QUANTITATIVE INVESTIGATION OF WOOD COMPOSITION BY INTEGRATED FT-IR AND THERMOGRAVIMETRIC METHODS

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A non-invasive integrated method for assessing cellulose and hemicelluloses/lignin ratio in different wooden pieces was developed by coupling infrared spectroscopy (FTIR-ATR) with thermo-gravimetric analysis (TGA). The method could be helpful for a precise assessment of the cellulose and hemicelluloses/lignin ratio necessary for the characterization of wooden artefacts. Thirteen wood species of hardwood lime (*Tilia cordata*), oak (*Quercus robur*), beech (*Fagus sylvatica L.*), poplar (*Populus*), maple (*Acer palmatum*), cherry tree (*Prunus avium*), horn beam (*Carpinus betulus*), walnut (*Juglans regia L.*), balsa, sycamore maple (*Acer pseudo platanus*), African pole (*Pyrus communis*), and two wood species of softwood fir (*Abies*), pine (*Pinus silvestris*) were investigated in fresh and dried state. The ratio between the normalized peak area A_{1370} (corresponding to the mass loss of cellulose and hemicelluloses) and A_{1505} (corresponding to the mass loss of lignin) was determined – from the FTIR spectra – as $A_{1370}/A_{1505} = R^{FTIR}$. From TGA data, the ratio between the mass loss of cellulose and hemicelluloses (Δm_{HC}) and the mass loss of lignin was calculated: Δm_L as $\Delta m_{HC}/\Delta m_L = R^{TG}$. A good correlation was obtained, with a small variation between the difference in the two parameters, $\Delta R = R^{FTIR} - R^{TG}$, related to the nature of wood (+0.015 in fresh softwood and +0.065 in fresh hardwood), (+0.265 in dried softwood and +0.18 in dried hardwood). The results obtained show that TGA (a quantitative and invasive method) may be successfully used as a complementary tool of FT-IR analysis (a qualitative and non-invasive method) for the rapid assessments required by the restoration processes as to the degradation stage of wooden artefacts.

Keywords: cellulose and lignin content, fresh/dried wood, FTIR-ATR, thermal analysis

INTRODUCTION

The development of non-invasive techniques for the investigation of cultural heritage pieces was a real challenge for scientists. The relationship between the restoring/preserving protocols and the scientific methodological approaches of the archaeological objects requires the cooperation of researchers from different areas of science, such as archaeology, chemistry, physics, textile technology, and history of art.[1] Particularly by ageing and weathering, wooden artefacts undergo profound changes in their physical, chemical and structural properties, when fiber degradation causes a decrease in thread and fabric strength, or even distortions of the whole object. As generally known, fiber degradation means a sharp decrease in the content of cellulose and lignin wood components, consequently, the cellulose/lignin ratio and the decay mechanisms of cellulose and lignin are most important issues for both scientific investigators, in order to understand the degradation processes undergone by wooden objects, and for restorers, to develop suitable consolidation and preserving procedures.[2-3] The accurate methods reported by literature data[4-6] for determining the cellulose/lignin ratio in wooden materials are mainly based

on invasive and destructive techniques (sampling and chemical analysis).

Nevertheless, in most cases, the use of destructive methods to determine the cellulose and lignin content in archaeological and historical wooden pieces is not allowed.[7,8]

Once the advanced modern methods tackle the area of the cultural heritage restoring/preserving protocols, many techniques become very important tools in providing important data on the chemical composition of artefacts. In this respect, spectroscopic methods and thermal analysis have been successfully approached for characterizing several wooden materials. The differences between wood species have been successfully performed by FT-Raman[9] and FTIR spectroscopy[10-11] for assessing the mass loss caused by fungi or by different wood species, as well as by FTIR-NIR spectroscopy[12] for predicting the decay resistance of the solid heartwood. Studies on the decay mechanisms and composition of wooden materials were mostly performed by thermal analysis.[13-14] Usually, the spectroscopic methods are considered as qualitative and semi-quantitative, since cellulose, hemicelluloses and lignin exhibit many common bands,[15] allowing the identification of the wood components, while thermal analysis is a blind method, slightly invasive, but with good results in assessing wood composition.[16] Combining the two methods – FTIR and thermal analysis – in an integrated system of analysis will provide more precise and accurate information on wood composition. Starting from these considerations, different hardwood and softwood species were investigated in both fresh and dried state. All species were analysed by FTIR-ATR spectroscopy and TGA. It has been found out that it is only the ratio between the normalized peak area of cellulose and hemicelluloses found at 1370/1373 cm^{-1} and the normalized peak area of lignin localized at 1505/1510 cm^{-1}, from FTIR-ATR spectra, labelled as $R^{FTIR} = A_{1373}/A_{1505}$, that are in strong agreement with the ratio between the mass loss of cellulose and hemicelluloses Δm_{HC} and the mass loss of lignin Δm_L, from thermal analysis, labelled as $R^{TG} = \Delta m_{HC}/\Delta m_L$.

EXPERIMENTAL

Materials and sampling methods

Wood materials: fresh and dried (7 years of natural drying in dark rooms) wood powder samples were collected by micro-drilling from carefully selected wood pieces, representative of panel paintings. The fresh wood species employed were as follows: *horn beam*, *maple*, *beech*, *poplar*, *cherry tree*, *lime*, *oak*; softwood species: *pine*, *fir* of Romanian origin (moisture content listed in Table 1). The dried wood species employed – *African pole*, *walnut*, *balsa*, *sycamore maple*, *lime*, *oak*, *pine*, *fir* (moisture content listed in Table 2) – were purchased from icon workshops in Bucharest.

Characterization methods

FTIR-ATR: A Bruker Hyperion FTIR microscope has been used, equipped with a cryogenic mercury-cadmium telluride detector and a germanium (Ge) ATR 20× objective, interfaced to a Vertex 70 spectrometer (Bruker Optics). The Ge crystal, with a refractive index of 4.01, has an anvil design with an 80-μm tip.

Table 1
Parameters of non-isothermal thermo-oxidative degradation in static air atmosphere for fresh wood species

Fresh wood	Dehydration			Thermo-oxidative process II			Thermo-oxidative process III		
	% Δm	T_{min} (°C) DTG	T_{min} (°C) DTA	% Δm_{II}	$T_{II'}$ (°C)	T_{II} (°C)	% Δm_{III}	T_{min} (°C) DTG	R^{TG}
Lime	4.00	70.4	76.4	63.76	292.9	325.5	22.05	458.1	2.89
Oak	5.55	70.8	81.0	55.47	291.0	320.3	29.61	473.8	1.87
Horn beam	5.66	68.8	80.9	66.02	287.9	324.1	23.63	449.5	2.79
Maple	3.52	71.1	82.2	67.60	290.1	327.0	20.64	449.4	3.28
Beech	3.41	69.1	81.1	66.43	292.8	327.7	21.23	449.4	3.13
Poplar	7.06	71.7	82.7	55.06	297.0	329.8	25.10	482.9	2.19
Cherry tree	3.03	71.5; 81.6	83.8	63.72	290.7	328.8	23.33	458.8	2.73
Fir	6.99	71.8	83.0	62.74	328.0	331.1	27.54	468.1	2.28
Pine	13.10	67.6	78.7	56.42	323.8	328.9	26.17	461.5	2.16

%Δm = total mass loss at dehydration; T_{min} (DTG) = minimum temperature of gravimetric decay; T_{min} (DTA) = minimum temperature of the endothermic process

Table 2
Parameters of non-isothermal thermo-oxidative degradation in static air atmosphere for dried wood species

Dried wood	Dehydration			Thermo-oxidative process II			Thermo-oxidative process III		
	% Δm	T_{min} (°C) (DTG)	T_{min} (°C) (DTA)	% Δm_{II}	$T_{II'}$ (°C)	T_{II} (°C)	% Δm_{III}	T_{min} (°C) DTG	R^{TG}
Lime	4.49	70.9	74.3	69.04	292.7	329.4	20.07	473.4	3.44
Oak	3.97	70.1	72.7	62.90	287.0	318.2	29.35	477.6	2.14
African pole	5.80	70.5	75.4	50.11	288.7	332.4	31.15	480.9-	1.61
Walnut	5.68	82.2	87.0	56.85	320.3	323.4	30.08	451.8	1.81
Balsa	5.97	66.9	73.3	70.54	286.3	314.0	16.97	422.2	4.20
Sycamore maple	5.66	69.4	80.7	67.46	292.5	331.5	20.76	459.6	3.25
Fir	4.65	68.8	82.6	61.05	336.1	339.5	26.82	512.1	2.28
Pine	5.56	64.9	69.9	60.41	331.4	334.5	27.70	473.9	2.18

A vertical sliding mechanism allows positioning of the crystal out of the field of view, to provide visualization of the sample, which can be enhanced by the use of visible polarization and fluorescence illumination to increase contrast. A remote aperture is used for further reducing the mask size, to meet the dimensions and orientation of the specific area of interest. The lowest contact pressure level available (0.8 N) has been used for all measurements. Spectra were acquired in the 4000-600 cm^{-1} range with 4 cm^{-1} resolution and automatic background subtraction. Finally, for each spectrum, an ATR correction was applied, followed by Kubelka-Munk, for correcting the diffusive component and for normalizing the band with maximum intensity (KnowItAll(R) Informatics System 8.2-Bio-Rad laboratories).
TG/DTG and *DTA*: A Netzsch 409 PC equipment has been employed (temperature range – 25 °C to 600 °C, heating rate – 10 K/min^{-1}; working atmosphere – static air; crucibles – Pt-Rh).

RESULTS AND DISCUSSION

FTIR Spectra

Due to the high number of spectral curves collected from the 13 samples, two representative ones were selected for softwoods (fir, pine) and for hardwoods (lime, oak), respectively. The FTIR ratios (R^{FTIR}) of all wood species are summarized in Table 3 and Figure 4, for correlation with thermo-gravimetric analysis (R^{TG}). The wood of different species, in fresh or dried state, has many similarities and specific features, localized in the fingerprint area. In the valence band area, the ATR-FTIR spectra of all wood types exhibit common features in the 3500-2500 cm^{-1} range: a band at 3300 cm^{-1}, assigned to the ν O-H stretching vibration, for the water molecules absorbed in the wood lumen cells, and a prominent band at 2881 cm^{-1}, corresponding to the ν C–H stretching vibration of organic moiety.[17-18] In the 1800-600 cm^{-1} fingerprint area, specific and common bands appear, assigned to cellulose, hemicelluloses and lignin moieties, as follows: 1724-1736 cm^{-1} assigned to unconjugated keto ν C=O in xylan, 1594-1602 cm^{-1} – conjugated ν C–O; 1510-1501 cm^{-1} – a band specific to aromatic skeletal vibrations (this band depends on the wood species and is assigned to the total content of the lignin components); 1450-1456 and 1417-1424 cm^{-1} – the bands of δ C–H in lignin; 1363-1370 cm^{-1} – of δ C–H in cellulose and hemicelluloses; 1320-1328 cm^{-1} – the band of ν C–H in cellulose and ν C_1–O of syringyl derivatives (characteristic of hardwoods); 1264-1270 cm^{-1} – vibrations of the guaiacyl rings and stretching vibrations of the C-O bonds (observed in softwoods); 1226-1234 cm^{-1} – syringyl ring vibration; 1150-1156 cm^{-1} – ν C–O in lignin and xylan; 1116 cm^{-1} – ν C–O–C in cellulose and hemicelluloses, 1024-1034 cm^{-1} – ν C–O in cellulose and hemicelluloses, and 895-900 cm^{-1} – δ C–H in cellulose (Figs. 1-2). The 1724-1736 cm^{-1} band, assigned to unconjugated keto ν C=O in xylan, remains very weak in softwoods (Fig. 1), but well-defined in hardwoods (Fig. 2).

The water content in wood can be assessed from the 1660-1590 cm^{-1} region. In this region, the bands corresponding to keto conjugated carbonyl ν C=O with benzene ring in lignin at 1662 cm^{-1} are localized, as well as the bending vibration of δ H-O-H from the water molecules absorbed at 1645 cm^{-1} (fresh wood, Figs. 1-2). In fresh lime and oak wood samples (Fig. 2), a large and more intense band lies in the 1650-1600 cm^{-1} domain, considered to include both ν C=O and δ H-O-H. In the dried lime and oak samples, this band decreases in intensity and splits into a band at 1594 cm^{-1}, belonging to ν C=O, and a very weak peak at 1640 cm^{-1}, belonging to δ H-O-H. In softwoods (Fig. 1), the dried state still maintains a high water content, which is a specific feature, related to the water content in

all wood species. The fresh wood samples naturally contain a large amount of water, assigned to the broad band at 1640-1600 cm^{-1}, which may overlap with the adjoining bands. In dried state, this band splits into other sub-bands, as a consequence of a lower water amount. Considering fresh softwoods and hardwoods, the absorbed water content is specific to each, being related to band broadening and its intensity, caused by the amount of δ H-O-H. In the fresh hardwood species (lime and oak), this band is more intense than in the fresh softwood species (fir and pine). Consequently, because water is not chemically bonded within the cell, its amount depends on the wood texture. According to literature,[19] hardwoods present large holes, which can be filled with large amounts of water molecules, while softwoods present small and very small holes, so that fewer water molecules are adsorbed. Therefore, the band at 1640 cm^{-1} is a good indicator for estimating the changes produced in hardwood and softwood, in either fresh or dried state.

To establish what characteristic is related to wood degradation, caused by climatic, biological and radiation factors, the 1368-1370 cm^{-1} band was assigned to the total content of lignin, and the 1504-1508 cm^{-1} one – to the total cellulose and hemicelluloses content. The ratio of the band area is strongly dependent on the degradation level, which is a very good criterion due to its correlation with the classical method, thermal analysis, or in cases when less destructive methods are required. The cellulose and hemicelluloses/lignin ratio, R^{FTIR}, from FT-IR was measured from the normalized peak area, A_{1373}, of cellulose and hemicelluloses (1370/1373 cm^{-1}) and from the lignin peak area, A_{1505} (1505/1510 cm^{-1}), as presented in Table 3.

Thermal analysis

Non-isothermal degradation in static air atmosphere, for all wood species, occurs through three successive processes accompanied by mass losses (Fig. 3). Each wood species shows: (i) an endothermic process, denoted as I, when water loss takes place, (ii) an exothermic process, denoted as II, consisting of pyrolytic decomposition assigned to cellulose and hemicelluloses, over the 250-380 °C range,[14] (iii) an exothermic process, denoted as III, assigned to lignin thermoxidation, over the 400-500 °C range[20] (Fig. 3). TG and DTG associated with DTA have a distinctive peak for hemicelluloses (II') and, respectively, cellulose (II). The mass loss ratios of hemicelluloses and cellulose ($\Delta m_{II'} + \Delta m_{II} = \Delta m_{HC}$) to lignin ($\Delta m_L$) are listed in Table 1 (fresh wood) and Table 2 (dried wood), with their onset temperatures determined by DTG. All wood species exhibit a $T_{\min}^{DTG}$ (II) value (temperature corresponding to the minimum of the DTG curve characteristic of process II) that practically does not depend on the wood species ($\overline{T_{\min}^{DTG}}$ (II) = 325.1±7.1 °C). The main differences in the thermal behaviour of the investigated wood species were evidenced by comparison of the following parameters: maximum mass loss (%Δm) at dehydration and in process II; ratios of mass losses in processes II and III ($R^{TG} = \Delta m_{HC}/\Delta m_L$), which are practically equal with the ratio of cellulose and hemicelluloses to lignin in wood.

Table 3
Ratios of cellulose and hemicelluloses to lignin determined by FTIR (R^{FTIR}) and thermo-gravimetric analysis (R^{TG}) for fresh and dried wood species

Wood	Softwoods		Hardwoods						
Fresh	Fir	Pine	Maple	Beech	Lime	Horn beam	Cherry tree	Poplar	Oak
R^{FTIR}	2.31	2.18	3.34	3.19	2.95	2.85	2.79	2.21	2.11
R^{TG}	2.28	2.18	3.28	3.13	2.89	2.79	2.73	2.19	1.87
$\|\Delta R\|$	0.03	0	0.06	0.06	0.06	0.06	0.06	0.02	0.24
Dried	Fir	Pine	Balsa	Lime	Sycamore maple	Oak	Walnut	African pole	
R^{FTIR}	2.71	2.28	4.35	3.71	3.40	2.27	2.01	1.82	
R^{TG}	2.28	2.18	4.20	3.44	3.25	2.14	1.81	1.61	
$\|\Delta R\|$	0.43	0.1	0.15	0.27	0.15	0.13	0.2	0.21	

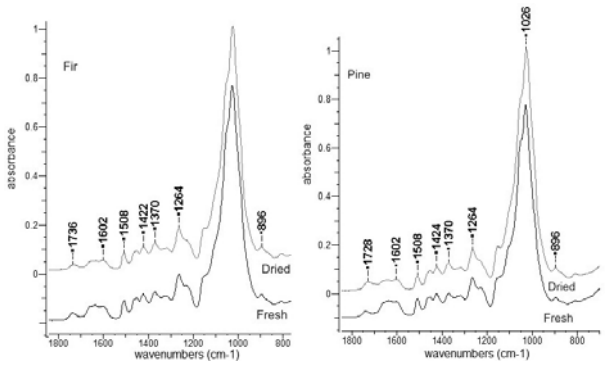

Figure 1: FTIR spectra of fresh and dried fir and pine in the fingerprint region

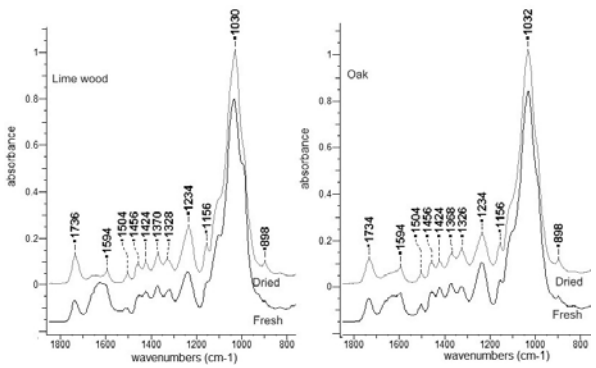

Figure 2: FTIR spectra of fresh and dried lime and oak in the fingerprint region

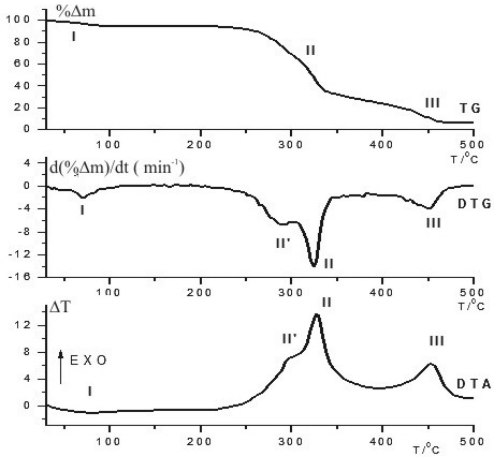

Figure 3: Representative wood thermograms (TG, DTG, SDTA) with dehydration and thermo-oxidation characteristics of hemicelluloses (II`), cellulose (II), lignin (III)

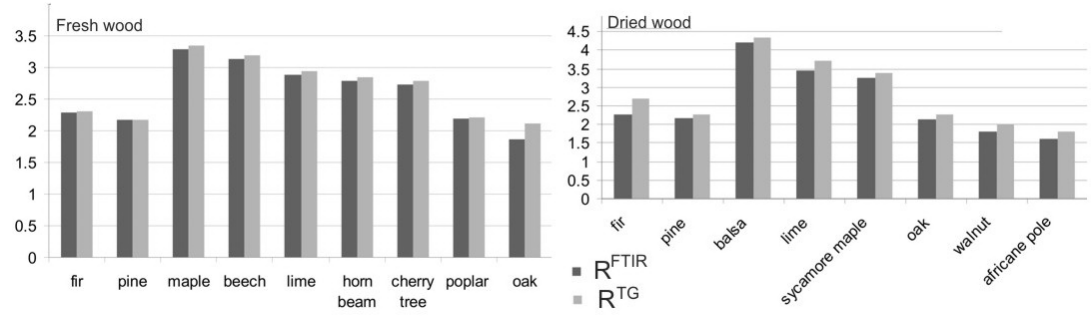

Figure 4: Correlation of the two ratios, R^{FTIR} and R^{T}, in fresh, dried softwood and hardwood series

A comparison of the FTIR and TG ratios (Table 3, Fig. 4) evidences slightly positive differences between R^{FTIR} and R^{TG}, corresponding to an average of +0.015 in fresh softwood and of +0.065 in fresh hardwood, together with less than the average of +0.265 in dried softwood and of +0.18 in dried hardwood, respectively. This may be an imminent consequence of the difference in sensitivity of the quantitative thermal analysis method and of the qualitative FTIR spectroscopic method. It is only by coupling certain peak areas of the FTIR spectra with the mass loss values of the thermal diagrams that FTIR spectroscopy becomes a complementary quantitative method for evaluating the cellulose and hemicelluloses to lignin ratios in wooden pieces from different species. On the other hand, the R^{TG} ratios (Tables 1 and 2) are in good agreement with the literature data[20] related to the percent composition of cellulose and hemicelluloses (78.76-67.84%) and of lignin (32.15-21.32%) in hardwoods. Slight differences were found for softwoods, in which cellulose and hemicelluloses

represent 73.04-68.55%, while lignin – around 30%. The high percentage of lignin found in dried softwood pieces can be related to the soundness and careful drying of the wood samples.

Figure 3 shows the changes in the chemical composition of the different wood species from the fresh and dried series, determined by the two ratios. The ratios are higher in dried than in fresh wood species, and correspond well to the literature data[19] reporting increasing lignin and cellulose deposition with tissue maturation, when the maximum rate of lignin deposition follows that of cellulose. In addition, wood species can be ordered in a natural way, related to the R^{FTIR} and R^{TG} ratio, as well as to the specific morphological characteristics of each wood species and tree growth conditions.

CONCLUSIONS

Only by coupling certain peak areas of the FTIR spectra with the mass loss values of the thermo-gravimetric diagrams, FTIR spectroscopy becomes a complementary quantitative method for evaluating the cellulose and hemicelluloses to lignin ratios in wooden pieces of different species. The R^{FTIR} and R^{TG} ratios match well, agreeing with the corresponding literature data. The ratios are higher in dried than in fresh wood types.

The observation was made that it is only the ratio between the normalized peak area of cellulose and hemicelluloses localized at 1370-1373 cm^{-1}, and the normalized peak area of lignin localized at 1505-1510 cm^{-1}, from ATR-FTIR spectra, R^{FTIR}, that is closely correlated with the ratio between the mass loss of cellulose and hemicelluloses and the mass loss of lignin, from thermal analysis, R^{TG}.

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