EVALUATION OF DEGRADATION IN CHEMICAL COMPOUNDS OF WOOD IN HISTORICAL BUILDINGS USING FT-IR AND FT-RAMAN VIBRATIONAL SPECTROSCOPY

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ABSTRACT

Vibrational spectroscopy approaches like FT-IR and FT-Raman, as analytical method, can be used to assess chemical changes in historical wood structures. In this study, wood samples of three historical buildings, in Gorgan, Iran, namely Tekie Estebar, Molla Esmaiel Mosque, and the Esmaieli Buildings were selected. Wood species was determined by their macroscopic characteristics which were hornbeam (*Carpinus betulus*), oak (*Quercus castaneifolia*), beech (*Fagus orientalis*), and elm (*Ulmus glabra*), as hardwood species, and yew (*Taxus baccata*) as a softwood species. Also, some samples of oak were collected from northern and southern sides of the Esmaieli Building in order to compare deterioration environmental factors.. The approximate assignment of the experimental bands was completed by comparing. For this purpose, the experimental bands with the calculated band frequencies of cellulose, hemicellulose and lignin. In addition, the reported assignment for softwood and hardwood was used to confirm the vibrational assignments. The results of spectroscopy revealed that biodegradation had occurred in all species. Comparison between the most important vibrational band frequencies related to carbohydrates and lignin in hardwood species suggested that degradation of carbohydrates was greater than lignin, which could be attributed to brown rot and hydrolysis. Reduction of chemical compounds in south oak samples was higher and could be associated with prevailing wind and UV ray in this side. In the only softwood species (yew), because of its highest exposure to frequent raining, deterioration was observed in both carbohydrates and lignin.

Keywords: Guaiacyl lignin, hardwood, softwood, wood carbohydrates, wood durability.

INTRODUCTION

Wood has a complicated chemical structure which depends largely on the plant species.. However, the major components of wood are the same in all species, namely; cellulose (a linear polymer containing glucose units), hemicellulose (polysaccharides containing many different sugar monomers), and lignin (a class of complex organic polymers belonging to a group of aromatic alcohols) (Sjostrom 1993).

Vibrational spectroscopy (FT-IR, FT-Raman) has been applied in typical conservational experimental analysis. This approach is often used in studying ancient wood samples to evaluate the level of their degradation (Casadio and Toniolo 2001, Petrou *et al.* 2009, Pucetaite 2012, Sandak *et al.* 2010). Because of the small amount of wood needed to obtain the spectrum through these spectroscopy techniques and the low level of biodegradation of samples, they are frequently utilized (Picollo *et al.* 2011). The chemical characterization of historical wood is importance, as it can not only reveal the degradation processes that have occurred but it can

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also direct conservation practices. For instance, the identification may guide the suitable conservation methods and a comprehension of the preservation of excavated material may assist in the proper handling of archaeological timbers (Derrick *et al.* 1999). Various biological applications of these techniques, particularly on wood, have been reported including evaluation of organic substances in plants, characterization of wood type and its chemical compounds such as carbohydrates, sugars, extracts, resins (Akhtari 2010, Faix *et al.* 1991, Lionetto *et al.* 2012, Mirshokraie *et al.* 2014, Rodrigues *et al.* 1998). In addition, these techniques have been used in analyzing chemical changes in weathered rotten wood, treated wood, and also degraded wood (Derrick *et al.* 1999, Faix 1992, Pandey and Pitman 2003, Popescu *et al.* 2006). There are a great number of wooden parts in ancient buildings whose conservation is of great importance regarding cultural, historic, religious and touristic aspects.

This study aims to investigate changes and degradation in chemical compounds of the woods in historical buildings of the old parts of the city Gorgan, located in the northern part of Iran, compared with the fresh woods using FT-IR, FT- Raman spectroscopy as an analytical approach and we used the Raman portable device in historical building for the first time. The advantages of raman spectroscopy over FT-IR are many organic and inorganic materials are suitable for Raman analysis, no sample preparation needed, not interfered by water, non-destructive, the region from 4000 cm^{-1} to 50 cm^{-1} can be covered by a single recording and Raman spectra can be collected from a very small volume (< 1 μm in diameter). The use of vibrational spectroscopy for historical buildings in this study is the first case in Iran and can be localized and considered as a start point for future studies, including historical buildings, monuments and museums.

MATERIALS AND METHODS

Materials

Wood samples were collected from three historical building in the old part of the city Gorgan, namely Tekie Estebar, Molla Esmaiel Mosque, and the Esmaieli Building (Figure 1). Table 1 presents locations of the collected samples. In addition, some samples of oak were collected from the northern and southern sides of the Esmaieli Building in order to compare degradation environmental factors in those sides. To determine the wood species, cross, tangential, and radial sections were collected from the healthy parts of historical samples and then compared with the fresh samples of the same species.
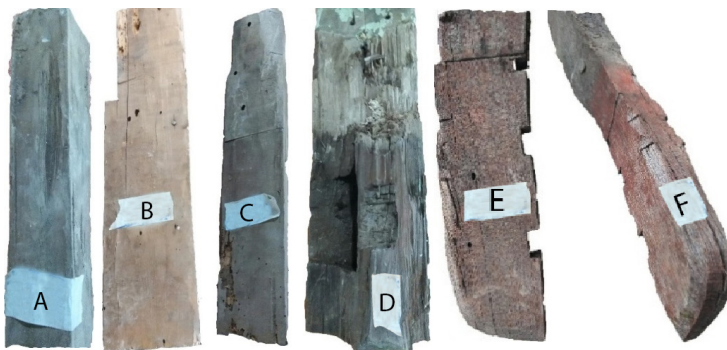

Figure 1: Photos of historical wood: (a) Elm, (b) Hornbeam, (c) Beech, (d) Yew, (e) Northern side oak, (f) Southern side oak.

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Table 1: Characteristics of the collected samples from historical building and their locations.

Species	Type of wood	Location	Historical building	Age (Years)
Oak *(Quercus castaneifolia)*	Hardwood	Exposed rafters, south and north side	Esmaieli Building	250
Hornbeam *(Carpinus betulus)*	Hardwood	Main beam, first floor	Tekie Estebar	150-200
Beech *(Fagus orientalis)*	Hardwood	Exposed rafters, northern side	Tekie Estebar	150-200
Elm *(Ulmus glabra)*	Hardwood	Tie beam in roof	Tekie Estebar	150-200
Yew *(Taxus baccata)*	Softwood	Pole of the western side	Molla Esmaiel Mosque	200-250

METHODS

FT-IR spectroscopy

Spectroscopy of the samples was performed using FT-IR instrument (Model Bomem MB-154, Germany). For this purpose, wood flour collected by cordless drill equipped with a drill bit (3 mm diameter to depth of 2-3 mm into the sample) was used. Afterwards, the wood flour was dried in the oven at 103 °C for 24 hours to reach the lowest moisture and immediately KBr pellets composed of the wood flour were made. Finally, the spectrum of the samples was obtained at a spectral range of 4000-500 cm⁻¹ and resolution of 4 cm⁻¹ and 11 scans were made and then edited using Win-Bomem Easy software.

FT-Raman spectroscopy

FR-Raman spectra were obtained using a portable Rigaku Firstguard Spectrometer instrument with Nd/YAG laser excitation at 1064 nm. 180° scattering was used in the sample illumination geometry. Spectra were recorded over the wavenumber range of 200-2000 cm⁻¹ at 4 cm⁻¹ spectral resolution with 256 scans accumulated, and the applied laser powers were between 0 mW and 180 mW. The OMNIC software (Thermo Scientific Company) was utilized to edit the spectra and determine the peak positions.

Finally, the spectral differences associated with the deterioration in the historical samples were compared with equivalent fresh samples. We normalized the spectrums based on the peak about 1460 cm⁻¹ that relates asymmetric bending of CH_3 in methoxyl groups.

RESULTS AND DISCUSSION

All compounds of the wood structure exhibit bands in the FT-Raman spectrum. It has been demonstrated in relevant applications of Raman spectroscopy to historical materials that as cellulose, hemicellulose and lignin deteriorate, their characteristic peaks in the spectra typically reduce in intensity or completely disappear (Smith and Clark 2004), and this was observed in the historical wood specimens from Gorgan. Also some related bands to these compounds were changed which are presented in Table 2 and Table 3.

Analysis of FT-IR spectroscopy

Most of major factors in wood are present between 800 and 1800 cm⁻¹ are individually considered as a fingerprint. Comparison of the obtained infrared spectra revealed some significant differences between the historical and fresh samples (Zhou *et al.* 2012).

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Oak

The obtained spectra from the historical samples of the north and south sides and fresh samples are demonstrated in Figure 2. In these two historical samples, the bands located in the regions 1000-1180 cm^{-1} which are assigned to stretching and asymmetric vibrations of C-O, C-C and C-O-C and 1375 cm^{-1} attributed to symmetric and asymmetric bending of CH$_3$ groups (Table 2) are related to cellulose and hemicellulose. The region of 1245 cm^{-1} assigned to carbohydrates and lignin also decreased. So the region of 1730 cm^{-1} assigned to stretching of C=O in xylan related to hemicellulose showed a significant decrease. In higher frequencies the regions of 2800-3400 cm^{-1} assigned to C-H and OH showed a significant decrease in cellulose and hemicellulose. The region of 1505 cm^{-1} assigned to Stretching vibrations of aromatic structure C=C in lignin was increase due to loss of extractives and carbohydrates. As can be seen in Figure 2, decrease of chemical compounds in south oak sample was higher and as a result, which could be associated with prevailing wind and UV ray on this side.
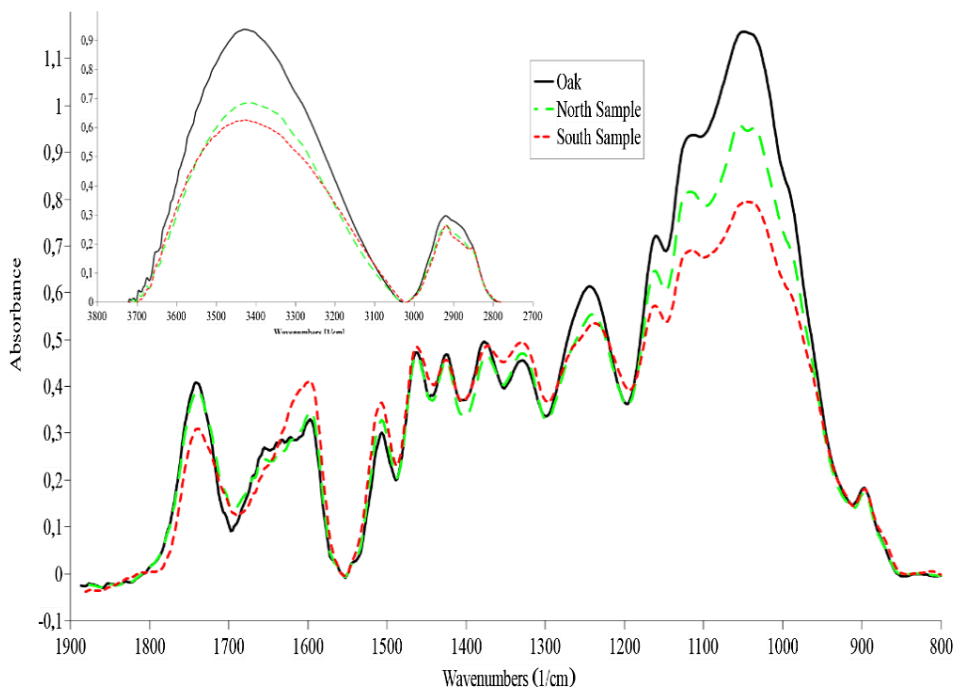

Figure 2: FT-IR spectra for historical and fresh sample of oak.

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Table 2: FT-IR band assignments for fresh hardwood and softwood species.

Hardwod (cm⁻¹)	Softwood (cm⁻¹)	Functional group	Assignment	Reference
897	895	In-plane symmetric vibration of C-H	Cellulose	(Pucetaite 2012, Lionetto *et al.* 2012)
1033	1029	Stretching vibrations of C-O	Cellulose- hemicelluloses	(Faix 1992, Pucetaite 2012)
1049	1056	Stretching vibrations of C-O and C-C	Cellulose- hemicelluloses	(Pandey *et al.* 1999, Pucetaite 2012)
1118	1110	Asymmetric stretching of C-O-C	Cellulose- hemicelluloses	(Pucetaite 2012)
1160	1159	Asymmetric stretching of C-O and C-C	Cellulose- hemicelluloses	(Pucetaite 2012, Moosavinejad *et al.* 2016)
1243	1234	Stretching vibrations of C-O in Xylene and syringyl ring	Lignin- hemicelluloses	(Pandey *et al.* 2003, Moosavinejad *et al.* 2016)
-	1273	Stretching vibrations of C-O in guaiacyl ring and wagging in OH and CH	Lignin, cellulose, hemicellulose	(Faix 1992, Pucetaite 2012)
1330	-	Vibrations of C-H and stretching in C-O related to syringyl ring	Cellulose- Lignin	(Lionetto *et al.* 2012)
1375	1375	Symmetric and asymmetric bending of CH₃ groups	Cellulose- Lignin	(Faix 1992, Pucetaite 2012)
1425	1428	Vibrations of aromatic structure	Lignin	(Pandey *et al.* 1999)
1464	1460	Asymmetric bending of CH₃ in methoxyl groups	Lignin	(Lionetto *et al.* 2012, Moosavinejad *et al.* 2016)
1508	1512	Stretching vibrations in aromatic structure C=C	Lignin	(Faix 1992, Gelbrich *et al.* 2009, Lewis *et al.* 1994)
1595	1608	Stretching vibrations in aromatic structure C=C	Lignin	(Pucetaite 2012, Moosavinejad *et al.* 2016, Emmanuel *et al.* 2015)
1654	1655	Stretching vibrations of conjugated C=O	Lignin	(Mirshokraie *et al.* 2014, Pucetaite 2012)
1739	1736	Stretching vibrations of unconjugated C=O and related to carbonyl groups	Hemicellulose	(Pucetaite 2012, Bodirlau *et al.* 2009)
2843	2841	Symmetric stretching vibrations of C-H related to methyl and methylene	Lignin, cellulose, hemicellulose	(Pandey *et al.* 1999, Carrillo *et al.* 2004, Schwanninger *et al.* 2004)
2933	2934	Asymmetric stretching vibrations of C-H related to methyl and methylene	Lignin, cellulose, hemicellulose	(Faix 1992, Pandey *et al.* 1999, Bodirlau *et al.* 2009, Carrillo *et al.* 2004, Schwanninger *et al.* 2004)
3423	3421	Stretching vibrations of O-H	Cellulose- hemicellulose	(Hergert 1971, Rodrigues *et al.* 1998, Michell *et al.* 2002)

Elm, hornbeam, beech

Comparison of the historical samples of elm, hornbeam and beech with the fresh samples (Figure 3) revealed that absorption in the region of 1160, 1118, 1050 and 895 cm⁻¹ (assigned to cellulose and hemicellu-

lose) decreased; while a significant decrease in the bands 1240 and 1740 cm^{-1} was observed which could be attributed to existence of hemicellulose, according to Table 2, the band at 1740 cm^{-1} is assigned to stretching vibrations of unconjugated C=O and related to carbonyl groups and the band at 1240 cm^{-1} is assigned to stretching vibrations of C-O in xylan and syringyl ring. On the other hand, almost in all species the absorption in the bands assigned to lignin was determined in the region 1508, 1600 and 1650 cm^{-1}. According to the results, it was clear that degradation of cellulose and hemicellulose was higher than lignin which could be a result of brown rot and hydrolysis in wood.

Comparing the infrared spectra in the historical and fresh samples of hardwood revealed that the samples collected from historical samples of oak from north and south sides (Figure 2) experienced the highest decrease in cellulose and hemicellulose. At the same time, beech species had the lowest decrease of chemical compound compared to the other species. Such decrease could be attributed to the location, exposure condition and natural durability of the species.
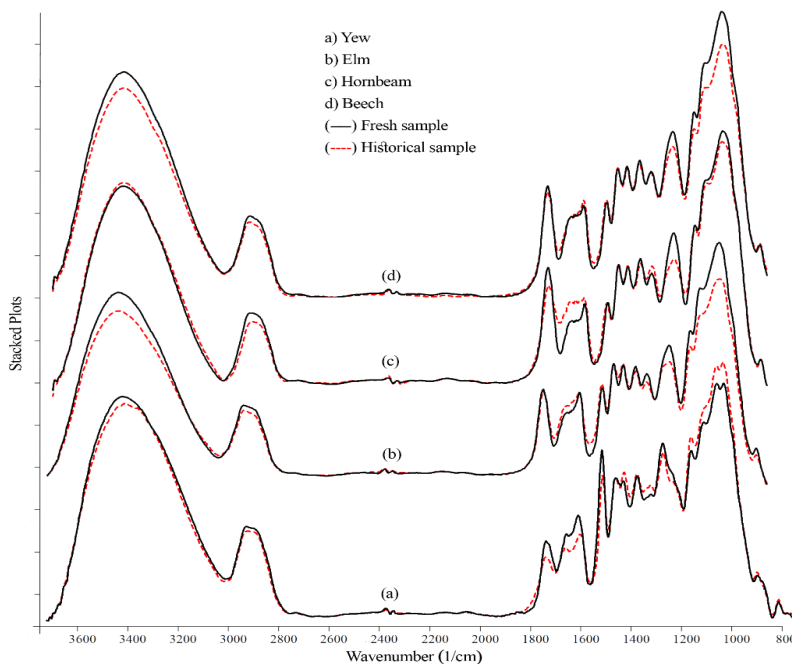

Figure 3: FT-IR spectra of historical fresh sample of elm, hornbeam and beech.

Yew

The obtained spectrum from yew species (Figure 3) in the region 1159, 1110, 1051 and 1029 cm^{-1} were assigned to cellulose and hemicellulose showed increase in absorption. Moreover, in the region 1650 and 1606 cm^{-1} increase in absorption was observed, according to Table 2 these bands are assigned to stretching vibrations of aromatic C=C and stretching vibrations of conjugated C=O, respectively. In contrast, in the region 1270 cm^{-1} assigned to stretching vibrations of C-O in xylan and syringyl ring and 1234 cm^{-1} attributed to stretching vibrations of C-O in guaiacyl ring and wagging in OH and CH and also in the region 1508 cm^{-1} related to the aromatic structure of lignin the absorption decreased. The Yew is naturally durable, but high degradation of chemical compounds of it is mostly related to rain damage in historical buildings.

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Analysis of FT-Raman spectroscopy

Oak

Raman spectra showed that in both historical samples the region 992 cm^{-1} were related to CH_2 groups in cellulose and the bands located in the regions 1152, 1098, 1051 and 1378 cm^{-1} related to cellulose and hemicellulose a considerable decrease occurred but the bands in the region 1602 cm^{-1} related to stretching vibrations of C=C in lignin experienced a significant increase. Like FT-IR spectroscopy, the results of FT-Raman demonstrated higher degradation in south oak (Figure 4).
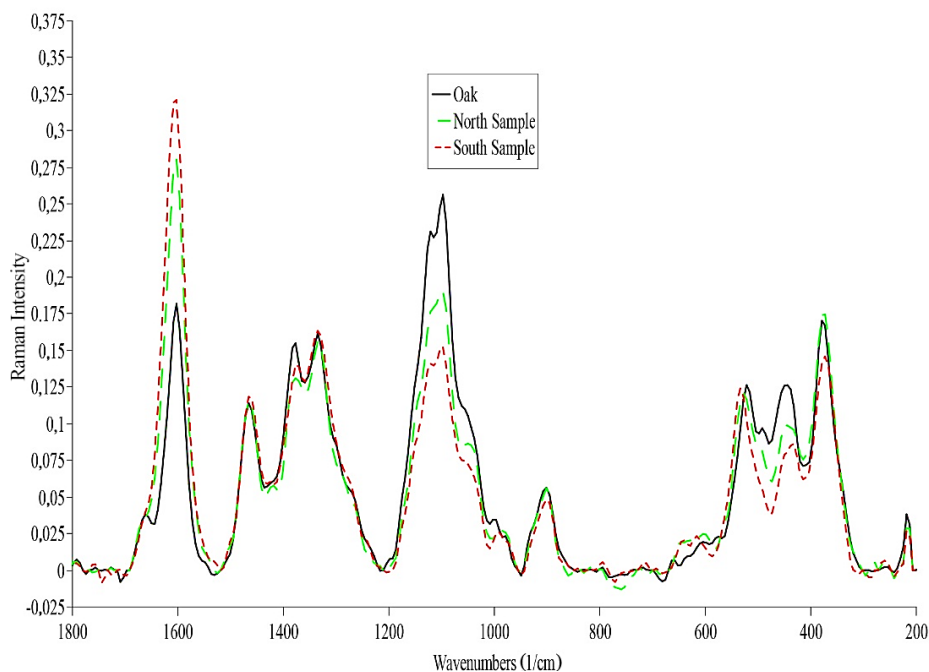

Figure 4: FT-Raman for historical and fresh sample of oak.

Elm, hornbeam and beech

The spectrum obtained for the species elm, hornbeam and beech (Figure 5) revealed that the intensity in the region 1600-1660 cm^{-1} related to stretching vibrations of C=C and C=O in lignin significantly increased. A weak band of the region 1275 cm^{-1} related to stretching vibrations of C-O and wagging of OH and CH in lignin guaiacyl and carbohydrates showed a slight increase in intensity. On the other hand, the bands located in the region 1050-1150 cm^{-1} which is mainly attributed to stretching vibrations of C-O and C-C, glycosidic symmetric vibrations of C-O-C and asymmetric stretch of C-O and C-C and are related to cellulose and hemicellulose, The region 896 cm^{-1} was assigned to in-plane symmetric vibration of C-H in cellulose showed increased intensity. In addition, in these three species, in lower frequencies and the regions 378, 431, 451, 527 cm^{-1} assigned to symmetric bending CC, bending CCO and CCC , Bending CCO and CCC ring deformation. Skeletal bending and COC bending, glycosidic links/CCC ring deformation, respectively (Table 3). Which is mostly related to cellulose the intensity decrease. FT-Raman spectroscopy demonstrated decreased degradation in all species and oak had the highest decrease. Moreover, beech had the lowest degradation by the climatic factors. These data are in agreement with IR spectra of the samples.
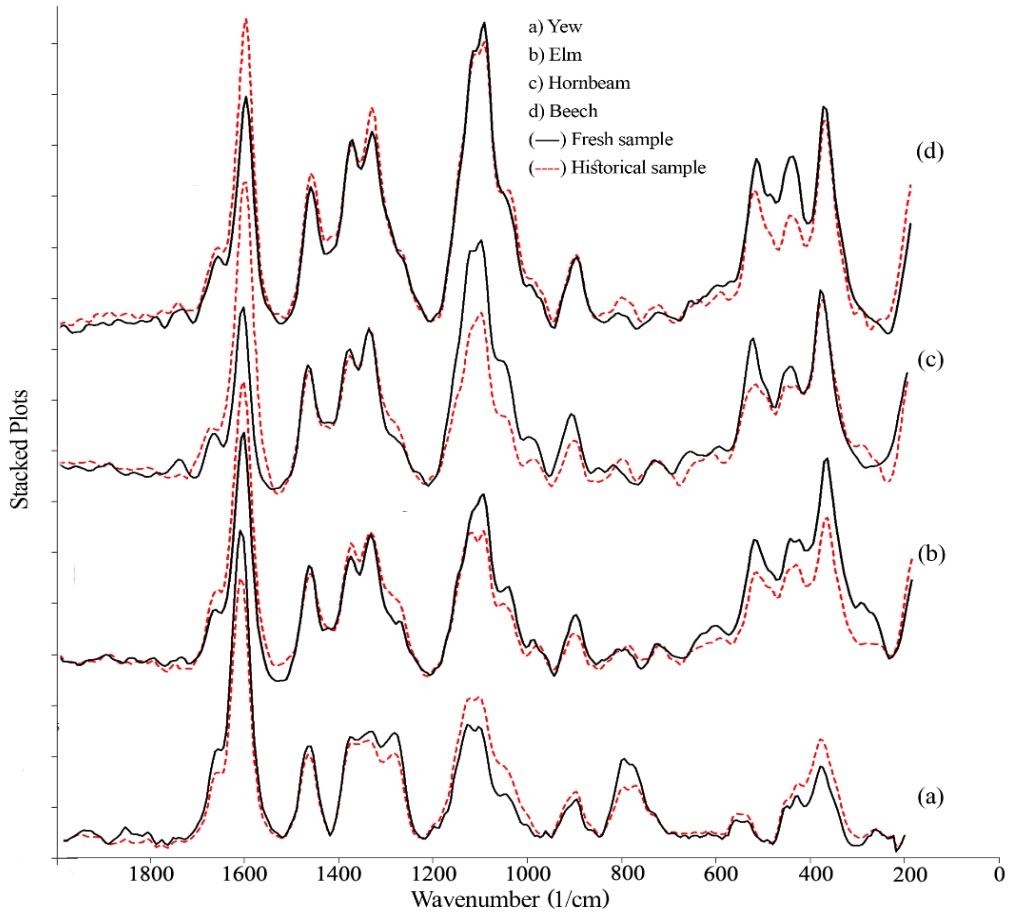
Figure 5: FT-Raman of historical fresh sample of elm, hornbeam and beech.

Table 3: FT-Raman band assignments for fresh softwood and hardwood species.

Hardwood (cm^{-1})	Softwood (cm^{-1})	Functional group	Assignment	Reference
378	378	Symmetric bending CC. Ring deformation	Cellulose	(Petrou *et al.* 2009)
431	433	Bending CCO, CCC. Ring deformation	Cellulose	(Petrou *et al.* 2009)
451	451	Bending CCO, CCC, ring deformation. Skeletal bending	Cellulose	(Petrou *et al.* 2009)
527	521	COC bending, glycosilic links/CCC ring deform.	Cellulose	(Schenzel and Fischer 2001, Wiley and Atalla 1987)
800	-	David star mode of phenyl ring	Lignin	(Wilson 1934)
904	896	In-plane symmetric vibration of C-H	Cellulose	(Ona *et al.* 1999, Petrou *et al.* 2009, Shen *et al.* 1998)
967	992	CH$_2$ in Cellulose	Cellulose	(Schenzel and Fischer 2001, Wiley and Atalla 1987, Yamauchi *et al.* 2005)
1050	1051	Stretching vibrations of C-O and C-C	Cellulose, hemi-cellulose	(Yamauchi *et al.* 2005)
1102	1098	Glycosidic symmetric vibrations of C-O-C	Cellulose, hemi-cellulose	(Petrou *et al.* 2009)
1127	1122	Glycosidic symmetric vibrations of C-O-C	Cellulose, hemi-cellulose	(Petrou *et al.* 2009)
1152	1152	Asymmetric stretch of C-O and C-C	Cellulose, hemi-cellulose	(Petrou *et al.* 2009)
1282	1275	Stretching vibrations of C-O in guaiacyl ring and wagging of OH and CH	Lignin, Cellulose, hemicellulose	(Shen *et al.* 1998, Yang *et al.* 1999)
1330	1335	Absorption related to syringyl ring and stretch of C-O	Lignin	(Zhou *et al.* 2012)
1378	1378	Stretch of C-H and wagging of OH and CH	Cellulose, hemi-cellulose	(Petrou *et al.* 2009, Socrates 2004)
1461	1464	Asymmetric bending of CH$_3$ in methoxyl groups	Lignin	(Ona *et al.* 1999, Yang *et al.* 1999)
1608	1602	Stretching vibrations of aromatic C=C structure	Lignin	(Ji *et al.* 2013, Kihara *et al.* 2002, Petrou *et al.* 2009, Shen *et al.* 1998, Yang *et al.* 1999)
1658	1662	Stretching vibrations of conjugated C=O	Lignin	(Kihara *et al.* 2002, Ona *et al.* 1999, Petrou *et al.* 2009, Shen *et al.* 1998, Yang *et al.* 1999)

Yew

In the spectrum of historical and fresh samples of yew (Figure 5) the bands located at 1608 cm⁻¹and 1281 cm⁻¹ mostly related to guaiacyl lignin had decreased intensity. Also the region around 1330 cm⁻¹ related to stretching of C-O in lignin and carbohydrates showed slightly decreased intensity. The region around 1127cm⁻¹ related to glycosidic symmetric vibrations of C-O-C in to cellulose and hemicellulose had the highest increase with an almost hidden peak. The region around 800 cm⁻¹ related to guaiacyl lignin also slightly declined.

CONCLUSIONS

The results obtained from FT-IR and FT-Raman could not be applied accurately in quantitative studies; but they could be a powerful tool to evaluate structural changes in chemical compounds of historical wood. This spectroscopy study showed the destruction of wood species in three historical structures in Gorgan, Iran. Comparing changes and degradation in intensity of bands related to lignin and carbohydrates in hardwood species revealed higher degradation of carbohydrates compared to lignin. In contrast, the only softwood species (yew) showed significant degradation both in lignin and carbohydrates which was attributed to its exposure to frequent rain and exposure condition. It was confirmed that degradation characteristics of the historical samples could be attributed to fungal and bacterial factors, and the decreased peaks also could be the result of leaching of organic substances and hydrolysis of wood by water. Finally, this study demonstrated noticeable potential of employing vibration spectroscopy techniques in historical wood samples.

ACKNOWLEDGEMENTS

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