# Identification of Cellulosic Fibres by FTIR Spectroscopy I: Thread and Single Fibre Analysis by Attenuated Total Reflectance

Paul Garside[1] and Paul Wyeth[1,2]

[1] Research Centre for Textile Conservation and Textile Studies, Textile Conservation Centre, University of Southampton Winchester Campus, Park Avenue, Winchester, SO23 8DL.

[2] Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ.

**Summary**

The ability to accurately identify fibres is of importance to conservators, allowing the most appropriate methods of treatment to be employed. Our research has concentrated on the development of an ATR FT-IR spectroscopic technique for the characterisation of cellulosic (plant) fibres.

Six species of fibre were examined, taken largely from the bast group (flax, hemp, jute and ramie), along with cotton and sisal. Initially, unprocessed fibres were considered; subsequently, processed fibres from a variety of sources were examined. Peak intensity ratio techniques were employed to differentiate the fibre types on the basis of relative lignin content with respect to other cellular components.

It was found that for each of the species of fibre, the ratios fell within characteristic ranges.

**Authors' Biographies**

***Paul Wyeth*** received a BA (Hons) from Cambridge, where he remained to study for a PhD. He joined the Chemistry Department at the University of Southampton in 1978 and currently holds a joint appointment as lecturer in the Chemistry Department and lecturer in Conservation Science at the Textile Conservation Centre. He is a Fellow of the Royal Society of Chemistry and a member of the United Kingdom Institute for Conservation and of the recently constituted Institute for Conservation Science. He has helped to establish the Southern Conservation Network, which supports heritage conservators and curators in the South of England. His research interests encompass applications of microstructural and microspectroscopic analysis in the areas of conservation science and natural technology.

***Paul Garside*** studied for his Master of Chemistry degree at Southampton, graduating in 1998. He stayed on for doctoral research with Paul Wyeth on the characterisation of natural polymer fibres in historic textiles. He has developed significant expertise in applying analytical methodology to conservation science problems and is now extending this through postdoctoral studies at the Research Centre for Textile Conservation and Textile Studies, University of Southampton.

# Identification of Cellulosic Fibres by FTIR Spectroscopy I: Thread and Single Fibre Analysis by Attenuated Total Reflectance

Paul Garside[1] and Paul Wyeth[1,2]

[1] Research Centre for Textile Conservation and Textile Studies, Textile Conservation Centre, University of Southampton Winchester Campus, Park Avenue, Winchester, SO23 8DL.

[2] Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ.

## Introduction

Cellulosic (plant) fibres have been used to produce textiles for thousands of years, and the treatment of such artefacts represents an important aspect of heritage conservation. The identification of the fibres may not only adduce the origin of an artefact, for example, but can also serve as a predictor of behaviour and so is essential in allowing an informed decision on conservation protocol.

Conventional approaches to the characterisation of these fibres, such as microscopy and staining techniques have several limitations: The methods rely heavily on experience as they generally produce qualitative data and may require the subjective comparison of results. In addition, degradation and physical damage can often conceal or destroy the characteristic fibre morphology necessary to an unambiguous identification. A routine, objective method, not reliant on such visual clues, would be of value. The aim of the research described below was to assess the suitability of vibrational spectroscopy, as a reliable, reproducible and relatively simple technique, for the differentiation of plant fibres. This builds on previous work carried out by our group [1] and the seminal contributions of others, as described below.

Vibrational spectroscopy covers a range of techniques, including conventional Fourier transform infrared (FTIR), Raman and attenuated total reflectance (ATR) spectroscopy. These methods have been variously employed for the study of textile fibres, not only to identify the fibres themselves and their state of deterioration, but also to confirm processing and dye treatments [2],[3],[4],[5],[6].

Spectroscopic approaches have been widely used to distinguish the broad categories of cellulosic, proteinaceous and regenerated natural fibres and the many different types of synthetic fibre [7],[4],[8],[9]. The marked chemical differences between these groups of materials means that they are often readily distinguished. In general, however, there have been few reports on the differentiation of the chemically similar fibres within a group, such as the cellulosic plant fibres. Edwards has employed Raman spectroscopy to discriminate amongst untreated plant fibres (ramie, jute, flax, cotton, kapok, sisal and coir) on the basis of peak ratios derived from the associated C-H and glycosidic C-O-C vibrations [10]. However, the Raman technique is not routine for many conservation science laboratories and, in any case, we have found that luminescence can prove problematic even when excitation is performed at longer, near infrared wavelengths, particularly with historic materials. Infrared spectroscopy would seem the more appropriate choice, but, to date, a similarly comprehensive analysis of cellulosic materials has not appeared, although there have been several reports in which band assignments are presented for the various constituents [11],[12],[13] and in which degradation has been assessed. In the latter case, the loss of identifiable chemical components and the accumulation of distinctive degradation products (such as carbonyl containing species produced by oxidative processes) have been followed, and changes in microstructure deduced from spectroscopically-derived crystallinity indices [14],[15],[16].

In the research presented below, we have used ATR spectroscopy, a refinement of conventional FTIR spectroscopy [17],[18],[19], to characterise cellulosic plant fibres. Infrared radiation will excite molecular vibrations within a material; the frequencies of these vibrations, and hence the absorption peaks in the spectrum, are characteristic of the chemical composition of the specimen. In the ATR technique, the fibre sample is just pressed against a crystal 'window' (typically diamond) and the infrared beam interacts with the sample at the interface. While the radiation undergoes total internal reflection at the crystal surface, an evanescent wave penetrates the sample to a shallow depth (typically of the order of the radiation wavelength, i.e. a few microns), and it is absorption of this component which produces the infrared spectrum. The technique offers a number of advantages over conventional or micro-spectroscopy: relatively small sample sizes can be employed, little preparation is required, and, after brief practice, due to the controlled presentation of the sample to the radiation by the ATR anvil, the data is highly reproducible; a portable ATR set-up, or one with an

optical fibre probe, may preclude the need to sample at all. In addition, the technique is simple to use and reasonably widely available, considerations which are of importance if the approach is to become routine.

Six species of fibre were considered in the study, chosen to represent the types of fibre typically encountered in textile artefacts: cotton (a seed fibre); flax, hemp, jute and ramie (bast - or stem - fibres); and sisal (a leaf fibre). Initially, raw unprocessed fibres were analysed. Subsequently, processed fibres from yarns and textiles were examined, from both modern and historic sources.

All plant fibres have a cellular structure and are largely composed of cellulose, along with hemicelluloses, pectins, lignin (see *Figure 1*), and other minor components, which may include bound water, residual protein, waxes and pigments, and inorganic materials. Cellulose is found primarily in the cell walls and adopts a crystalline, fibrillar structure interspersed with amorphous regions. Hemicelluloses are branched polysaccharides (primarily with xylan and mannan monomers) that adopt an amorphous structure, and form a matrix in which the cellulose microfibrils are embedded. Pectins are jelly-like acidic polymers of galacturonic acid, incorporating some arabinose and galactose units. Lignin is an amorphous phenolic polymer with a poorly characterised structure, which is also found within the natural composite matrix.

Typical compositions of the various fibre types are given in *Table 1*, though as the fibres are natural products, these values will vary along the fibre length and between samples [20],[21]. Nonetheless, the relative proportion of lignin with respect to other cellular components seems distinctive and, indeed, the qualitative assessment of lignin content by staining (such as the phloroglucinol test or the use of the Herzberg reagent) is an accepted method of fibre characterisation [9],[22].

We have applied ATR spectroscopy to the comparison of the lignin to cellulose content of the plant fibres. As the predominant component of these fibres is cellulose, and other major constituents (hemicelluloses and pectins) are also polysaccharides, the spectra of the samples are superficially similar (*Figure 2*); band assignments are presented in *Table 2*. As a result they cannot be readily distinguished by eye, and we have found that library search techniques are also of limited value. However, there are certain ‘signatures’ that can be assigned to specific components; the relative

intensity of each can be considered as representative of the proportion of that component within the fibre: the C=O ester band at ~1735 $cm^{-1}$, from pectin (however, this band can also be strengthened by the carbonyl groups of oxycelluloses found in degraded materials); the C=C in plane aromatic vibrations at ~1595 $cm^{-1}$ and ~1505 $cm^{-1}$, from lignin; the C-C ring breathing band at ~1155 $cm^{-1}$ and the C-O-C glycosidic ether band at ~1105 $cm^{-1}$, both of which arise from the polysaccharide components (that is, largely cellulose). The intensity of the C-H stretching vibration at ~2900 $cm^{-1}$ was taken as a measure of the general organic material content of the fibre.

The fibres were characterised by calculating ratios based on the intensities of the bands at 2900, 1595 and 1105 $cm^{-1}$; these bands were taken to represent the overall organic content, the lignin content and the cellulose content, respectively. (The pectin derived band at ~1735 $cm^{-1}$ was also considered, but was found not to provide consistent data.) Two ratios were calculated as it was found that this was a more reliable means of distinguishing the different fibre types than the use of a single ratio. (We have found that the ratios presented here form a better basis for differentiation than those employed in our earlier work [1].)

**Experimental Method**

Initially, unprocessed fibres were studied; the spectra of ten samples of each of the six fibre types (cotton, flax, hemp, jute, ramie and sisal) were obtained. Subsequently, processed fibres (in the form of yarns or textiles) from a variety of sources were assessed, although fewer samples were available: cotton, 5; flax, 8; hemp, 4; jute, 11; ramie, 3; and sisal, 5. These processed materials were taken from the Textile Conservation Centre's reference collection, and included several examples of aged historic textiles (generally dating from the early part of the twentieth century). The samples were not subjected to any preparative treatment, and were analysed under ambient conditions, no attempt being made to control the temperature or humidity.

Absorbance spectra were acquired using a *BioRad 'FTS 135'* FTIR spectrometer equipped with a *Specac 'Golden Gate'* ATR accessory. The latter was fitted with a diamond crystal, and operated with single reflection optics at an interaction angle of 45 º and a probe area of 0.6 mm diameter; the sampling depth (at 1000 $cm^{-1}$) was calculated to be approximately 3 μm. The spectra were recorded over the range 4000 - 750 $cm^{-1}$, with a resolution of 4 $cm^{-1}$, and averaged over 32 scans. Subsequent manipulation was carried out with *Galactic Industries 'GRAMS/32'* software. Base-line

corrections were applied at 3680, 2630, 1780, 1185 and 765 $cm^{-1}$, and the intensities of the bands at 2900, 1595 and 1105 $cm^{-1}$ measured above local baselines imposed between 3000 – 2630, 1780 – 1485 and 1185 – 765 $cm^{-1}$ respectively. [The derivation of intensities from deconvoluted spectra was considered, but gave inconsistent results].

The following ratios were then calculated:

$$R_1 = I_{1595} / I_{1105}$$

$$R_2 = I_{1595} / I_{2900}$$

**Results and Discussion**

Typical spectra for each of the six fibre types are shown in *Figure 2*, demonstrating their superficial similarity and domination by the contribution from the cellulosic component; the spectrum of pure cellulose is given for comparison.

For the native fibres, the average values of the two ratios, $R_1$ and $R_2$, and their standard deviations, $\sigma_1$ and $\sigma_2$, are presented in *Table 3.a*; these ratios are plotted against each other in *Figure 3.a*. The corresponding data for the processed fibres are presented in *Table 3.b* and *Figure 3.b*. The envelopes shown on these graphs denote the regions into which the data for the various species of fibre fall.

As can be seen, whilst a single measurement of lignin content, based on either the lignin to cellulose ratio ($R_1$) or the lignin to organic material ratio ($R_2$), does allow a certain degree of differentiation between the fibre types, it is more useful to consider both values. A unique region for each fibre type can be defined in a plot of the two ratios. The native fibres appear to be the more readily differentiated in the graphs, with the lignin content often being somewhat lower for the processed ones. Even so, there is little overlap of the mapped regions suggesting that the method may have general utility. Furthermore, the ratios were found to be quite insensitive to the age of the samples, both early and late twentieth century specimens complying with the analysis.

There is a general trend for the data points to fall along a diagonal axis on the plots, with the more highly lignified materials found at higher values of the two ratios. However, this trend does not

strictly follow the literature data for fibre composition (see *Table 1*), as sisal has higher values of $R_1$ and $R_2$ than jute (with lignin contents of 9.9 and 11.8 % respectively), and a similar discrepancy is observed for cotton and ramie. There may be two explanations for this apparent anomaly:

1. Lignin is a poorly characterised material and its exact properties vary depending on both the species of the plant and its location within the plant [21]. The fact that cotton is a seed fibre, sisal a leaf fibre, whilst the other four are stem fibres may have some bearing, with differences in the chemical composition of the lignin possibly accounting for the discrepancy.
2. In the 'fingerprint' regions of the spectra, which contain the cellulose and lignin bands, numerous overlapping peaks are observed. As intensities were derived by direct measurement from the spectra, rather than from deconvoluted peak data, there will be contributions from the underlying bands. For example, the shoulder of the water deformation band at 1635 $cm^{-1}$ may augment the 1595 $cm^{-1}$ lignin absorbance, although we have found that spectra which evidence significantly different amounts of adsorbed water nonetheless give consistent $R_1$ and $R_2$ ratios. (However, the precision of the data might improve if it was possible to maintain environmental conditions constant.)

Despite their ostensible similarity, it is apparent that just minor differences in the composition of the various cellulosic plant fibres allow them to be distinguished by ATR FT-IR spectroscopy, whether the fibres are presented unprocessed or in textile threads. Preliminary investigations also suggest that this technique is applicable to the characterisation of such fibres in paper. (There may be some ambiguity though when dyes or other finishing agents contribute overlapping infrared bands, or where there is marked fibre deterioration.)

Since the polarised infrared spectroscopic technique is also applicable to ATR, the oriented crystallinity of cellulose within natural fibres may also be probed. The value of this to the further differentiation of bast fibres (and particularly the potentially problematic species flax and hemp) will be the subject of a subsequent publication.

**Acknowledgements**

While this work was completed PG was supported by an Engineering and Physical Sciences Research Council (EPSRC) studentship. PW would like to thank Nell Hoare, Director, Textile

Conservation Centre, University of Southampton, for permission to publish, and other colleagues at the TCC for their support.

**References**

[1] P. GARSIDE and P. WYETH, 'Characterisation of Plant Fibres By Infra-Red Spectroscopy', *Polymer Preprints* **41**(2) (2000) 1792-1793.

[2] D.H. ABRAHAMS and S.M. EDELSTEIN, 'A New Method for the Analysis of Ancient Dyed Textiles' in M. LEVEY, *Archaeological Chemistry*, University of Pennsylvania Press, Philadelphia (1967) 15-27.

[3] C-S CHEN, C.W. BROWN and M.J. BIDE, 'Non-destructive Near-IR Analysis for the Identification of Dyes on Textiles', *Journal of the Society of Dyers and Colourists* **110** (1994) 196-199.

[4] T. GÁL, I. AMBRUS and S. URSZU, 'Forensic Analysis of Textile Fibres by Fourier Transform Infrared Diamond Cell Technique', *Acta Chimica Hungarica* **128**(6) (1991) 919-928.

[5] P.A. MARTOGLIO, S.P. BOUFFARD, A.J. SOMMER, J.E. KATON and K.A. JAKES, 'Unlocking the Secrets of the Past - The Analysis of Archaeological Textiles and Dyes', *Analytical Chemistry* **62** (1990) 1123A-1128A.

[6] S.D. WRIGHTMAN, A. MURRAY and H.F. SHURVELL, 'The Identification of Pigments in Paper Coatings by Infrared Spectroscopy', *Internet Journal of Vibrational Spectroscopy* **3**(3) (1999) 3 www.ijvs.com.

[7] P.L. LANG, J.E. KATON, J.F. O'KEEFE, D.W. SCHIERING, 'The Identification of Fibers by Infrared and Raman Microspectroscopy', *Microchemical Journal* **34** (1986) 319-331.

[8] H.E. HOWELL and J.R. DAVIS, 'Qualitative Identification of Fibers Using NIR Spectroscopy', *Textile Chemist and Colorist* **23** (1991) 69-73.

[9] D.R. PERRY, *Identification of Textile Materials (7th Edition)*, The Textile Institute, Manchester (1985).

[10] H.G.M. EDWARDS, D.W. FARWELL and D. WEBSTER, 'FT-Raman Microscopy of Untreated Natural Plant Fibres', *Spectrochimica Act - Part A* **53** (1997) 2383-2392.

[11] J. BLACKWELL, P.D. VASKO and J.L. KOENIG, 'Infrared and Raman Spectra of cellulose from the Cell Wall of Valonia Ventricosa', *Journal of Applied Physics* **41**(11) (1970) 4375-4379.

[12] H.G.M. EDWARDS, D.W. FARWELL and A.C. WILLIAMS, 'FT-Raman Spectrum of Cotton: A Polymeric Biomolecular Analysis' *Spectrochimica Acta* **50A**(4) (1994) 807-811.

[13] M.L. NELSON and R.T. O'CONNOR, 'Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type. Part I. Spectra of Lattice Types I, II, III and of Amorphous Cellulose', *Journal of Applied Polymer Science* **8** (1964) 1311-1324.

[14] M. MASCARENHAS, J. DIGHTON and G.A. ARBUCKLE, 'Characterisation of Plant Carbohydrates and Changes in Leaf Carbohydrate Chemistry Due to Chemical and Enzymatic Degradation Measured by Microscopic ATR FT-IR Spectroscopy', *Applied Spectroscopy* **54**(4) 2000 681-686.

[15] J.E. MILLER and B.M. REAGAN, 'Degradation in Weighted and Unweighted Historic Silks', *Journal of the American Institute for Conservation* **28** (1989) 79-96.

[16] M.L. NELSON and R.T. O'CONNOR, 'Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type. Part II. A New Infrared Ratio for Estimation of Crystallinity in Celluloses I and II', *Journal of Applied Polymer Science* **8** (1964) 1325-1341.

[17] J. COATES and A. SANDERS, 'A Universal Sample Handling System for FT-IR Spectroscopy' *Infrared Spectroscopy* **12**(5) 2000 12-22.

[18] D. COOMBS, 'The Use of Diamond as an ATR Material' *Internet Journal of Vibrational Spectroscopy* **2**(2) 1998 3 www.ijvs.com.

[19] SPECTRA-TECH, 'Introduction to Attenuated Total Reflection (ATR) Spectroscopy', Spectra-Tech Inc. (2000) www.thermospectra-tech.com/resource/theory.pdf .

[20] M. LEWIN and E.M. PEARCE (EDITORS), *Handbook of Fiber Chemistry (2nd Edition)*, Marcel Dekker, Inc., New York (1998).

[21] A. TÍMÁR-BALÁSZY and D. EASTOP, *Chemical Principles of Textile Conservation*, Butterworth-Heinemann, Oxford (1998).

[22] J.A. MARSHALL, 'The Identification of Flax, Hemp, Jute and Ramie in Textile Artefacts', MSc Dissertation, The University of Alberta, Edmonton (1992).

**Manufacturers and Suppliers**

ATR FT-IR: BioRad ‘FTS 135’ FT-IR spectrometer (Bio-Rad House, Maylands Avenue, Hemel Hempstead, Hertfordshire, HP27TD) with Specac ‘Golden Gate’ ATR accessory (River House, 97 Cray Avenue, Orpington, Kent, BR5 4HE).

Software: Galactic Industries ‘GRAMS/32 5.21’ (395 Main Street, Salem, NH 03079, USA).

Table Legends

Table 1. The composition of cellulosic fibres [20],[21]. In addition to the listed components, bound water, residual waxes, pigments, protein and inorganic material will also be found.

Table 2. Infrared band assignments for the cellulosic fibres [11],[10],[12],[13].

Table 3. The average values of the band intensity ratios $R_1$ ($I_{1595}$ / $I_{1105}$) and $R_2$ ($I_{1595}$ / $I_{2900}$) and their standard deviations, $\sigma_1$ and $\sigma_2$, are tabulated for (a) native and (b) processed fibres.

Figure Captions

Fig. 1. Structures of the momomeric units for the major polymeric constituents of cellulosic plant fibres. Typical monomers are shown for hemicellulose, pectin and lignin.

Fig. 2. Infrared absorbance ATR spectra of the plant fibres and pure cellulose recorded over the range 4000 – 750 $cm^{-1}$.

Fig. 3. Plots of the intensity ratios, $R_1$ versus $R_2$ for (a) native fibres and (b) processed fibres. The envelopes denote the regions into which the combined data for the various species of fibre fall.

*Table 1:* The composition of cellulosic fibres [20],[21]. In addition to these major components, which are sub-totalled, bound water, residual waxes, pigments, protein and inorganic material will also be found.

| | Cellulose/% | Hemicellulose/% | Pectin/% | Lignin/% | Sub-total/% |
|---|---|---|---|---|---|
| **Cotton** | 82.7 | 5.7 | | 0.0 | 88.4 |
| **Flax** | 64.1 | 16.7 | 1.8 | 2.0 | 84.6 |
| **Hemp** | 67.0 | 16.1 | 0.8 | 3.3 | 87.2 |
| **Jute** | 64.4 | 12.0 | 0.2 | 11.8 | 88.4 |
| **Ramie** | 68.8 | 13.1 | 1.9 | 0.6 | 84.4 |
| **Sisal** | 65.8 | 12.0 | 0.8 | 9.9 | 88.5 |

*Table 2:* Infrared band assignments for the cellulosic fibres [11],[10],[12],[13].

| **Position / $cm^{-1}$** | **Assignment** |
|---|---|
| ~ 3335 | ν(OH) free |
| ~ 2900 | ν(C-H) |
| ~ 2850 | ν($CH_2$) symmetrical stretching |
| ~ 1735 | ν(C=O) ester |
| ~ 1635 | adsorbed water |
| ~ 1595 | ν(C=C) aromatic in-plane |
| ~ 1505 | ν(C=C) aromatic in-plane |
| ~ 1475 | δ($CH_2$) scissoring |
| ~ 1455 | δ(C-H); δ(C-OH) 1° & 2° alcohol |
| ~ 1420 | δ(C-H) |
| ~ 1365 | δ(C-H) |
| ~ 1335 | δ($CH_2$) wagging |
| ~ 1315 | δ(C-H) |
| ~ 1280 | δ($CH_2$) twisting |
| ~ 1235 | δ(C-OH) out-of-plane |
| ~ 1200 | δ(C-OH); δ(C-CH) |
| ~ 1155 | ν(C-C) ring breathing, asymmetric |
| ~ 1105 | ν(C-O-C) glycosidic |
| ~ 1050 | ν(C-OH) 2º alcohol |
| ~ 1025 | ν(C-OH) 1º alcohol |
| ~ 1005 | ρ(-CH-) |
| ~ 985 | ρ(-CH-) |
| ~ 895 | ν(C-O-C) in plane, symmetric |

*Table 3:* The average values of the band intensity ratios $R_1$ ($I_{1595}$ / $I_{1105}$) and $R_2$ ($I_{1595}$ / $I_{2900}$) and their standard deviations, $\sigma_1$ and $\sigma_2$, are tabulated for (a) native and (b) processed fibres.

| **a** | $R_1$ | $\sigma_1$ | $R_2$ | $\sigma_2$ |
|---|---|---|---|---|
| **Cotton** | 0.39 | 0.14 | 0.09 | 0.03 |
| **Flax** | 0.70 | 0.12 | 0.33 | 0.12 |
| **Hemp** | 0.61 | 0.13 | 0.12 | 0.04 |
| **Jute** | 0.96 | 0.18 | 0.24 | 0.02 |
| **Ramie** | 0.10 | 0.06 | 0.02 | 0.01 |
| **Sisal** | 1.37 | 0.35 | 0.51 | 0.19 |

| **b** | $R_1$ | $\sigma_1$ | $R_2$ | $\sigma_2$ |
|---|---|---|---|---|
| **Cotton** | 0.40 | 0.15 | 0.11 | 0.03 |
| **Flax** | 0.36 | 0.10 | 0.17 | 0.08 |
| **Hemp** | 0.38 | 0.03 | 0.11 | 0.01 |
| **Jute** | 0.78 | 0.04 | 0.27 | 0.03 |
| **Ramie** | 0.13 | 0.05 | 0.04 | 0.01 |
| **Sisal** | 1.05 | 0.10 | 0.47 | 0.11 |