

THE ASSESMENT OF THE DECAYED LIME WOOD POLYMERIC COMPONENTS BY TG AND FT-IR PARAMETERS CORRELATIONAna EMANDI^{1*}, Petru BUDRUGEAC², Ioan EMANDI³,
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The restoration and conservation practices of wooden artifacts increasingly need more nondestructive, inexpensive and no-time consuming diagnosis methods. A number of twelve samples of lime wood in various states of degradation from furniture and panel painting were investigated by thermal analysis and infrared spectroscopy. The present work was undertaken to quantify the degree of complementarity of the TG and FT-IR methods by assessing the ration between cellulose, hemicelluloses and lignin of the decayed lime wood by the correlation of the parameters $R^{TG} = \Delta m_{HC} / \Delta m_L$ from TGA data, and $R_1^{FTIR} = A^{ab}_{1370} / A^{ab}_{1505}$, $R_2^{FTIR} = A^{bc}_{1370} / A^{bc}_{1505}$, $R_3^{FTIR} = I^{ab}_{1370} / I^{ab}_{1505}$, $R_4^{FTIR} = I^{bc}_{1370} / I^{bc}_{1505}$, from the corresponding peaks of cellulose and hemicelluloses at $\sim 1370 \text{ cm}^{-1}$ and of lignin at 1505 cm^{-1} in FT-IR spectra, where R^{TG} is the ratio between the mass loss of cellulose & hemicelluloses Δm_{HC} and the mass loss of lignin Δm_L ; R_1^{FTIR} , R_2^{FTIR} , are the ratio between the absolute peaks area $A^{ab}_{1370} / A^{ab}_{1505}$, and the normalized peaks area $A^{bc}_{1370} / A^{bc}_{1505}$, respectively, while R_3^{FTIR} , R_4^{FTIR} are the ratio between the absolute peaks intensity $I^{ab}_{1370} / I^{ab}_{1505}$, and the normalized peaks intensity $I^{bc}_{1370} / I^{bc}_{1505}$, respectively. We found that the TG parameter decreases in the same order as FT-IR parameters R_1^{FTIR} , R_2^{FTIR} , R_3^{FTIR} , R_4^{FTIR} , and relates well in the values with R_1^{FTIR} .

Keywords: lime wood; decayed wood; wood diagnosis; infrared spectroscopy, thermal analysis.

Introduction

The lime tree (*Tillia cordata Mill*) wood was often used as support for icons as well as for manufactured iconostasis from Romanian churches and monasteries.

Sandu et al. [1] use thermogravimetric method for investigation of the non-isothermal thermo-oxidative degradation of some samples of soft lime tree wood from the structure of the supports of old painting (mobile icons and iconostasis) 100-200 years old. It was obtained that the characteristic parameters of TG and DTG curves as well as global kinetic parameters of the thermo-oxidations of wood samples depend on their deterioration degree.

In a previous work [2] it was pointed out that the thermal analysis methods are suitable for conservation state determination of historical and/or cultural objects manufactured from lime-tree wood. Our research was based on the earlier results reported by Tomassetti et al. [3-5]

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and Wiedemann [6-7] who pointed out that thermogravimetry (TG) enables a rapid and accurate moisture, cellulose and hemicelluloses, lignin contents and % ashes residues determination in the fresh and old wood samples. It was shown [2] that the following non-isothermal parameters can be used for distinction between a new and old lime tree wood: mass loss in the first process of thermo-oxidation, ratio between the mass losses in the first and the second processes of thermo-oxidation, the maximum rate of the first process of thermo-oxidation. Consequently, the certification of a patrimonial object manufactured from lime tree wood could be performed by applying the thermal analysis methods.

In another previous paper [8], it was shown that combining the two methods FTIR and thermal analysis in an integrated system of analysis will provide more precisely and accurately information about the recent wood composition. On these basics we have investigated a series of different new hard and soft wood species in fresh and dried states. All species were analysed by ATR-FTIR spectroscopy and thermo-gravimetric. It has been found that only the ratio between the absolute and the normalized peak area of cellulose & hemicelluloses localized at $1370/1373\text{ cm}^{-1}$ and the absolute and normalized peak area of lignin localized at 1505 cm^{-1} , from FTIR spectra, labelled as $R_1^{\text{FTIR}} = A_{1370}^{\text{ab}}/A_{1505}^{\text{ab}}$, $R_2^{\text{FTIR}} = A_{1370}^{\text{bz}}/A_{1505}^{\text{bz}}$, $R_3^{\text{FTIR}} = I_{1370}^{\text{ab}}/I_{1505}^{\text{ab}}$, $R_4^{\text{FTIR}} = I_{1370}^{\text{bz}}/I_{1505}^{\text{bz}}$, are in straight agreement with the ratio between the mass loss of cellulose & hemicellulose Δm_{HC} and the mass loss of lignin Δm_{L} , from thermal analysis, labelled as $R^{\text{TG}} = \Delta m_{\text{HC}}/\Delta m_{\text{L}}$. The aim of this work is checking of this result for some decayed lime wood from the supports of different furniture and panel painting.

Experimental

Samples

A number of the twelve lime wood samples labeled as $V_1 - V_{12}$ were collected from different wooden supports with serious problems of deterioration. The samples were taken from areas of the surface of the wooden supports that had been examined microscopically for any signs of previous conservation treatment. The deposits (dust, waxes, finely divided Carbon) were removed with a suitable solvent compresses. Layer was scraped off carefully with a scalpel and the powdered sample was placed into a clean sample vial. The weight of the samples were between 0.5 and 1 mg.

The characterization methods

Thermo-gravimetric analysis: the simultaneous analysis TG / DTG with current oxygen DSC were performed for all samples with Netzsch 409 PC in the range 25°C to 600°C , at $10\text{ K}\cdot\text{min}^{-1}$ heating rate. The working atmosphere: static air. Crucible: Pt-Rh.

FTIR measurements were performed using a Bruker Hyperion FTIR microscope equipped with a cryogenic mercury-cadmium telluride detector and a germanium (Ge) ATR $20\times$ objective, interfaced to a Vertex 70 spectrometer (Bruker Optics). The Ge crystal, with a refractive index of 4.01, has an anvil design with a $80\text{-}\mu\text{m}$ tip. The samples were processed as powders in KBr pellets and all spectra were acquired in the range $4,000\text{--}600\text{ cm}^{-1}$ at 4 cm^{-1} resolution, with automatic background subtraction.

Results and discussions

Thermo-gravimetric analysis

Parameter values of the first and the second processes of thermo-oxidation, % total mass loss of $\Delta m =$ in process (II); % total mass loss of $\Delta m =$ in process (III); $T_{\text{min}}(\text{DTG}) = \text{DTG}$ minimum appropriate temperatures, $T_{\text{max}}(\text{DSC})$ DSC exothermic peak = appropriate temperature are shown in (table 1). Parameter values of the first thermo-oxidation process of wood samples are close to those of corresponding fresh and dried wood samples. Therefore, the first mechanism of thermo-oxidation process does not change by natural aging. On the other hand the speed of the first thermal oxidation process for all wood samples is higher than the corresponding fresh and dried lime tree. Reported values attest that aging natural lime wood pulp is part of thermo-oxidized processes and decomposes to form volatile compounds and non-

volatile carbonyl compounds. The thermo-oxidation processes means the oxidation of carbon atoms in the macromolecular bone and the increasing of the reaction speed. This behavior is a consequence of the increasing of the carbon substitution degree, by means of the broken hydrogen bonds between cellulosic chains as well as linkages between cellulose-lignin-hemicelluloses during wood aging. The average ratio ($\Delta m_{II}(\text{cellulose and hemicellulose})/\Delta m_{III}(\text{lignin})$), of old wood samples is lower than non-degraded wood samples as a consequence of the different speed of the decay processes as well as the different amounts of wood components eaten by wood rot and mould fungus. [9-12, 20].

Table 1. Thermo-oxidative degradation parameters of the decayed lime wood

No.	Sample	The first process of thermo-oxidation (Process II)			The first process of thermo-oxidation (Process III)			
		% Δm	T _{min} (DTG) °C	T _{max} (DSC) °C	% Δm	T _{min} (DTG) °C	T _{max} (DSC) °C	* $\Delta m_{II} / \Delta m_{III}$
1	V ₁	65.70	311	313.5	21.9	443	439; 466	3.0
2	V ₂	56.70	299	301.5	21.0	403; 440	402; 439	2.7
3	V ₃	35.88	300	305.0	13.8	427	428	2.6
4	V ₄	50.50	296	305.0	20.2	443	442	2.5
5	V ₅	39.12	306	314.0	16.3	469	455	2.4
6	V ₆	31.60	291	302.0	15.8	405; 457	369; 455	2.0
7	V ₇	24.16	317	322.0	15.1	423	423	1.6
8	V ₈	24.12	311	316.0	13.4	437	436	1.3
9	V ₉	15.84	317	320.0	13.2	452	449	1.2
10	V ₁₀	15.00	314	321.0	15.0	442	442	1.0
11	V ₁₁	9.17	271	≈280.0	13.1	448	447	0.7
12	V ₁₂	8.88	280	302.0	14.8	440	435	0.6

* Δm_{II} = the mass loss of cellulose and hemicelluloses; Δm_{III} = the mass loss of lignin in the thermo-oxidative degradation

FTIR-ATR analysis

Changes in the absorbance peaks of wooden materials during the ageing are generally characterized by no completely disappearance of the peaks as well as neither appearance of new peaks. Wood components are attacked at rates dependent on their concentration, which is followed by some characteristics of the white-rot, such as the slow lowering of the degree of polymerization and the gradual decrease of the alkali soluble content. These processes may be ordered as following: the broken of the reticular structure of the biopolymer (breaking hydrogen bonds between cellulose chains and/or linkages between lignin and cellulose); the oxidation of cellulose, hemicelluloses, lignin and extractives with releasing volatile products; the drastically weight loss in wood, however, indicates the degree of removal of wood substance in the form of water and carbon dioxide due to the enzymatic degradation and metabolism of fungi.

These processes should be added to the partial hydrolysis of wood components occurs through its interaction with water vapor in the air [13, 14]. In studying natural wood aging by infrared spectroscopy the following peaks are very good candidates: $\nu C=O$ (pectin & oxycelluloses degraded materials) at $1730-1710 \text{ cm}^{-1}$, $\delta C=C$ phenyl propane polymer of lignin, respectively in aromatic rings at 1595 cm^{-1} , 1510 cm^{-1} , $\delta C-H$ (cellulose and hemicelluloses) at $\sim 1370 \text{ cm}^{-1}$, (syringyl ring & $\nu C-O$ lignin and xylan) at 1200 cm^{-1} . Large absorbance peaks are growing up at wave numbers attributed to carbonyl ($C=O$) stretching during wood UV-VIS oxidation while a decrease in peaks intensity lie in the range $1558 \text{ cm}^{-1} - 1535 \text{ cm}^{-1}$ are properly to the mould fungus and wood rot attacks. Note that one of the water δOH absorbance peaks at 1637 cm^{-1} changes in the FTIR spectra due to the various moisture levels in the samples [15]. The results of the detailed inspection of the infrared spectra of the investigated wooden samples led us to chose the peaks 1370 cm^{-1} and 1505 cm^{-1} in order to estimate the relative amount of cellulose, hemicellulose and lignin in the decayed wood species by measuring the absolute area, the basic line normalized area, the absolute intensity and the basic line normalized intensity [16, 17] of the corresponding cellulose&hemicelluloses peak as well as the corresponding lignin peaks in each sample, are shown in the (table 2, table 3, table 4, table 5).

Table 2. The absolute peaks area of cellulose, hemicelluloses and lignin and the corresponding FTIR parameter $*R_1^{FTIR} = A^{ab}_{1370}/A^{ab}_{1505}$

No.	Samples	A^{ab}_{1370} (cellulose & hemicellulose)	A^{ab}_{1505} (lignin)	$*R_1^{FTIR} = A^{ab}_{1370}/A^{ab}_{1505}$
1	V ₁	1.223	0.591	2.069
2	V ₂	0.893	0.446	2.002
3	V ₃	1.538	0.876	1.755
4	V ₄	1.690	0.971	1.740
5	V ₅	0.774	0.534	1.449
6	V ₆	1.587	1.098	1.445
7	V ₇	1.593	1.115	1.428
8	V ₈	1.380	0.967	1.427
9	V ₉	0.890	0.666	1.336
10	V ₁₀	0.912	0.946	0.964
11	V ₁₁	0.536	1.466	0.365
12	V ₁₂	0.399	1.242	0.321

* A^{ab}_{1370} is the absolute peak area of the band at 1370 cm⁻¹ assigned to $\delta(C-H)$ for cellulose and hemicelluloses; A^{ab}_{1505} is the absolute peak area of the band at 1505 cm⁻¹ assigned to $\delta(C=C)$ phenyl propane polymer of lignin, respectively in aromatic rings

Table 3. The normalized basic line peaks area of cellulose, hemicelluloses and lignin and the corresponding FTIR parameter $*R_2^{FTIR} = A^{bz}_{1370}/A^{bz}_{1505}$

No.	Samples	A^{bz}_{1370} (cellulose & hemicellulose)	A^{bz}_{1505} (lignin)	$*R_2^{FTIR} = A^{bz}_{1370}/A^{bz}_{1505}$
1	V ₁	0.138	0.084	1.642
2	V ₂	0.093	0.068	1.367
3	V ₃	0.196	0.218	0.899
4	V ₄	0.175	0.196	0.892
5	V ₅	0.064	0.075	0.853
6	V ₆	0.083	0.133	0.624
7	V ₇	0.144	0.267	0.539
8	V ₈	0.145	0.271	0.535
9	V ₉	0.162	0.347	0.466
10	V ₁₀	0.057	0.193	0.295
11	V ₁₁	0.073	0.277	0.263
12	V ₁₂	0.067	0.302	0.221

* A^{bz}_{1370} is the normalized basic line of the peak 1370 cm⁻¹ assigned to $\delta(C-H)$ for cellulose and hemicelluloses; A^{bz}_{1505} is the normalized basic line of the peak 1505 is the infrared bands assigned to $\delta(C=C)$ phenyl propane polymer of lignin, respectively in aromatic rings

Table 4. The absolute peaks intensity of cellulose, hemicelluloses and lignin and the corresponding FTIR parameter $*R_3^{FTIR} = I^{ab}_{1370}/I^{ab}_{1505}$

No.	Samples	I^{ab}_{1370} (cellulose & hemicellulose)	I^{ab}_{1505} (lignin)	$*R_3^{FTIR} = I^{ab}_{1370}/I^{ab}_{1505}$
1	V ₁	0.034	0.022	1.545
2	V ₂	0.034	0.022	1.545
3	V ₃	0.037	0.024	1.541
4	V ₄	0.029	0.022	1.318
5	V ₅	0.035	0.027	1.296
6	V ₆	0.035	0.027	1.296
7	V ₇	0.032	0.026	1.230
8	V ₈	0.026	0.022	1.181
9	V ₉	0.027	0.023	1.173
10	V ₁₀	0.028	0.024	1.166
11	V ₁₁	0.035	0.035	1.000
12	V ₁₂	0.030	0.036	0.833

* I^{ab}_{1370} is the absolute intensity of the band at 1370 cm⁻¹ assigned to $\delta(C-H)$ for cellulose and hemicelluloses; I^{ab}_{1505} is the absolute intensity of the band at 1505 cm⁻¹ assigned to $\delta(C=C)$ phenyl propane polymer of lignin, respectively in aromatic rings

Table 5. The normalized basic line peak intensities of cellulose, hemicellulose and lignin and the corresponding FTIR parameter $R_4^{FTIR} = I_{1370}^{bz}/I_{1505}^{bz}$

No.	Samples	I_{1370}^{bz} (cellulose & hemicellulose)	I_{1505}^{bz} (lignin)	$R_4^{FTIR} = I_{1370}^{bz}/I_{1505}^{bz}$
1	V ₁	0.004	0.003	1.333
2	V ₂	0.002	0.002	1.000
3	V ₃	0.006	0.007	0.856
4	V ₄	0.005	0.007	0.714
5	V ₅	0.002	0.005	0.400
6	V ₆	0.005	0.013	0.384
7	V ₇	0.003	0.008	0.375
8	V ₈	0.001	0.003	0.333
9	V ₉	0.003	0.009	0.333
10	V ₁₀	0.001	0.006	0.166
11	V ₁₁	0.001	0.009	0.111
12	V ₁₂	0.001	0.011	0.090

* I_{1370}^{bz} is the normalized basic line intensity of the peak 1370 cm^{-1} assigned to $\delta(\text{C-H})$ for cellulose and hemicelluloses; I_{1505}^{bz} is the normalized basic line intensity of the peak 1505 cm^{-1} is the infrared bands assigned to $\delta(\text{C=C})$ phenyl propane polymer of lignin, respectively in aromatic rings

The analyzed lime wooden pieces were discussed in the following groups:

(i) Samples (V1-V4) showed the delignification mainly caused by the microorganisms and also by photo-bleaching. By comparing the infrared spectra of dried sound lime wood as blank sample with the peaks of the investigated samples we can observe that the decreasing of the $\delta\text{C=C}$ aromatic rings peak intensity at 1509 cm^{-1} is associated with the strong increasing of the $\nu\text{C=O}$ peak intensity at 1730 cm^{-1} . According to the literature data this behavior is properly to a process faster and more deeply of delignification by photo-oxidation [8, 20].

(ii) Samples (V5-V8) showed that the degradation of cellulose components is more sensitive to micro-organisms in comparison with UV radiations. Cellulosic components are a favorite food of micro-organisms and a decreasing of the corresponding peaks intensity is always properly to this phenomenon. We can observe a lower peak intensity at around 1730 cm^{-1} than in blank sample associated with a constant peak intensity 1505 cm^{-1} and a slight decreasing of the $\delta\text{C-H}$ (cellulose and hemicelluloses) peak intensity. There is a profound degradation of cellulose components mainly by micro-organisms attacks [18].

(iii) samples (V9-V12) showed that the spectra of the amorphous powder samples are deeply and entirely degraded and exhibit the peaks assigned to $\delta(\text{C=C})$ of aromatic rings 1619 cm^{-1} , $\nu(\text{C-O})$ and $\delta(\text{CH}_2)$ usually related to the band of intramolecular hydrogen bonds $\text{O}_3\text{-H}_3\text{...O}_5$ in cellulose 3392 cm^{-1} , 1415 cm^{-1} , Syringyl unit and also to stretching vibrations $\nu_{\text{sym}}/\nu_{\text{asym}}$ C-O-C bonds 1104 cm^{-1} , $\delta(\text{C-O-C})$ pyranose ring in cellulose 1029 cm^{-1} and ν_{asym} ring out of phase or $\omega(\text{CH})$ in cellulose/ C_1 group frequency in cellulose and hemicellulose 872 cm^{-1} . Therefore, the spectrum proves the presence in a high excess of the degraded cellulosic fibers, as an amorphous powder, comparable with the small rest of the decayed lignin polymer. These pieces suffered really different types of violent attacks [19, 21].

Combining the two methods [8] thermo gravimetric analysis TG and infrared spectroscopy FTIR (table 6) by determining the complementary parameters of the infrared spectra, $R_1^{FTIR} = A_{1370}^{ab}/A_{1505}^{ab}$, $R_2^{FTIR} = A_{1370}^{bz}/A_{1505}^{bz}$, $R_3^{FTIR} = I_{1370}^{ab}/I_{1505}^{ab}$, $R_4^{FTIR} = I_{1370}^{bz}/I_{1505}^{bz}$ (where A_{1370}^{ab} , A_{1505}^{ab} are the absolute peaks area of cellulose & hemicelluloses, $A_{1370}^{bz}/A_{1505}^{bz}$ are the normalized basic line peaks area of cellulose & hemicelluloses and respectively lignin, while $I_{1370}^{ab}/I_{1505}^{ab}$ are the absolute peaks intensity of cellulose & hemicelluloses, $I_{1370}^{bz}/I_{1505}^{bz}$ are the normalized basic line peaks intensity of cellulose &

hemicelluloses and respectively lignin) and of the thermo gravimetric data $R^{TG} = \Delta m_{HC} / \Delta m_L$ (where Δm_{HC} and Δm_L are the mass losses of cellulose & hemicellulose and respectively lignin) for all samples we obtained the first information about their diagnosis.

Table 6. The correlation of the complementary parameters ($R_{1-4}^{FTIR} = A_{1370} / A_{1505}$) and ($R^{TG} = \Delta m_{HC} / \Delta m_L$)

Parameters	Samples											
	V1	V2	V3	V4	V5	V6	V7	V8	V9	V10	V11	V12
$R^{TG} = \Delta m_{HC} / \Delta m_L$	3.0	2.7	2.6	2.5	2.4	2.0	1.6	1.3	1.2	1.0	0.7	0.6
$R_1^{FTIR} = A^{ab} / A^{ab}$	2.069	2.002	1.755	1.740	1.449	1.445	1.428	1.427	1.336	0.964	0.365	0.321
$R_2^{FTIR} = A^{bz} / A^{bz}$	1.642	1.367	0.899	0.892	0.853	0.624	0.539	0.535	0.466	0.295	0.263	0.221
$R_3^{FTIR} = I^{ab} / I^{ab}$	1.545	1.545	1.541	1.318	1.296	1.296	1.230	1.181	1.173	1.166	1.000	0.833
$R_4^{FTIR} = I^{bz} / I^{bz}$	1.333	1.000	0.856	0.714	0.400	0.384	0.375	0.333	0.333	0.166	0.111	0.090

We also obtained for the investigated samples a good relationship between $R^{TG} = \Delta m_{HC} / \Delta m_L$ and $R_1^{FTIR} = A^{ab}_{1370} / A^{ab}_{1505}$ with normally slightly differences because TG/DTG is recognized as a quantitative method while FTIR may be quantitative only by coupling with other methods. We found as a novelty issue a very interesting correlation in the decreasing order of all parameter R_{1-4}^{FTIR} and R^{TG} that can be very useful in the very rapid diagnosis of the decayed lime wooden pieces. We believe that the weaknesses of the FTIR method is successfully completed by TG method and becomes negligible in the diagnosis test of wooden artifacts. Diagnosis results achieved by determining R^{TG} and R^{FTIR} related to the state of the works of art, as well as with the proper restoration methodologies allowed us to classify the samples into four categories:

- Wood samples better preserved - parameters range $R^{TG} = 3.0 - 2.5$
- Wood samples available by classical restoration protocol – parameters range $R^{TG} = 2.4 - 2.0$
- Wood samples available by classical and scientific restoration protocols – parameters range $R^{TG} = 1.9 - 1.0$
- Wood samples available only by scientific personalized protocol – parameters range $R^{TG} < 1.0$

The scientific protocol proposed in this paper for the first stage regarding the wooden pieces diagnosis is based only on the assessment of the amounts of lignin and cellulosic components remaining after certain stages of aging. For these reasons we recommend this protocol in the first stage of diagnosis because it must be necessarily followed by the analytic detailed protocol in order to identify the other remaining wood components, to monitor the restoration processes and to propose the most appropriate scientific methods and advanced personalized materials for the consolidation of the critical wooden areas.

Conclusions

Scientific protocol proposed in this paper by coupling the certain parameters of the FT-IR and TG methods can be successfully used in the first stage of diagnosis of wooden artifacts, offering the first information about the quantitative composition of wooden polymeric components in a short time and on the basis of the two most known and affordable investigative techniques in the field. Because the information provided by this protocol can be used only in the first stage of diagnosis it must be necessarily completed by detailed investigation of works of art which show the critical parameters.

Aknowlegments

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