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NON-DESTRUCTIVE TESTING OF SILK: PROBLEMS AND POSSIBILITIES

ABSTRACT

Silk deterioration can be catastrophic, with splits and tears leading to powdery and friable surfaces which are difficult to conserve. The deterioration is reported to be accelerated for silks which have been treated with metallic salts; however, these materials are difficult to identify. Methods of non-destructive testing to identify the types of silk and their condition have been explored. The use of these techniques in situ to reduce sampling or object movement is discussed along with the problems and possibilities of each technique.

RÉSUMÉ

La dégradation de la soie peut être catastrophique, puisque les déchirures et les accrocs rendent les surfaces poudreuses et friables, et donc difficiles à conserver. La dégradation est décrite comme accélérée pour les soies ayant subi des traitements à base de sels métalliques ; toutefois, ces matériaux sont difficilement identifiables. Des méthodes d'essais non destructifs destinés à identifier les types de soie et leur état de conservation ont été explorées. L'utilisation de ces techniques *in situ* afin de réduire l'échantillonnage et les déplacements des objets est discutée, ainsi que les problèmes et les possibilités relatifs à chaque technique.

RESUMEN

El deterioro de la seda puede ser catastrófico, con rajaduras y desgarres que hacen que las superficies se vuelvan pulverulentas y friables, y sean difíciles de restaurar. Se sabe que el deterioro se acelera en sedas que han sido tratadas con sales metálicas. Sin embargo, estos materiales son difíciles de identificar.

INTRODUCTION

Object and conservation records, along with archives, can provide a wide variety of information on collections. Despite this, elucidating the composition and condition of textiles requires scientific analysis. However, a balance has to be achieved between the care, conservation and display of the objects and the removal of material for analysis to inform these areas. Generally, destructive analytical techniques require large samples and are limited in application to surrogate materials for laboratory experiments. In some cases, micro-sampling of objects for destructive analysis is acceptable due to the value of information obtained. For example, silk fibroin molecular weight, an indicator of the state of deterioration, is revealed by high-performance size exclusion chromatography (HPSEC), which requires just a millimetre of thread.

Ideally, analysis would be performed without removing samples and even while an object is on display. The techniques would need to be both non-invasive (samples do not need to be removed) and non-destructive (no damage caused), whilst still providing useful results. Such analysis can help inform curators and conservators both of the technical art history as well as the condition of the objects. Research has been undertaken to determine the potential of two non-destructive techniques for revealing the condition and composition of historic silks on open display.

ANALYSIS METHODS

An initial review identified a number of techniques, most notably spectroscopic techniques such as Raman spectroscopy and polarised attenuated total reflectance infrared spectroscopy (pol-ATR), which could be used to provide detailed information on the condition and composition of silk (Luxford 2009). However, almost all of the techniques identified required samples, although often very small (less than 1 mg), and very few could be used on site or truly non-destructively. Two techniques, X-ray fluorescence (XRF) and near-infrared (NIR) spectroscopy, had the potential to provide information on the condition and composition of the silk. Both techniques are non-invasive and non-destructive making them suitable for in situ analysis of historic collections. Furthermore, both are becoming increasingly portable and more widely used within heritage science enabling access to this equipment.

TEXTILES

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Se han estudiado métodos no destructivos para identificar los tipos de seda y su estado de conservación. El artículo discute el uso de estas técnicas *in situ* para reducir la toma de muestras y el movimiento de los objetos, así como los problemas y las posibilidades de cada técnica.

XRF spectroscopy

XRF has been applied to textiles for the identification of mordants (Masschelein-Kleiner and Maes 1978) and weighting agents (Becker et al. 1987), as well as pesticides (Odegaard et al. 2006), painted details (Skelton 1995) and mineral dyes (Gardiner et al. 2000). However, previous studies have usually relied on objects being taken to larger-scale laboratory-based equipment. More recently, portable, hand-held devices have become available and the potential of the Bruker TRACeR III-V handheld XRF was assessed for use with historic textiles. The instrument is battery powered with an associated PDA for data analysis, although a laptop and power cables can also be used. When used with the KeyMaster-Bruker vacuum pump attachment, elements with atomic mass down to magnesium can be identified. The sampled area is an ellipse approximately 5 by 6 mm and, in this study, a real count time of 40 seconds was used.

NIR spectroscopy

NIR spectroscopy has already found application for paper and plastics within conservation science and some studies on textiles have also been reported (Richardson et al. 2008, and references therein). A variety of natural and synthetic fabrics can be identified, as long as there is a suitable reference dataset for comparison. NIR has also been shown to be of value for the diagnosis of areas of strain within silk (Richardson and Garside 2009). Previously, NIR has indicated potential for condition monitoring of silk (Zhang and Wyeth 2007, Kim and Wyeth 2009).

To characterise the condition of the historic silk collection, a NIR spectrometer was taken to Brodsworth Hall, an English Heritage property. NIR spectra have been collected using a Perkin Elmer Spectrum One Fourier-transform near infrared spectrometer (FT-NIR) with an Axiom fibre optic probe scanning between 4000-12000 cm^{-1} with a resolution of 8 cm^{-1} and a scan accumulation of 64. The background reference was Spectralon®. All data were collected in absorbance at 22 ± 2°C and 52 ± 5% RH. Baseline corrections and spectral averaging were carried out in Thermo Galactic Grams AI version 8. Additional spectral pre-processing and multivariate analysis (MVA) was performed with The Unscrambler® version 9.7 software by Camo Technologies Inc.

EXPERIMENTAL RESULTS AND DISCUSSION

XRF results

XRF was used at two English Heritage historic houses, Audley End House and Brodsworth Hall, to provide elemental analysis of textiles on display. One of the immediate benefits of on-site analysis was the greater number of areas that could be analysed. For example, in Figure 1 individual colours could be selected to determine differences in mordants and weighting agents used. By using a non-invasive and non-destructive technique, it was possible to select areas to sample for analysis by other techniques, such as

Figure 1

Detail from the festoon curtain in the Little Drawing Room at Audley End House. Numbers indicate representative areas of the different coloured threads analysed

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HPSEC. The use of the portable XRF also allowed ready determination of the composition of a number of metal threads, including gilt silver, and brass (see Figure 2, for example), found within the silk artefacts. In most cases, these would have been impossible to sample without causing obvious aesthetic damage to the textiles design.

A variety of elements were identified within the silk, including some that were expected such as tin (probably weighted silk), iron (probably used as a mordant on black silk) and chromium (used as a mordant on modern reproduction silks). For example, the prize ribbon in Figure 2 has high levels of tin, indicating the ribbon has been weighted. Treatment of silk with metallic salts, especially tin, was common, particularly for costume and fashion textiles (Hacke 2008). These materials are seen as inherently deteriorating due to the presence of the metallic salts, but are particularly difficult to identify as there are no obvious visible indicators. Hence, finding a non-destructive method of identifying these materials is of crucial importance for curators and collections managers.

Whether the element identified is a result of weighting or mordanting (or an alternative source such as pollution) is less certain, thus limiting to some degree the value of the information for conservators and curators. This arises as the equipment standards are based on metal alloys and without access to the XRF software it was not possible to establish an internal XRF calibration for silk textiles (further details can be found in Luxford 2009). Therefore, an element can be qualitatively identified as present, but the quantitative concentration could not be determined, making assignment of its source difficult. In most cases, the source can be assumed, e.g. chromium in modern textiles is most likely to arise from the mordant used. However, historically tin was used both as a mordant for light coloured textiles and a weighting agent, as was iron for dark coloured dyes, primarily black.

Identified elements are present at more than twice the baseline level, whereas trace elements were present above the baseline but below this point. Baselines for each element were determined by comparison of the amount found in all analysed objects with the line drawn above the low concentration present in all samples (Luxford 2009). Results from the in situ XRF analysis at Brodsworth Hall are presented in Table 1. In some cases, other materials also seem to have been sampled. For example, on the sofa in the south hall the silk upholstery is light coloured and therefore unlikely to contain iron as a mordant. However, iron has been identified, which may arise from something like an upholstery tack beneath the upholstered layer. Lead was identified in situ during analysis at both Brodsworth Hall and Audley End House. Although lead was sometimes used as a weighting agent, it is rare for upholstery fabrics to be weighted. In most cases, when lead was identified it was on wall silk, and a possible explanation is the presence of lead paint beneath the silk.

Due to perceived inherent deterioration of weighted silk, objects in a poor condition are often assumed to be weighted. However, in some cases silk

Figure 2
Prize ribbon [90015011] from Brodsworth
Hall with brass metal threads

in a very poor condition showed no presence of any metallic elements. For example, only sulfur was identified on the cabinet in the north corridor, which is in a particularly perilous condition. Other authors have previously noted that much degraded silks, labelled as weighted due to their condition, contained no metallic elements, but high levels of sulfur (Ballard et al. 1990). In these cases, the damage is thought to be the result of sulfur bleaching processes rather than any weighting agents.

Table 1

XRF results from in situ analysis at Brodsworth Hall

room	location	identified elements	trace elements
south hall	sofa good condition area	S, Sn, Ca	K, Fe
	wall gold silk	S, Pb	
drawing room	wall behind exit door	S	Ca
	sofa behind door		S, Sn, Ca
	sofa behind exit door shattered area	Sn	S, K, Ca, Pb
drawing room	sofa behind exit door good condition area		S, Sn, Ca, Pb
	wall silk (by entrance door) gold area	S	
	wall exit door gwwood condition	S	Pb
north corridor	cabinet grille	Cu, Zn	S
	cabinet RHS flat area silk	S	
store	narrow cummerbund metal thread	Cu, Zn	S
	wide cummerbund metal thread	Cu, Zn	S
	prize ribbon tassel	Cu, Zn	P, S
	prize ribbon	Si, K, Sn, Ca	P, S

Practical problems included the weight of the XRF when held for long periods and the relatively short battery-life, although on more recent models the battery life has been significantly improved and now lasts for a full day of analysis. The portable XRF allows elements to be identified within the silk. However, due to the problem of establishing an internal XRF calibration for silk textiles, it was often necessary to check the identification after the analysis, which increases the interpretation time. There were significant advantages in using the portable equipment on site; for example, the inorganic composition of many of the objects could not otherwise have been determined, as sampling would have been overly damaging. It also allowed a much wider range of objects to be analysed, for example wall silk could never have been taken to a laboratory for analysis. Although the amounts of elements were not quantified in this work, it was possible to qualitatively identify the presence of elements and make assignments based on known processing methods.

NIR identification results

In some cases, identification of materials can help curators establish the date or the status of an object, for example the brass (rather than gold) metal threads above in Figure 2. NIR can be used for identification when a suitable database of spectra is available for comparison. During the research, identifying the material used to make the pile for velvets was problematic and for a number of objects fibre identification by NIR proved especially

useful. The majority of objects were wool, but in some cases silk velvet was found. Silk upholstery and cellulosic padding layers were also successfully separated and identified using this technique (Figure 3). This could be done by separately analysing areas of remaining silk and the underlying padding visible in areas of damage, such as split areas of the silk. In some cases, the padding contribution was subtracted from the spectrum to give a clearer indication of the remaining upholstery layer composition.
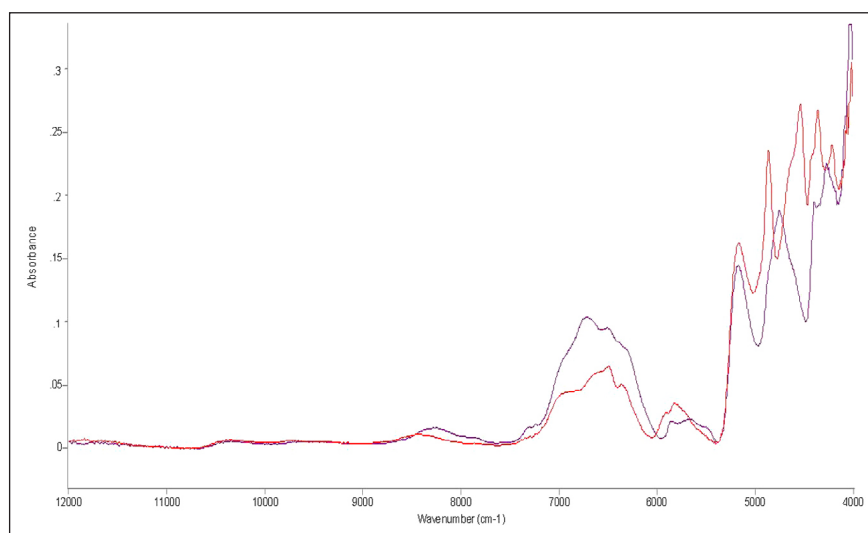
Figure 3
NIR spectra of silk upholstery (red) and padding (purple)

Identification by NIR spectroscopy has a number of advantages, including the fast analysis and the fact that samples are not required. However, in order to identify a material, a large reference database is required (Kawano 2002). This can be difficult as known and well-characterised materials are required as reference materials. The broad overlapping peaks that typify NIR spectra can also make it difficult to identify materials and some spectral processing can be required for materials with similar chemical groups such as wool, silk and nylon. This processing can significantly add to the interpretation time, meaning that although the data collection is rapid, the actual identification is time-consuming. Although the NIR spectrometer used can be moved easily, it is relatively large and so not ideal as a portable instrument; furthermore, it requires a power supply during operation. This can limit its use, although more portable models are now available. The lack of portability is compensated, to some degree, by the use of a fibre-optic probe limiting the need to move the spectrometer.

NIR condition assessment results

In order to assess small changes within NIR spectra multivariate analysis (MVA) has been used. This allowed the development of a model which can be used to predict the tensile strength of silk from the NIR spectrum. The model was built using NIR spectra and the tensile properties of a reference set of artificially aged surrogate silks (Luxford 2009). Tests of the model with other samples of the same silk gave results within the model's

deviation (around 30 N). This indicated condition predictions based on the NIR spectra were possible. The deviation is calculated by Unscrambler using the model error, sample leverage and residual X-variance. Large deviations indicate the predicted sample is different from the calibration samples.

Subsequent prediction of condition for the historic silks suggested better performance than expected, but with relatively large prediction errors (Figure 4). For example, unaged silk in the accelerated ageing experiments had a tensile strength of 160 N. For most of the objects analysed in situ the results were equal to, or greater than 160 N. This indicates that the historic silks are not well described by the current model. As the model used here has been built solely using artificially aged samples of unweighted modern silk, it is unsurprising there are differences between the real objects and the model. A more robust model would require a great number and variety of historic silks with suitable data on the condition, either tensile properties or molecular weight from size exclusion chromatography (HPSEC) analysis of micro-samples.
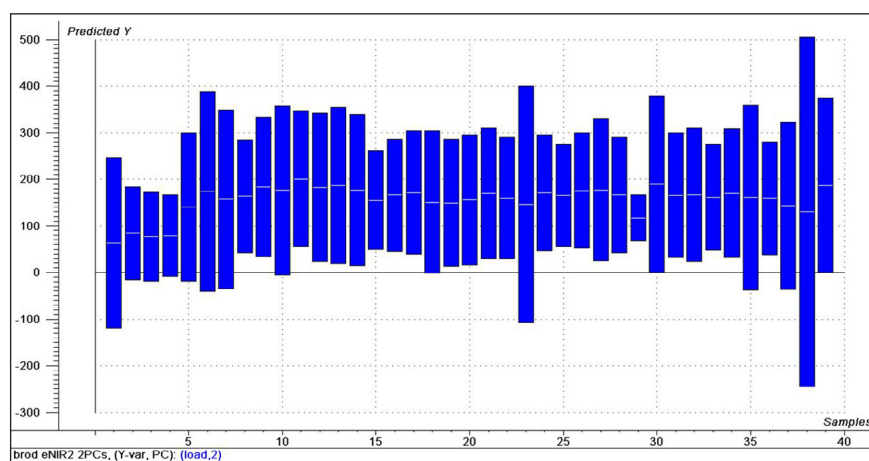

Figure 4
Predicted tensile strengths (in N) of historic silks (white line) of in situ NIR spectra with the deviation shown as a blue bar (sample number from 1 to 39 is shown on the x-axis)

As the model was not as successful in situ as expected from the laboratory trial, the NIR spectra from a number of objects were investigated to determine some of the factors which may influence the model. Coloured samples were first investigated, since additional, complicating dye-related absorptions would be expected. However, the current model limits the analysis to a small spectral region (4100-5100 cm^{-1}) and colour had little significant effect.

As the XRF analysis had demonstrated some of the objects were made of silk that contained elements such as tin, these were also studied to determine if there was any impact. In Figure 5, a clear change can be seen between the unaged (unweighted) silk and the two tin weighted silk spectra, which have an increased peak intensity at 5180 and 6970 cm^{-1}. Although outside the limited spectral region used in the current model, weighting appeared to have some influence. A future model could include

weighted samples which may improve both the prediction of condition and help identify weighted silk within collections.
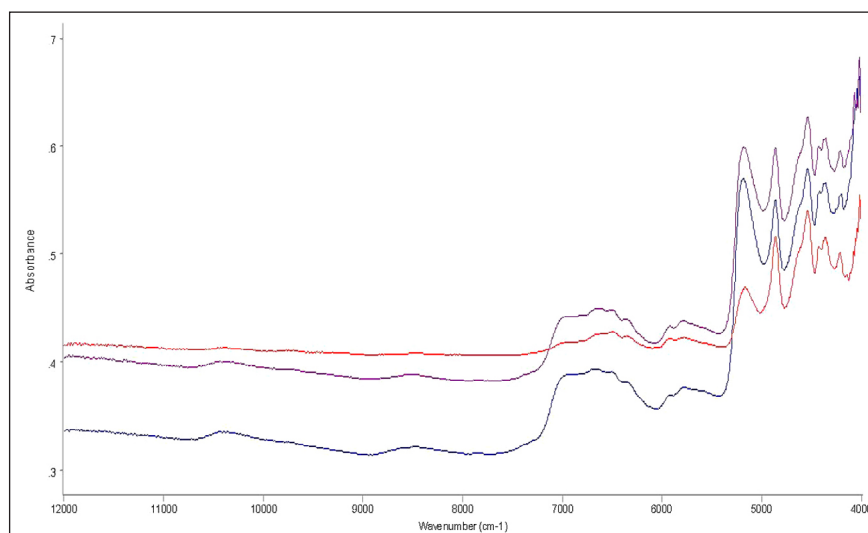

Figure 5

Effect of inorganic elements on NIR spectra (unaged silk: red; weighted samples: blue and purple)

Although the predicted values of the tensile strength are greater than would be expected, the samples were successfully ranked in order of condition. For example, those samples in the poorest visible conditions also had the lowest predicted tensile strength values. The current model cannot be used to give exact values of condition, but it can provide comparative ranking, which could help in prioritising future interventive treatment. NIR spectroscopy offers rapid, non-destructive and non-invasive silk characterisation, although its application may be constrained by the requirement for a comprehensive reference spectral dataset and the generation of a robust condition model.

CONCLUSION

The research has demonstrated the feasibility and illustrated the value of non-destructive analysis of textiles on open display. XRF has been found to be suitable for in situ analysis of textiles and provides a qualitative identification of silks treated with metallic salts. It can also be used to determine the composition of metal threads whilst on display. The types of textile can be identified using NIR spectroscopy with comparison against a suitable database, without removing samples for analysis. Furthermore, the relative condition of the silks can be gauged by NIR/MVA. Appropriate extension of the NIR reference dataset should enable prediction of absolute values for condition related parameters such as tenacity and fibroin molecular weight, offering more detail and better informing curatorial and conservation strategies.

ACKNOWLEDGEMENTS

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MATERIALS LIST

KeyMaster-Bruker TRACeR III-V handheld XRF and KeyMaster-Bruker vacuum pump:
Mike Dobby, Portable XRF Applications Manager (Europe), Bruker Advanced X-Ray
Solutions Banner Lane, Coventry, CV4 9GH, UK

PerkinElmer Spectrum One NTS spectrometer with Axiom probe.
Perkin Elmer Life and Analytical Sciences
Chalfont Road, Seer Green, HP9 2FX, UK

Unscrambler version 9.7
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