

SPECTRAL CHARACTERISATION OF ANCIENT WOODEN ARTEFACTS WITH THE USE OF TRADITIONAL IR TECHNIQUES AND ATR DEVICE: A METHODOLOGICAL APPROACH

TECHNICAL PAPER

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This work presents a methodological approach to the study of ancient wooden artefacts using FT-IR techniques. Sampling is one of the most important steps during investigation of works of art. However, samples should be taken only when this operation does not appreciably modify any part, or change the integrity of the wooden artefact in question. Although it was invasive, a low-destructive method of sampling was used on wood meal in order to obtain reproducible results. Moreover, two modes of operation were compared, namely the transmission mode (carried out on pellets of wood meal mixed with KBr) and the Attenuated Total Reflectance (ATR) mode (carried out directly on wood meal). For the former, the effect of the concentration of wood in KBr was also considered. The results show a similar quality of spectra, although a different sensitivity between the two techniques in some spectral ranges was observed. The final focus of this research will be on validating the use of IR spectra to date wooden materials.

1 Introduction

Since 1980s, Fourier Transform Infrared spectroscopy (FT-IR) has been one of the most widely used analytical techniques for routine and research laboratory analyses in the art conservation field.¹⁻³ When waterlogged archaeological wood samples are studied, the FT-IR technique is often used to characterise the degradation of the objects in order to choose the appropriate conservation method.⁴ However, the FT-IR technique has not yet been extensively applied to the study of ancient wooden artefacts, such as furniture, beams, painting supports, and sculptures.

FT-IR spectroscopy is a useful technique for studying the chemistry of decay in wood, because a minimal manipulation of samples is required, and very small quantities (for example, a few milligrams of wood) can be analysed to provide detailed information. FT-IR has been extensively used to characterise the chemistry of wood⁵⁻⁷ and to obtain quantitative data, mainly in the determination of lignin.⁸ Moreover, it has also been

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used to analyse the chemical changes in wood that occur during weathering, decay and chemical treatments,⁹ and biodegradation processes.¹⁰ In addition, several studies have focused on the possibility of using FT-IR methodologies for dating of wooden artefacts.^{11,12}

The aim of this paper is to define a procedure for wood analysis and to compare the data acquired using the same wooden materials, more specifically samples taken from ancient wooden artefacts, by applying two different FT-IR techniques that are commonly used in the investigation of artworks: the traditional KBr pellet transmission mode and the Attenuated Total Reflectance (ATR) mode. In order to limit the variability of the specimens, only two wooden species, namely larch (*Larix decidua* Mill) and Norway spruce (*Picea abies* Karst.), were used to make this comparison. The final focus of the present research will be to determine the possibility of dating wood materials by starting from IR spectra. This aspect is significant, because only a limited quantity of data on this specific application is available in the literature, and not all of the authors have reached similar conclusions.

Wood is a renewable natural resource and a complex material made up of hollow cells with a strong wall that consists mainly of three biopolymers: cellulose, lignin, and hemicelluloses. In addition to these polymeric components, wood may also contain extractives in greater or lesser quantities. These include several classes of organic compounds such as sugars, flavonoids, tannins, terpenes, fats or waxes.^{13,14}

A distinction must be made between the constituents of chemical components of wood. To be more precise, cellulose, hemicelluloses, and lignin are the main macromolecular cell wall components, and are present in all woods. Instead, other minor low molecular-weight components, namely extractives and mineral substances, are generally more closely related to specific wood species, both in type and amount (Table 1). The relative concentration and the chemical composition of lignin and hemicelluloses differ between softwoods and hardwoods, while cellulose is a uniform component of all wood species.^{13,14}

	Hardwoods	Softwoods	Larch	Norway spruce
Cellulose	40-50%	40-50%	42-44%	40-46%
Hemicelluloses	30-40%	20-35%	20-25%	30-35%
Lignin	20-25%	25-35%	26-28%	26-28%
Extractives and mineral substances	4-10%	4-25%	8-12%	2-4%

Table 1. Basic chemical composition of generic hardwoods and softwoods and of specific species involved in this work. Values were taken both from the literature¹³ and from internal data available at IVALSA-CNR.

2 Materials and Methods

2.1 Samples and sampling

The samples analysed were taken from two Norway spruce (*Picea abies* Karst.) beams and two larch (*Larix decidua* Mill.) beams. All beams belonged to wooden roof structures in Venice, and were dated by means of dendrochronological analysis (Table 2). Two samples were collected from each beam, except for one beam of larch, which had been partially attacked by fungi.

At the beginning of the study, it had been decided to collect only small size flakes from the samples to be analysed by FT-IR. However, these flakes did not give reproducible results. Consequently, wood meal collected from the sample was used. Although it is invasive, this operation is low-destructive, and it greatly improved the reproducibility of the measurements.

Wood meal was obtained with a power drill equipped with a Resistograph® needle having a diameter of 3 mm. The first 2-3 mm of wood meals, starting from the surface, were removed, and then the inner wood meal was gathered on a piece of paper and poured into vials (Figure 1).

sample	provenance	wood species	time extension AD	dating
1400	Beam 1	Larch	1295-1525	<i>terminus ante quem non</i>
1350 1500	Beam 3	Larch	1293-1557	<i>terminus ante quem non</i>
1400 1440	Beam 4	Norway spruce	1394-1477	<i>terminus ante quem non</i>
1340 1400	Beam 7	Norway spruce	1337-1464	<i>terminus ante quem non</i>

Table 2. This table shows the samples collected from each beam and the corresponding dendrochronological dating.



Figure 1: Sampling the wood meal.

2.2 Wood meal preparation

The wood meal samples were extracted by means of organic solvents, in order to remove fatty acids, resin acids, waxes, tannins, and coloured substances. Extraction was carried out by means of sonication (Julabo model USR-1; 51 kHz), four times for 15 min in a 1:1:1 v:v:v ethanol/acetone/cyclohexane solution. Although sonication is a non-standard extraction method, this procedure is widely used for plant tissues, including wood, when only a small quantity of a sample is available.¹⁵⁻¹⁷ Prior to the IR analyses, the wood meals were oven-dried at 103 °C up to constant weight.

2.3 FTIR analysis

IR spectra were collected with two different instrumental configurations:

1. An Attenuated Total Reflectance (ATR) accessory mounted on a Bruker Optics Alpha ATR FTIR spectrometer, spectral range 4000-400 cm^{-1} , with a spectral resolution of 4 cm^{-1} (40 scans),
2. The transmission mode was achieved using a purged Nicolet Nexus FTIR spectrometer on 13-mm diameter KBr pellets, spectral range 4000-400 cm^{-1} , with a spectral resolution of 4 cm^{-1} (64 scans).

The analysis was performed in two steps: first, the wood meal was directly analysed by ATR technique; then, the same wood meal previously analysed using ATR was measured in the form of KBr pellets.

Spectra were manipulated using Opus 6.5 software (Bruker Optics). The baseline correction function was applied only on the transmittance spectra, in order to evaluate the concentrations of the KBr pellets. In addition, the normalization function was used for a systematic comparison among the entire set of spectra. This function made it possible to normalise the spectra and to perform offset corrections on them. The Min_Max 1900 - 1300 cm^{-1} normalization function was used for almost all the spectra: it enabled the scaling of each of the spectrum intensities, with the effect that the minimum absorbance unit was set as 0 and the maximum as 2. The ATR spectra were not further modified by applying any ATR correction functions supplied by the FT-IR software companies.

3 Results and discussion

3.1 KBr pellet concentration

Part of this work dealt with an evaluation of the effect of wood meal concentration on KBr pellets. A set of measurements was performed on mixtures containing different concentrations of dried wood meal and desiccated KBr. The mixtures ranged from 1.5% to 8.5%

of the total weight of a 200-mg sample of wood meal (Table 3).

wood (mg)	KBr (mg)	%
17	183	8.5
14	186	7
12	188	6
10	190	5
5	195	2.5
3	197	1.5

Table 3. KBr pellet concentrations (w%). The mixture of wood meal and KBr that gave the best results is shown in boldface.

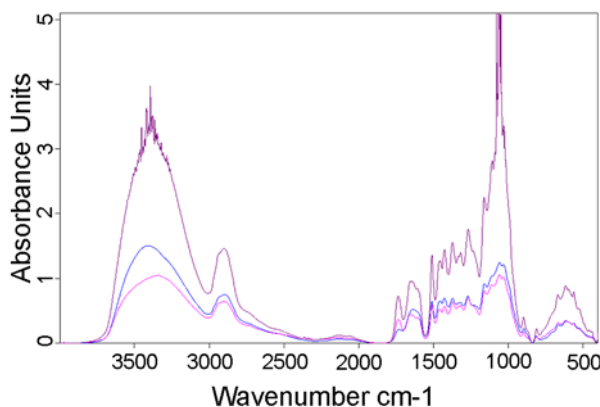


Figure 2: Spectra at different mixture concentrations: Wood meal 6%: purple curve; wood meal 2.5%: blue curve; wood meal 1.5%: pink curve.

Each mixture was homogenised in a ceramic mortar and transferred to a die with a barrel diameter of 13 mm. The mixture was then placed in a suitable press and compressed at approximately 10,000 psi for 1-2 min. The compression of the powder produced a clear glassy disk with a thickness of ca 1 mm. The optimal spectra were obtained for the 2.5% concentration (5 mg of wood meal and 195 mg of KBr) (Fig. 2). This result differed from the data reported by Faix and Böttcher,¹⁸ since they stated that the wood concentration in KBr pellets should not overly exceed the 0.1-0.5% range. This difference was most probably related to the different granulometry used: in the case reported by Faix and Böttcher, this was the sieved fraction <25 μm , while in this case it was uncontrolled, due to the necessarily limited quantity of wood meal taken from the object.

3.2 Systematic comparison of spectra

The spectra obtained in ATR mode for all samples in the 700-3700 cm^{-1} range are reported in Figure 3. In addition, and as expected, the comparison of the IR spectra of a same sample collected using the two different modes (ATR and KBr pellet transmission) revealed differences in the shape of the spectra and in the intensities of the absorption bands. These differences are reported below.

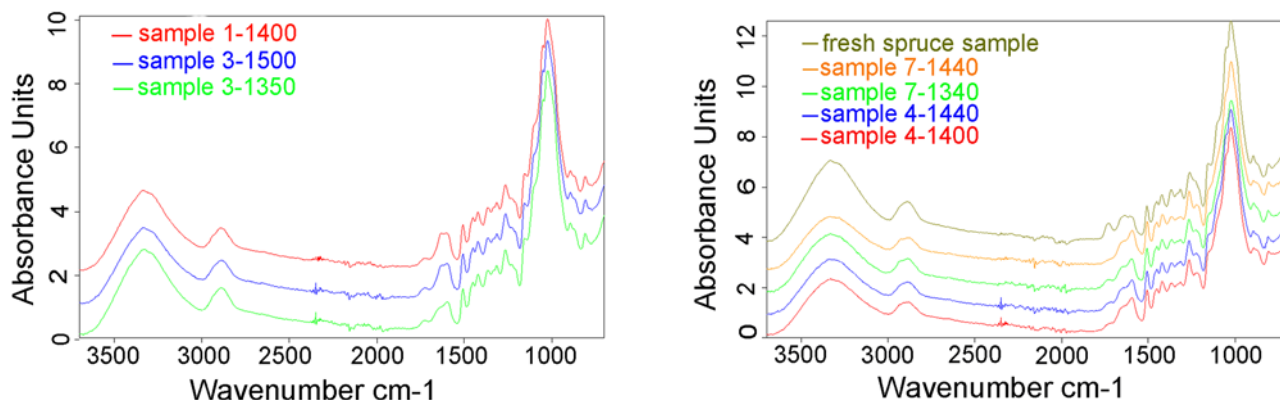


Figure 3: Normalized (Min_Max 1900-1300 cm⁻¹) spectra in ATR of the larch samples (left) and of the Norway spruce samples (right). In the latter case, the spectrum of a fresh reference sample was also reported.

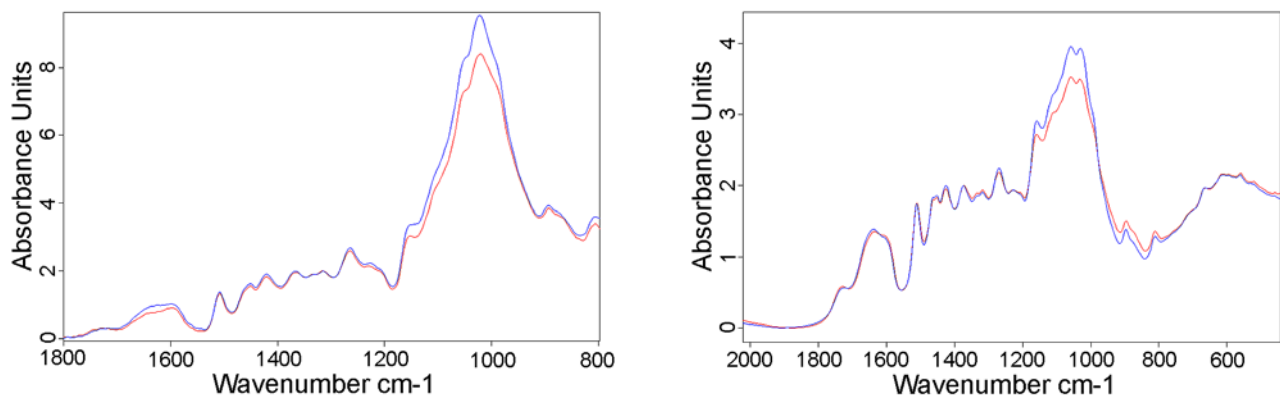


Figure 4: Normalized (Min_Max 1900-1300 cm⁻¹) spectra in ATR (left) and in transmission mode on KBr-pellets (right) of the "3-1350" (larch) sample. Blue spectra: non-extracted material; red spectra: wood meal extracted according to procedures reported within the text.

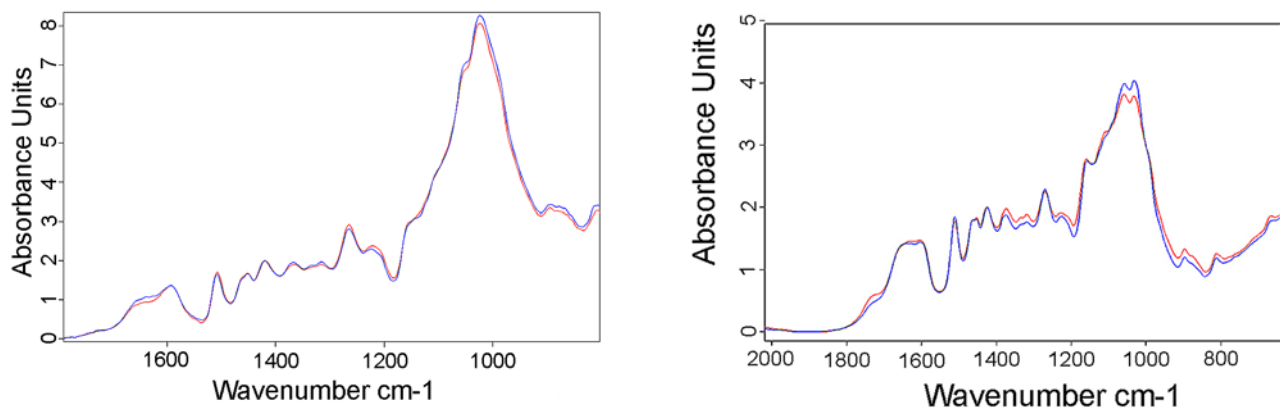


Figure 5: Normalized (Min_Max 1900-1300 cm⁻¹) spectra in ATR (left) and in transmission mode on KBr-pellets (right) of the "7-1440" sample (Norway spruce). Blue spectra: non-extracted material; red spectra: meal extracted according to procedures reported within the text.

At first, different sensitivities were observed for the two FTIR techniques in the absorption band near 1640 cm⁻¹, which in the literature is commonly assigned to H₂O absorption.¹⁹ In fact, the spectra collected using the ATR unit showed a difference in absorbance between the extracted and non-extracted samples in the 1640 cm⁻¹ region (Figure 4, left). On the other hand, the KBr pellet (transmission mode) spectra on the extracted and non-extracted samples did not show any differences (Figure 4, right). The reason for this behaviour could be that a residue of moisture present in the KBr powder masked the spec-

tral contribution of some of the wooden extractives. In fact, this difference in behaviour in the spectra acquired on the extracted or non-extracted samples was more evident for the larch samples than for the spruce samples because of differences in the concentration and composition of the extractives between the two species (Figure 5).

Secondly, a significantly different shape of the spectra in the bands near 1030 cm⁻¹ was observed (Figure 6). This absorption band is primarily due to the C-O deformation vibration mode, which is usually attributed to wood carbohydrate.¹⁹ The displayed differ-

ences in the shape of the spectra acquired with the two IR modes were not compensated even by applying the ATR conversion routine provided with Opus (Figure 7). Therefore, it can be suggested that the behaviour observed for the spectra acquired with the two IR modes is inherent to the specific techniques used for collecting the spectra.

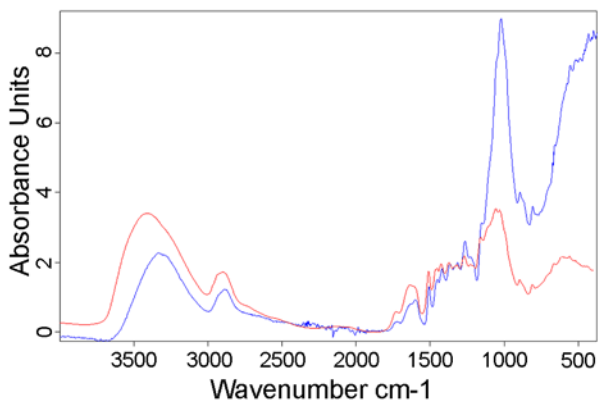


Figure 6: Comparison between normalised (Min_Max 1900-1300 cm^{-1}) ATR (blue curve) and transmission-mode on KBr pellet (red curve) spectra.

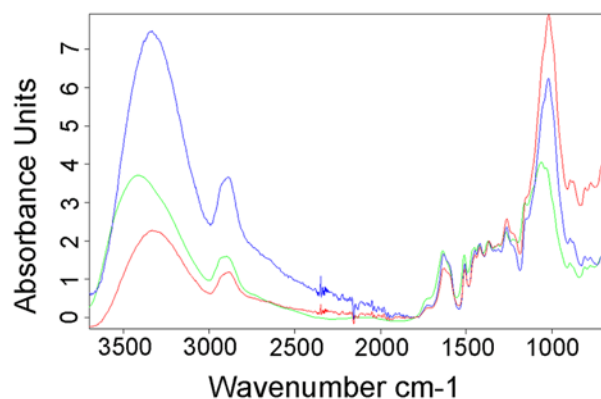


Figure 7: Normalized (Min_Max 1900-1300 cm^{-1}) comparison for sample "1-1400" of larch; the original spectra obtained in ATR mode (red curve) and in transmission-mode on KBr-pellets (green curve) with the converted spectrum from the ATR mode (blue curve).

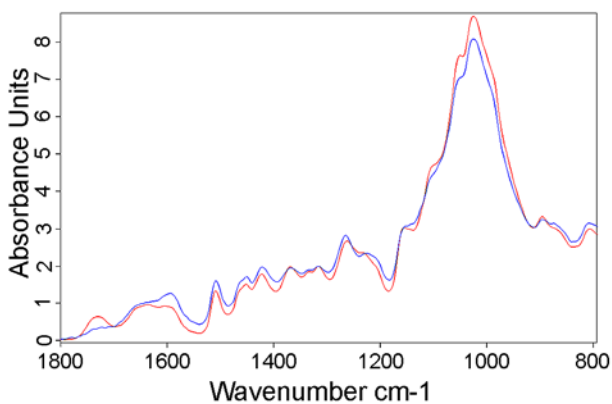


Figure 8. Comparison between the old wood sample "7-1440" (Norway spruce, blue curve) and the fresh wood sample (red curve) ATR normalized (Min_Max 1900-1300 cm^{-1}) spectra. The figure illustrates the difference between the fresh and the old woods in the shape and intensity of the hemicelluloses absorption band at 1734 cm^{-1} .

Next, different sensitivities between the two FTIR techniques were noted in the 3336 - 2882 cm^{-1} range (Figure 6), where O-H stretch and C-H stretch in methyl and methylene groups are evident.¹⁹ Nevertheless, the spectra collected with both techniques showed similar absorption band positions in the fingerprint region (1800-850 cm^{-1}). Moreover, the spectra associated with the two techniques displayed the same qualities (*i.e.* signal-to-noise ratio, resolution, etc.).

Lastly, spectra from old wood samples were compared with those from fresh wood. This comparison was performed using both techniques: ATR and KBr pellets in transmission mode. Both showed a difference between the fresh and the old woods in the shape and intensity of the hemicelluloses absorption band at 1734 cm^{-1} (Figure 8). This difference may be due to decay in the absorption intensity of the hemicelluloses related to the elapse of time.^{11,20}

4 Conclusions

One of the main requirements for workers in the field of cultural heritage is that they maintain the integrity of precious artefacts. This requirement makes the selection of a sampling method a critical choice. In this case, due to the spectroscopic characterisation of the four wooden beams of the two wood species, Norway spruce and larch, the samples had to be in the form of meal (instead of flakes) in order to obtain reproducible results. Although extracting meal was slightly invasive, it was low-destructive, and the integrity of the artefacts was preserved.

A systematic comparison of spectra acquired using both the ATR technique and the transmission mode KBr pellet method was carried out. The KBr pellets were prepared with a well-defined concentrated mixture of the wood beam sample, *i.e.* 5 mg of sample in 195 mg of KBr (2.5% w/w). This value was selected on the basis of specific tests. The results obtained by the two IR techniques on the same samples evidenced a similar quality in spectra. Nevertheless, some differences were noticed. In general, the KBr pellet transmission mode showed a lack of sensitivity in the 1640 cm^{-1} region, compared to the ATR technique. One reason for the difference could be that moisture present in the KBr powder may mask the spectral contribution of certain wooden extractives. This contrast was more evident for larch wood than for Norway spruce. Other appreciable differences in sensitivity between the two FTIR techniques were found in the absorption bands near 1030 cm^{-1} and near 3336-2882 cm^{-1} .

As a final conclusion, a further outcome of this inquiry should be mentioned: in comparing fresh and old

samples, a clear decrease in the absorption band of hemicelluloses at 1734 cm⁻¹ was observed. This subject was not further investigated within the present work. However, an effect related to the passing of time (e.g. due to the hydrolysis of acetyl groups in hemicelluloses²¹) can be hypothesized, and the possibility of using this fact for dating will be the subject of a new study, with the involvement of a specific sampling.

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6 Literature

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