least Squares 1 (PLS1) method. PLS1 is a regression method based on an iterative algorithm between two matrices, **X** and **Y**. The **X** matrix relates to the spectral responses and the **Y** matrix is a **1xn** matrix composed of the corresponding loads, recorded by the mechanical tester.

The calibration model was built from 115 spectra, with validation carried out using an independent test set of 73 spectra. The test set method pre-

vents over optimistic prediction and provides a robust method of validation. Subsequently, the PLS model was used to predict the stress experienced on a number of surrogate samples, to assess the application of the technique as an *in situ* method for monitoring the physical condition of silk textiles.

2.3 Surrogate Objects

A variety of surrogate samples, constructed from habutae silk and designed to mimic the range of structures often encountered in textile artefacts, were then subjected to a known load via a simple rig (Figure 2). Spectra (using the same parameters as above) were then recorded from a range of points across the surface of the sample, and this data assessed via the MVA calibration model.



Figure 2: Typical surrogate silk object and loading rig.

3. Results and Discussion

The dominance of diffusely scattered light detected in near infrared spectroscopy means that the spectra are dependent on physical as well as chemical differences. It can be seen from Figure 3 that as the fabric is placed under increasing load the samples exhibit changes in their scattering properties due to a tightening of the weave. This is seen in the spectra as a baseline shift. These variations highlight the need for data pre-processing prior to multivariate calibration. This reduces physical phenomena, such as shifting baselines,

unifying the data and ensuring that any variability being modelled relates to that of interest. A range of pre-processing methods were investigated, including normalisation, Standard Normal Variate (SNV) and derivatives, coupled with wavelength selection, to optimise spectral vibrations.

The Root Mean Squared Standard Error of Prediction (RMSEP) provides a method of monitoring the error in the validation method, and is therefore a measure of the degree of uncertainty to be expected when applied to future samples. It is calculated as the square root of the residual variance between the predicted and the measured y value.¹⁷ The success of the calibration model was deemed to be optimised when the RMSEP was at its lowest, found by reducing the sum of the squares of the residuals, as in more conventional linear regression methods. In this current work the most favourable RMSEP value was achieved when the spectra were processed using the 1st derivative Norris gap function, with a window of 19, followed by transformation with SNV and limiting the spectral region to 4100-5100 cm^{-1} (Figure 4). Table 1 gives the regression parameters for the PLS model.

The X-loadings plots enable the most influential variables (wavenumbers) in the decomposition of the X matrix to be pinpointed. It provides a means of ensuring that the relevant spectral bands are being modelled. The loadings relate to the new

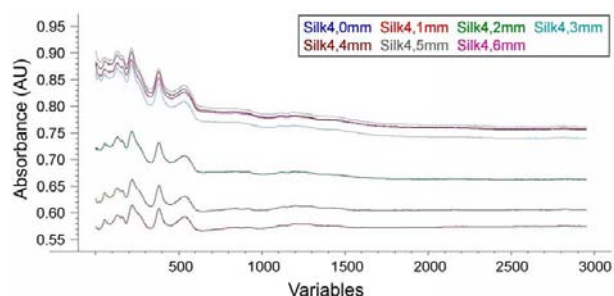


Figure 3: Spectral baseline shift under increasing load.

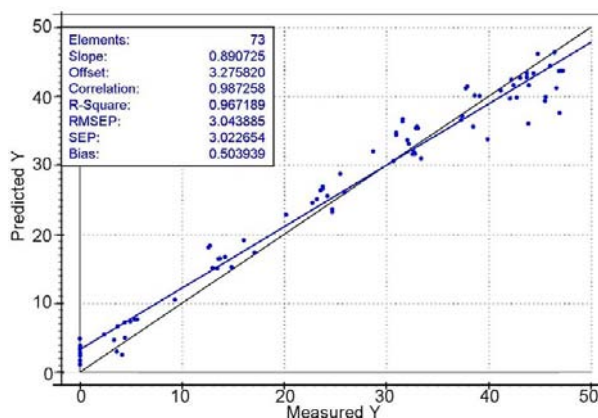


Figure 4: Validation regression line for final model: black and blue lines are the target and actual regression lines, respectively.

	Wavenumber Region/cm ⁻¹	No. of PCs	Calibration		Validation				
			Samples	RMSEC	Samples	Slope	Intercept	Correlation	RMSEP
Warp / Weft	4100 - 5100	3	115	2.6	74	0.88	1.24	0.99	3.19

Table 1: Regression parameters for the PLS calibration model.

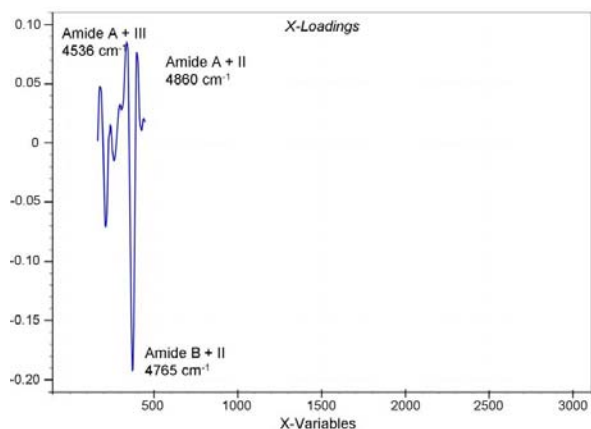


Figure 5: X-loadings plot for the first component after pre-processing.

component axis to the original data. If the variable lies along zero then the original axis contributes nothing to the new PC. Conversely, the greater the distance from zero the greater the degree of information that variable is contributing. Figure 5 shows the X-loadings plot for the first component covering the entire spectral range, after data pre-processing.

The significant contributions in the X-loadings plot at approximately 4536 and 4860 cm⁻¹ are likely to arise from the NIR peaks associated with the Amide A+III and Amide A+II combination stretching modes, respectively;¹⁸ the positions of X-loading peaks do not correspond precisely with the spectral peaks, and it is likely that this occurs as the model is influenced by subtle changes within the band, rather than the band as a whole. It is also possible that the contribution at 4765 cm⁻¹ may be derived from the Amide B+II combination, although in this case the correspondence is not as close. These vibrations were shown to shift to lower frequencies as the amorphous regions of the silk protein changed from a random coil structure to a more ordered 'pseudo-crystalline' conformation due to loading. This would explain the high influence that these variables contribute to the calibration and validation model. As the sample is subjected to a uniaxial load then the polymer lengths can be assumed to rearrange, into a more ordered configuration, as is commonly exploited during fibre processing methods for synthetic fibres.

The calibration model was then applied to the surrogate samples to predict the applied load, thus highlighting areas of concern. As already descri-

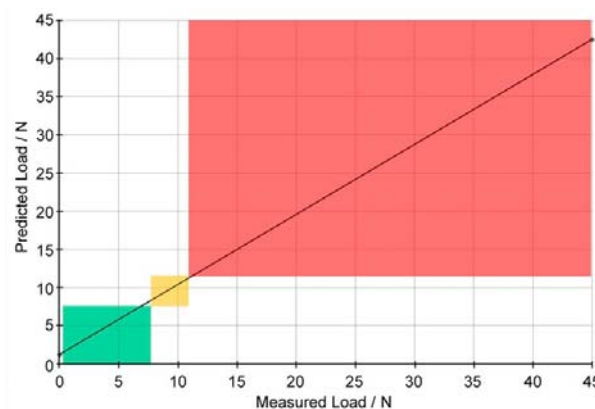


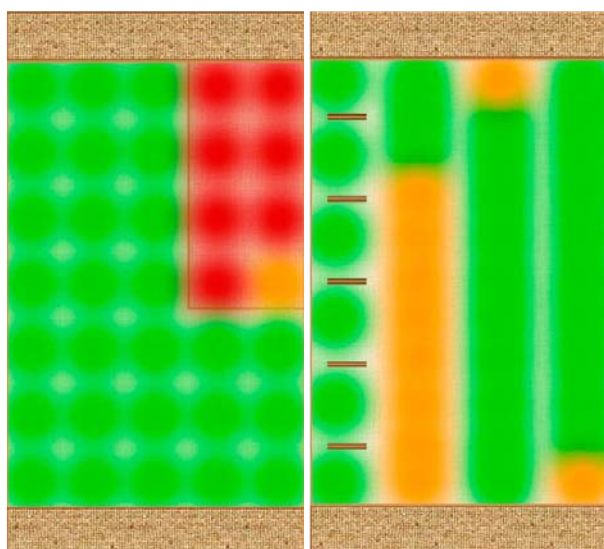
Figure 6: Regression boundaries for predicted loads.

bed, NIR spectra were acquired from a number of areas for each sample. This data was pre-treated in the same manner as the calibration samples and regressed against the calibration model. The commercial software provides numeric outputs for the predicted values of the new data providing a prediction of load at each sampling point.

In order for this application to be useful as a method of condition monitoring, boundaries needed to be determined to provide a measure of vulnerability of an object. The elastic limit of silk is reported to be in the region of a quarter to a third of the fibres yield point.² In the case of our calibration model, the average failure point was found to be 45 N. Therefore, as a conservative estimate this would place the elastic limit of the samples at 11.25 N, representing a load which ideally should not be exceeded.

With this in mind, it was arbitrarily decided to deem those samples experiencing loads of 0 to 7.5 N as free from stress, represented on the regression line in green (Figure 6). Samples predicted as bearing loads between 7.5 and 11.25 N were deemed to represent areas of possible concern. If such areas were detected in textile artefacts they would be considered in need of periodic monitoring as they would be reaching their elastic limit. These regions are illustrated in orange. Regions predicted at a level between 11.25 and 45 N would be at risk from irreversible deformation and damage, and have been designated red.

Figure 7 illustrates the predicted loads for each data point on the surrogate samples. The mean predicted loads have been used. The individual deviations are not presented, as the purpose of



a) b)
Figure 7: Predicted loads for surrogate samples.

the method was not to determine absolute values, but rather to give an indication of how a textile may be behaving when subjected to a load.

The predicted values for each sampling area closely match what may be expected when taking into account the localised stresses introduced by stitching and seams in textiles artefacts. For example, buttonhole surrogate is experiencing an increase in stress to the right of the holes when subjected to a static load (Figure 7b). This is due to the disruption in the weave structure and a non-uniform distribution of weight across the fibres.

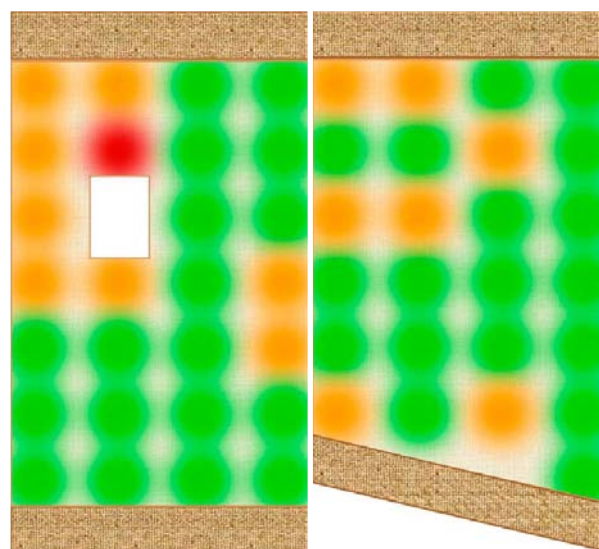
4 Conclusion

The work presented here has illustrated the successful application of near infrared spectroscopy as a rapid, non-invasive method for the monitoring of stresses in silk. Coupled with multivariate analysis, our calibration and validation has been shown to be robust for application to simple samples and readily extended to more complex surrogate textiles.

For the method to find application beyond these samples a broader range of material for calibration would be required, taking into account different silk processing, additives and weave structures. However, the potential for applying this technique as a collections management tool has been highlighted and warrants further investigation and development.

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c) d)

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