**Relating colour, chemical and physical characteristics of artificially light-aged New Zealand plant fibres**

Author/s (*indicates author for correspondence)
Bronwyn J. Lowe[*1], Catherine A. Smith[1], Keith C. Gordon[1], Lyall R. Hanton[1], Bruce Ford[2], Annika Korsten[1], Sara J. Fraser[1] and Bethany A. Lomax[1]

1. University of Otago, Dunedin, New Zealand
2. National Museum of Australia, Canberra, Australia

Email addresses: bronwyn.lowe@otago.ac.nz, catherine.smith@otago.ac.nz, Kgordon@chemistry.otago.ac.nz, lhanton@chemistry.otago.ac.nz, bford@nma.gov.au, sfraser@chemistry.otago.ac.nz

**Abstract [Heading]**
Light ageing of naturally-dyed plant fibres can cause colour change, alteration of molecular bonds within the fibre structure and loss of mechanical integrity. Lighting guidelines seek to protect artefacts by limiting light exposure, for example by estimating the lux hours likely to cause colour change of “one just noticeable fade” (1JNF). However the extent of associated molecular or mechanical damage is rarely simultaneously assessed.

This paper reports a pilot study investigating the effects of accelerated light ageing on *muka* (fibre extracted from the leaves of *Phormium tenax*), the most common fibre used in Māori textiles. Non-dyed and dyed *muka* were artificially light-aged and micro-faded to ascertain exposure resulting in 1JNF. Raman microscopy and tensile testing of individual fibres from the same samples were used to explore correlations among fading, molecular change and mechanical properties.

**Keywords [Heading]**
Māori textiles, accelerated light ageing, microfading, tensile testing, raman spectroscopy

**Introduction [Heading]**
Collections have considerable holdings of Māori textiles of cultural significance, constructed using *muka* (fibre) from *harakeke* (*Phormium tenax*). While guidelines exist for ‘safe’ display of light sensitive materials such as naturally-dyed plant fibres (Ashley-Smith, Derbyshire and Pretzel 2002, Ford and Smith 2011), no assessment has been made of the specific light-ageing characteristics of naturally-dyed New Zealand plant fibres. Textile artefacts from New Zealand are often displayed continuously because of their importance in Māori culture, resulting in the need to have accurate and specific data about their light ageing behaviour. Requests from Te Papa Tongarewa National

Museum of New Zealand about safe levels of display for Māori textiles prompted this study.

The effects of light ageing on plant fibres depends on fibre composition and tensile properties prior to ageing. *Muka* is a lignocellulosic fibre aggregate extracted from the leaf of *harakeke*. Compared with other plant fibres, *muka* contains relatively low cellulose (45% - 55%), and high hemicellulose (approximately 30%) and lignin (8 – 11%) (Daniels 1999, Carr, Cruthers, Laing and Niven 2005). The tenacity (tensile strength) of non-aged fibre prepared using customary techniques can range from 0.3 – 0.7 N/tex (Lowe, Carr, McCallum, Myers, Ngarimu-Cameron and Niven 2010). Tenacity varies according to the variety (approximately 60 *harakeke* weaving varieties are known), individual plant and leaf within a plant (Lowe et al. 2010), factors that must be considered when investigating light ageing of *muka*.

The response of dyed *muka* to light ageing depends on the dyes employed. The most common dye colours for *muka* include *paru* (black), *tanekaha* (tan/red) and *kowhai* (yellow). These dyes are prepared from a variety of sources including the bark of trees and muds with high iron content (Daniels 1999, Smith and Te Kanawa 2008). Investigations have focussed on *paru* coloured *muka* as it is known to lose physical integrity with age (Smith and Te Kanawa 2008). Accelerated thermal and chemical ageing have demonstrated loss of tensile strength and change of hue (Daniels 1999), and enabled some understanding of the chemical pathways (Daniels 1999, Smith and Te Kanawa 2008). However, the relationships among colour change, molecular structure and tensile properties when subjected to accelerated light ageing that simulates museum conditions (UV filtered light, temperature and relative humidity controlled) are unknown. Furthermore, *muka* dyed with colours other than *paru* have not been investigated.

The simplest and most obvious technique used by conservators to judge the condition of textile artefacts is colour change. Museum lighting guidelines for light sensitive artefacts are expressed in terms of exposure time in relation to a stated acceptable perception of fading. For example the display guideline for naturally-dyed fibres used by Te Papa Tongawera is 0.24 MLux hours exposure in 10 years. The concept of “one just noticeable fade” (1JNF) or “one perceptible change” has its roots in textile industry methods of comparing accelerated ageing of materials to the Blue Wool standards (Ashley-Smith et al. 2002). Although results from accelerated light ageing tests are commonly used, conservators recognise such data has limitations. These include assumptions of reciprocity, equivalence of spectra between ageing light sources and display lighting, and the use of test specimens as surrogates for the real artefact. Micro-fading is a relatively new technique that enables the fading response of artefacts to be measured in situ, minimising damage to the artefact itself. Although micro-fading has similar limitations to other accelerated ageing techniques, direct testing of artefacts is a distinct advantage (Ford and Smith 2011). However, confidence in applying this technique depends on comparisons with more familiar light ageing results (Whitemore

2002). Few studies are available that provide such comparisons, and at present no such data exists for naturally dyed New Zealand plant fibres.

Although colour change is an important criteria for judging artefact condition and display life, knowledge of any associated physical or chemical change may affect decisions regarding exhibition, conservation treatments and storage. Raman microscopy has been used successfully to characterise the molecular structure of natural plant fibres, and spectroscopic data is available for a range of fibre types (Edwards, Farwell and Webster 1997), although none is available for New Zealand plant fibres and dyes. The effects of accelerated ageing on cellulose-based materials can be followed using Raman microscopy, and the relative intensity of bands and band ratios show promise as a signature of ageing (Edwards, Nikhassan, Farwell, Garside and Wyeth 2006). Similarly, tensile testing of aged fibre specimens provides a measure of changes in strength (tenacity) and brittleness (strain to rupture, energy to rupture). Exploration of correlations among tensile properties and Raman signatures has indicated that Raman spectra can provide qualitative assessment of physical condition (Edwards et al. 2006) Although tensile properties of non-aged, non-dyed *muka* are relatively well documented (Lowe et al. 2010), and some information exists for tensile strength of *paru* dyed *muka* sampled from artefacts (Daniels 1999), the effects of ageing on *muka* tensile properties is not well documented, and the effects of dyes other than *paru* is unknown.

This pilot project had two broad aims. The first was to investigate physical and chemical changes to dyed *muka* in relation to colour change when exposed to accelerated light ageing. The second was to explore and refine techniques for assessing colour change, tensile properties and molecular structure of inherently variable plant fibres. Light ageing conditions were chosen to simulate display conditions currently practised at Te Papa Tongawera (95% of display time to be within standard conditions of 52% $\pm$ 7% RH and 20 °C (winter) and 22 °C (summer) $\pm$ 1 °C, UV filtered, exposure of 0.24 MLux hours per 10 years for light sensitive artefacts). Colour change was assessed using both established (Blue Wool standard) and emerging (micro-fading) methods familiar to conservators, enabling comparison of these techniques. Raman microscopy was explored for assessing changes in molecular structure of individual fibres.

**Materials and methods [Heading]**

A bundle of contemporary *muka* was prepared and dyed by an experienced Māori weaver. Leaves were harvested from a single *harakeke* bush and all *muka* extracted was combined into a single bundle. The bundle was separated into individual strands of fibre, which were then divided into two samples. Strands were assigned randomly to each sample. One sample was subsequently dyed with *tanekaha* using customary plant materials and techniques (red tannin solution dye bath from an infusion of *Phyllocladus trichomanoides* bark, dyed fibre then rubbed in warm wood ash to further develop colour (Smith and Te Kanawa 2008)), whilst the second sample remained non-dyed. Each sample was then divided into three portions.

The first portion was used to assess colour change in relation to the Blue Wool and Grey scale standards. *Muka* was wound onto a card, mounted into a specimen holder and artificially light aged following standard test methods (BS EN ISO Part B02 and UK-TN) using a Microsol 495 Light Fastness Machine fitted with an MB/mercury vapour lamp (400 W, 19500 lumen/100 hours). Specimen holders were fitted with UV-filter glass (Tru Vue Conservation Reflection Control®, blocking 97% of 300-380nm radiation). A water cooling system kept specimen holders at 20°C $\pm$ 4 °C and relative humidity was maintained at 52% with a saturated salt solution. Illumination levels were monitored with a Elsec 764 lux meter protected by the same UV-filtering glass. Average illumination at the specimens was 38,000 lux. Colour change was repeatedly assessed by a panel of four judges (BS EN ISO 105 Part A02) until an average colour change equivalent to Grey scale 4 (1JNF) was observed.

The second portion of each sample was artificially light-aged at 6 MLux for 10 minutes using a Newport Oriel Microfade Tester, fitted with a UV and IR filtered xenon source (400-700nm). Colour was measured using CIE L*a*b* co-ordinates and colour change (ΔE) calculated using both the CIE 1976 and 2000 colour space. Colour change was benchmarked against the Blue Wool standards, and expressed in terms of Blue Wool Equivalents (BWE) (Ford and Smith 2011).

The third portion of each sample was divided into individual fibre strands, and the strands mounted on cards so that only the centre 100 mm segment of each strand was exposed. The strands were light aged in the Microsol (0, 0.2, 0.4, 1.2, 1.5, and 2.0 MLux hours, n= 20 strands per exposure level). These fade levels were chosen to bracket Te Papa guidelines and the exposure to 1JNF determined from the first portion of *muka* as expected fading of Blue Wool standards 1 and 2 to 1JNF under UV filtered light (Ashley-Smith et al. 1999). After exposure, specimens were removed from the cards, length (mm) and weight (mg) of each individual fibre measured, and linear density calculated (tex = g/1000m).

The aged segment of each strand was tensile tested using an Instron 4464 Universal Testing Machine fitted with a 100N load cell (accuracy ± 0.5 %). Specimens were mounted in the clamps of the tensile testing machine with the exposed central portion of the strand corresponding to the 100mm gauge length. Specimens were preloaded (20 g) and tested at a strain rate of 10mm/min. Tensile properties calculated from the data were tenacity (N/tex), strain to rupture (%) and energy to rupture (N/tex, a measure of toughness). The effect of exposure on tensile properties was analysed using analysis of variance (ANOVA) procedures available in statistical software (SPSS v21).

Following tensile testing a sub-sample (n=6) of strands exposed for each of 0 and 2.0 MLux hours were used to investigate differences in the spectral signal of dyed and non-dyed, and aged and non-aged fibres using a Bruker Senterra Raman microscope and associated software. Various combinations of settings were trialled to determine a sampling regime that minimised damage to the specimen whilst providing spectra of

sufficient quality for analysis. Measurements were taken using the 785nm incident laser with each spectrum consisting of 50 co-added 5s acquisitions using the 20× objective and 50 µm confocal aperture with 3 $cm^{-1}$ spectral resolution. Data intervals were 0.3 $cm^{-1}$ and the automated Sure Cal® calibration was accurate to 0.1 – 0.3 $cm^{-1}$. This setup results in a laser spot size of about 2.4 µm in diameter. Variability within and among strands was explored by collecting a number of spectra (n=4) along the length of each specimen. Spectra were analysed using Unscrambler X 10.2 software. The spectra were processed using Linear Baseline Correction and Standard Normal Variate (SNV) transformations over the spectral region 300-1800 $cm^{-1}$ to align the baseline and scale each individual spectrum. Principal Component Analysis (PCA) was carried out over the same spectral region and used to explore interrelationships within the data, highlighting areas of similarity or difference among spectra. Partial Least Squares Regression (PLSR) was also used in an attempt to highlight differences between the control and light-aged data that was not evident with PCA.

**Experimental results and discussion [Heading]**

Both artificial ageing and micro-fading indicated *tanekaha*-dyed and non-dyed *muka* faded at a rate equivalent to Blue Wool standards 2 to 3, with 1JNF observed by the judges after approximately 1.8 MLux hours of exposure (Figure 2). Colour change rates measured by micro-fading were 2.4 and 2.8 BWE's based on CIE76 for *tanekaha* and non-dyed fibres respectively (2.8 and 4.0 based on CIE00). Comparison of these results with Te Papa Tongarewa guidelines of 0.24 MLux hours per 10 years implies an exhibition life of approximately 75 years under this regime before 1JNF.

The mechanical integrity (tenacity, extensibility, and toughness) of the *muka* strands appeared to be unaffected by accelerated light ageing up to 2 Mlux hours of exposure, with no statistically significant effect of light-aging for either the dyed or non-dyed *muka* (Figure 3) (*Tanekaha*; tenacity $F_{5,111} = 0.729$ P=0.603, extension to rupture $F_{5,111} = 1.196$ P=0.316, energy to rupture $F_{5,111} = 0.591$ P=0.707. Non-dyed; tenacity $F_{5,101} = 0.717$ P= 0.612, extension to rupture $F_{5,101} = 1.281$ P=0.278, energy to rupture $F_{5,101} = 1.010$ P=0.406). Therefore although colour change was perceptible for both *tanekaha* and non-dyed fibre after 1.8 MLux hours, this did not appear to be accompanied by a loss of mechanical integrity. A number of processes may contribute to this observation. The mechanical behaviour of lignocellulosic fibres such as *muka* is largely controlled by the cellulose microstructure. Light exposure is expected to cause oxidation rather than chain scission reactions in cellulose, with oxidation considered unlikely to degrade the mechanical properties of cellulose. In addition, limiting UV exposure limits the ability of cellulose to absorb light. However, the lignin component of the fibre is still susceptible, with degradation products contributing to colour change (Hallett and Bradley 2003).

Raman microscopy coupled with PCA enabled differences between dyed and non-dyed specimens to be readily detected. Here the dyed and non-dyed samples separate into two distinct groups along the first principle component (PC1) which captures the largest spectral variance in the samples (67%) (Figure 4b). The features contributing to this

separation are shown in the loadings plot, Figure 4a, with positive bands leading to separation into positive PC1 space and negative bands separating into negative PC1 space. The bands separating in the loadings are considered 'real' as they align with features in the original spectra (Figure 4a.)

The peaks observed in the natural samples spectra are associated with cellulose, hemicellulose and lignin (Edwards et.al. 1997) and are assigned in Figure 4(a). Of the bands associated with different components of the *tanekaha* dye, the bands at ~ 550, 625, 712, and 836 $cm^{-1}$ may be attributed to various anthocyanidins (Merlin et.al. 1994) which are thought to be the colour component of the *tanekaha* dye (Smith and Te Kanawa 2008). The bands at 949, 1180 and 1285 $cm^{-1}$ can be attributed to $\nu$(C-O-C) and two $\nu$(CC) alicyclic or aliphatic chain vibrations, respectively, but exact compound assignment of these bands is unsure. PCA of spectra showed separation based on dyed to natural, with the loadings separating based on fibre bands and dye bands (Figure 4).

PCA did not show any groupings related to light exposure of the samples, PLSR was used to find the areas of the spectra most likely to differentiate between control and light exposed. PLSR showed a weak separation between the aged and non-aged natural *muka*. Examination of the loadings plots (not shown) show that the differentiation appears to be a result of band differences at 378, 1096 and 1122 $cm^{-1}$ corresponding to $\delta$(CC) aliphatic chains, and two $\nu$(C-O-C) asymmetric vibrations in the natural fibers. The dyed samples appear to have degradation of the broad dye band at ~1330, and cellulose/hemicellulose bands at 1380, 1460 and 1603 $cm^{-1}$. However, the spectral changes were not definitive; this may be due to the paucity of the spectral differences or the fact that the Raman microscope did not sample a sufficiently large sample volume and thus was unrepresentative. With a more representative sampling regime – such as bulk Raman or infrared spectroscopy it may be possible to quantify photodegradation of dyed and non-dyed Māori textiles.

**Conclusions [Heading]**

This pilot study indicates that colour change to 1JNF measured using accelerated light-ageing and micro-fading techniques occurs for both *tanekaha* dyed and non-dyed *muka* at light exposures similar to that reported for other naturally-dyed textile fibres. However, no significant change in tensile properties or molecular structure could be detected. This information is useful for conservators for a number of reasons. Having an indication of light-fastness of *tanekaha* dyed fibres provides a level of confidence when planning and managing display of significant cultural material in relation to established international museum guidelines. The apparent lack of physical and chemical change associated with perceptible colour change indicates *tanekaha*-dyed artefacts are more robust than currently thought. Comparison of micro-fading data with conventional accelerated light ageing results is important for this emerging technique. Because micro-fading data provides an indication of how each tested artefact is likely to respond to light over time it is of obvious benefit, yet the infancy of the technique does not inspire confidence. The

similarity between accelerated light ageing and micro-fading results is reassuring, suggesting micro-fading is a useful tool for assessing light-fastness of textile artefacts constructed from New Zealand plant materials. Overall, this information may be used to meet requests from iwi, weavers and the wider community for extended access to artefacts. On the basis of data specific to New Zealand cultural material, conservators can more confidently extend display periods for Māori textiles, potentially approve travel of material to cultural centres outside the museum, and minimise expensive and unnecessary display changeover.

Additionally, the results of the pilot study have motivated a larger research program at the University of Otago, in partnership with Te Papa Tongarewa, National Museum of New Zealand. A wider range of traditional dyes used in Māori textile artefacts are being tested, higher levels of artificial light-ageing are being applied, and a wider range of spectroscopic techniques (FT-Raman and infrared) are being explored. The inherent variability of fibre properties is also being addressed using an improved experimental design in relation to sources of fibre variability. Further exploration of the correlations among colour change, tensile properties and molecular structure is expected to enhance the ability of conservators to give appropriate advice about the safe display of culturally-important Māori artefacts.

**Acknowledgements [Heading]**
Roka Ngarimu-Cameron for supply, preparation and dyeing of *muka*

**References [Heading]**

Ashley-Smith, J, Derbyshire, A, Pretzel, B, 2002, The continuing development of a practical lighting policy for works of art on paper and other object types at the Victoria and Albert Museum, *Preprints of the 13th triennial meeting of the ICOM Committee for Conservation in Rio de Janeiro*, Vol.1, 2002, pp. 3-8

British Standards. 1990. *UK-TN. Colour fastness to artificial light: mercury vapour fading lamp test*. British Standards: United Kingdom.

BS EN ISO 105 *Textiles – Test for colour fastness*. Part A02 *Grey scale for assessing change in colour, and* Part B02 C*olour fastness to artificial light.* British Standards: United Kingdom.

Carr, D. J., N. M. Cruthers, R. M. Laing, and B. E. Niven. 2005. Fibers from three cultivars of New Zealand flax (Phormium tenax). *Textile Research Journal* 75 (2): 93-98.

Daniels, V. 1999. The factors affecting the deterioration of the cellulosic fibres in black-dyed New Zealand flax (Phormium tenax). *Studies in Conservation.* no. 44:73-85.

Edwards, H.G.M., D.W. Farwell, and D. Webster. 1997. FT Raman microscopy of untreated natural plant fibres. *Spectrochimica Acta Part A* 53:2383-2392.

Edwards, H.G.M., N. F. Nikhassan, D.W. Farwell, P. Garside and P. Wyeth. 2006 Raman spectroscopic analysis of a unique linen artifact: the HMS *Victory* Trafalgar sail. *Journal of Raman Spectroscopy*. 37: 1193-1200.

Ford B. and N. Smith. 2011. Lighting guidelines and the lightfastness of Australian indigenous objects at the National Museum of Australia. In *ICOM-CC 16th Triennial Conference Preprints, Lisbon, 19-23 September 2011.* Paris: International Council of Museums

Hallett, Kathryn, and Susan Bradley. 2003. Ultraviolet-filtered lighting and cellulose degradation: Evaluating the effect of light exposure on ethnographic collections. *The Conservator* 27 (1): 3-12

Lowe, B.J., D.J. Carr, R.E. McCallum, T. Myers, R. Ngarimu-Cameron, and B.E. Niven. 2010. Understanding the variability of vegetable fibres: a case study of harakeke (*Phormium tenax*). *Textile Research Journal* 80 (20):2158-2166.

Merlin, J.-C., A. Statoua, J.-P. Cornard, M. Saidi-Idrissi and R. Brouillard. Resonance Raman spectroscopic studies of anthocyanins and anthocyanidins in aqueous solutions. *Phytochemistry* 35 (1):227-232

Smith, G., and R. Te Kanawa. 2008. Some Traditional Colourants of Maori and other Cultures. *Chemistry in New Zealand* 72 (4):127-131.

Whitemore, P. M. 2002. Pursuing the fugitive: Direct measurement of light sensitivity with micro-fading tests. In *The broad spectrum: Studies in the materials, techniques and conservation of color on paper*, ed. H.K. Startis and B. Salvesen. London: Archetype Publications.

**Materials List [Heading]**

Microsol Light Fastness Tester Model 495, James H. Heal and Co. Ltd.: Halifax, UK, fitted with UV filter glass, Tru Vue Conservation Reflection Control: McCook, Illinois, USA

Elsec 764 Environmental Monitor, Littlemore Scientific Engineering: Dorset, UK.

Oriel Fading Test System (O-MFT), Newport Corporation: Irvine, California, USA

Instron 4464 Universal Testing Machine, Instron Corporation: Canton, Massachusetts, USA

Bruker Senterra Raman microscope, Bruker Biosciences Pty Ltd: Lower Hutt, New Zealand.

**Captions for figures**

Figure 1. *Muka* specimens mounted on cards for accelerated light ageing. a) assessment relative to Blue Wool standards, and b) tensile specimens.

Figure 2. Results of colour change assessment of *tanekaha*-dyed and non-dyed *muka* samples using standard method BS EN ISO 105 *Textiles – Test for colour fastness.*

Figure 3. Effect of accelerated light ageing on tensile properties of *muka* (error bars: one standard deviation) a) tenacity, b) strain to rupture, c) toughness (energy to rupture).

Figure 4. Results of Raman analysis of *tanekaha*-dyed and non-dyed *muka,* aged and non-aged. a) Raman spectra and PC1 loadings with cellulose and hemicellulose type bands labeled in dark red and distinctive dye bands labeled in blue-green. b) PCA scores plot demonstrating the separation of samples based on dye, the spectral features relating to this separation are shown in the loadings plot (a).