UNIVERSITÀ DEGLI STUDI DI PALERMO

DiFC
Dipartimento di Fisica e Chimica - Emilio Segrè

Comparative Study of XIX Century Woods from the Historical Collection of Physics Instruments at the Palermo University by Thermogravimetry coupled with FTIR Spectroscopy

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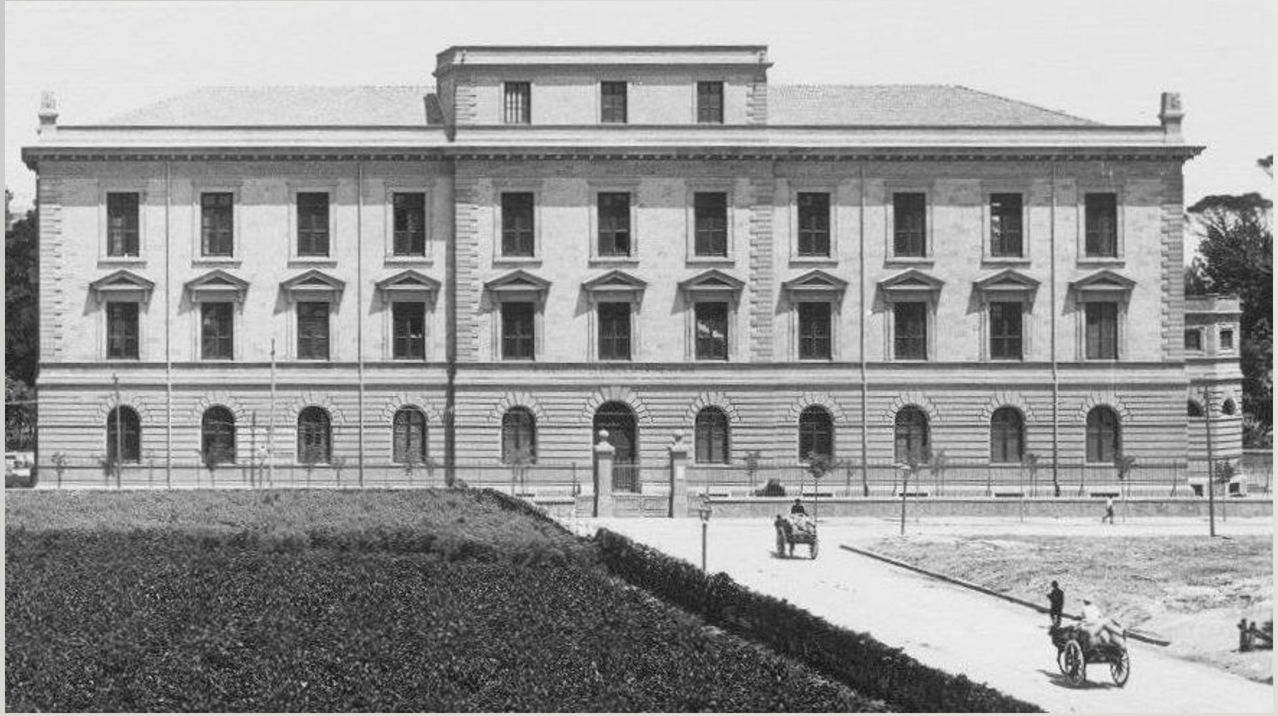
Preventive Conservation in Museums, Libraries and Archives: scientific collections as a case study
Palermo, Palazzo Chiaramonte Steri, 16 - 18 October 2019

Summary

- Thermal and structural properties of historical woods of XIX century acoustic apparatuses of the Historical Collection of the Physics Instruments of the Palermo University have been investigated by FTIR spectroscopy coupled with thermogravimetry (TG).
- The thermal behaviour of the wooden materials has been successfully interpreted on the basis of specific indexes determined by the quantitative analysis of the FTIR spectra.
- The activation energy of the pyrolysis process reflects both the peculiar composition (related to the specific wooden taxon) and the conservation state of the historical woods.
- The FTIR and thermogravimetric results were correlated to the specific wood taxon as well as to the preservation conditions of the historical apparatuses.
- The thermogravimetric parameters have been correlated to the lignin index of the woods by proper experimental equations, which can be considered as a novel protocol to estimate the preservation conditions of historical woods from different taxon.

The Historical Collection of the Physics Instruments

The Historical Collection of the Physics Instruments, of the University of Palermo, collects more than 500 physics instruments about mechanics, acoustic, calorimetry, electromagnetism and optics. The oldest instruments date back to the early 19th century, when experimental Physics began to be taught in the University by using instruments and apparatus. It is on exhibit at the Department of Physics and Chemistry - Emilio Segrè, in the historical building of via Archirafi 36.



- Sear T (2017). *The Historical Collection of Physics instruments of Palermo University.* Bulletin of Scientific Instrument Society **132**:32-33
- Agliolo Gallitto A, Chinnici I, Bartolone F (2018) *The Collection of historical instruments of Acoustics of the University of Palermo*, Museologia Scientifica **12**:48-54

The Investigated Instruments

The wood samples were extracted from three apparatuses of different age, from 1864 to 1906, and different wood taxon.

Chronograph tuning forks with electromagnetic drive

Resonance box of a tuning forks

Support for tuning forks

- Agliolo Gallitto A, Chinnici I, Bartolone F (2017). *Collezione Storica degli Strumenti di Fisica: Catalogo degli strumenti di Acustica*. Università degli Studi di Palermo. ISBN 978-88-941245-2-1

The Chronograph Tuning Forks with Electromagnetic Drive

Chronograph tuning forks with electromagnetic drive, by Max Kohl, Germany, acquired in the 1906.

The manufacturer's monogram engraved on the tuning fork.

- Agliolo Gallitto A, Chinnici I, Bartolone F (2017). *Collezione Storica degli Strumenti di Fisica: Catalogo degli strumenti di Acustica*. Università degli Studi di Palermo. ISBN 978-88-941245-2-1
- Kohl M (1909). *Physical Apparatus*, Vols. II, Chemnitz Germany. 1909-1911?, pag. 455

The Resonance Box of a Tuning Forks

Resonance box of a tuning forks, by Rudolph Koenig, France, acquired in the 1868.

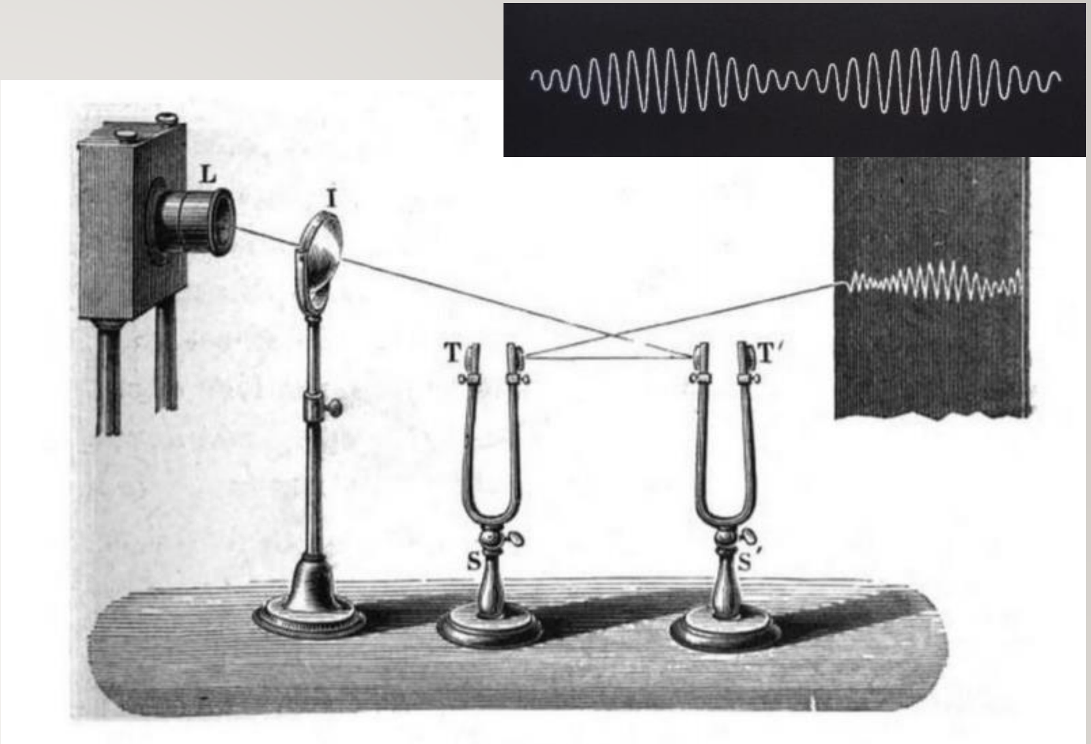


Fig. 29.

Apparatus for the phenomenon of acoustic beats.

- Agliolo Gallitto A, Chinnici I, Bartolone F (2017). *Collezione Storica degli Strumenti di Fisica: Catalogo degli strumenti di Acustica*. Università degli Studi di Palermo. ISBN 978-88-941245-2-1
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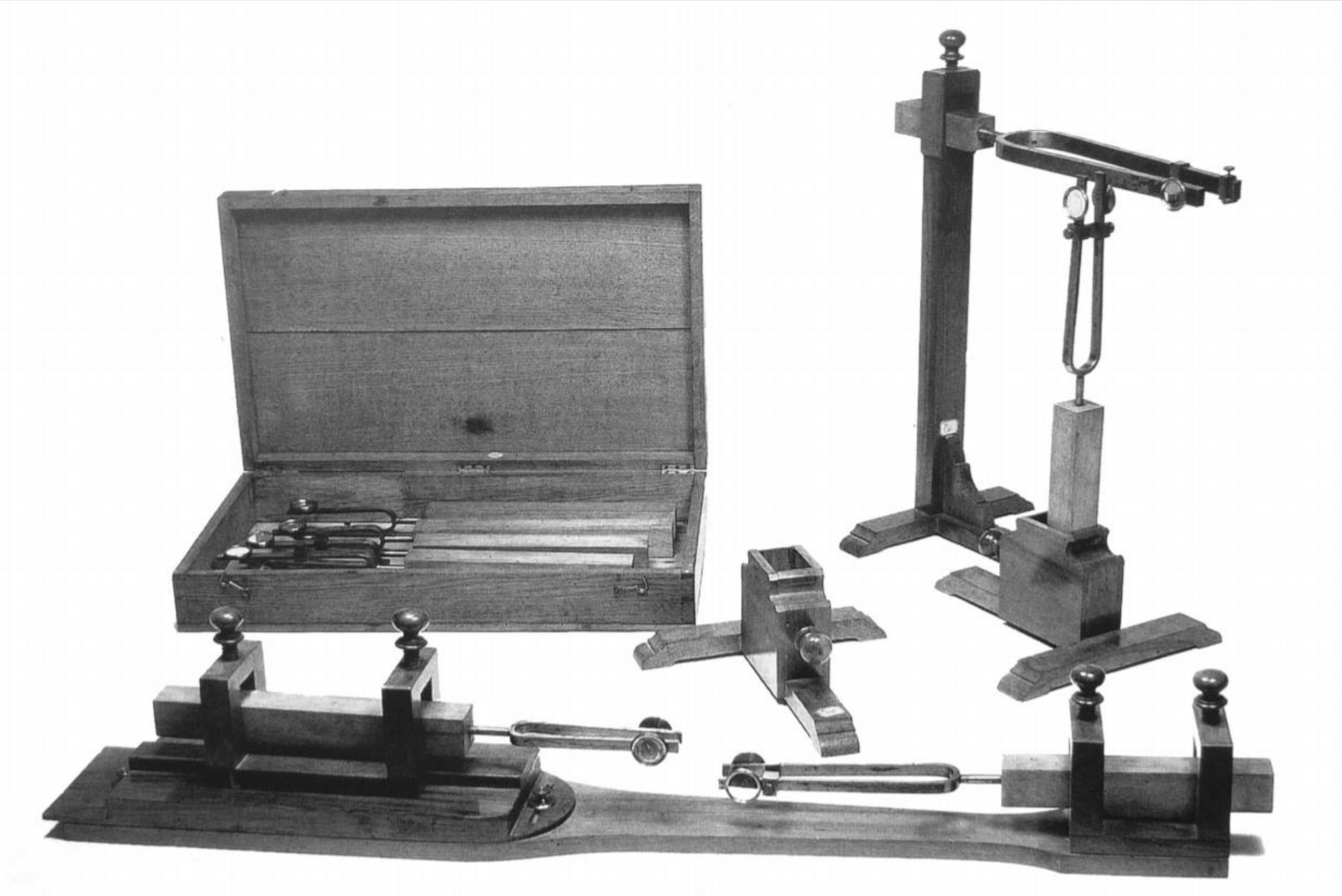
Aurelio Agliolo Gallitto *et al*

Palermo, 17.10.2019

The Support for Tuning Forks

Support for tuning forks, by Rudolph Koenig, France, acquired in the 1864.



- Agliolo Gallitto A, Chinnici I, Bartolone F (2017). *Collezione Storica degli Strumenti di Fisica: Catalogo degli strumenti di Acustica*. Università degli Studi di Palermo. ISBN 978-88-941245-2-1
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The Historical Wood Samples

Symbol	Wood taxon	Physics apparatus	Manufacturer	Year
SM	*Swietenia mahagoni*	Chronograph tuning forks with electromagnetic drive	Max Kohl, Chemnitz (Germany)	1906
PA	*Picea abies*	Tuning forks on resonance box	Rudolph Koenig, Paris (France)	1868
JR	*Juglans regia*	Support for tuning forks	Rudolph Koenig, Paris (France)	1864

Experimental Methods

FTIR Spectrosopy

Fourier-transform infrared (FTIR) spectroscopy allows one to obtain infrared spectra. FTIR measurements were performed at room temperature by a Frontier FTIR spectrometer (PerkinElmer). The spectra were recorded in the range between 450 and 4000 cm^{-1}, with a spectral resolution of 2 cm^{-1}. The experiments were performed on KBr pellets with a content of milled wood sample smaller than 2 wt%.

Thermogravimetry

Thermogravimetry (TG) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. This measurement provides information about physical phenomena, such as phase transitions, absorption/desorption, thermal decom-position, solid-gas reactions, etc. TG measurements were performed by a Q5000 IR apparatus (TA Instruments) under inert atmosphere. To this purpose, nitrogen flows of 25 and 10 $cm^3\ min^{-1}$ were used for the sample and the balance, respectively. The experiments were carried out by heating the sample (ca. 5 mg) from room temperature up to 600 °C. Five different heating rates (5, 10, 15, 20 and 25 °C min^{-1}) were selected.

- Cavallaro G, Agliolo Gallitto A, Lisuzzo L, Lazzara G (2019). *Comparative study of historical woods from XIX century by thermogravimetry coupled with FTIR spectroscopy*. Cellulose, in press. doi: 10.1007/s10570-019-02688-3

FTIR SPECTRA FOR THE INVESTIGATED SAMPLES

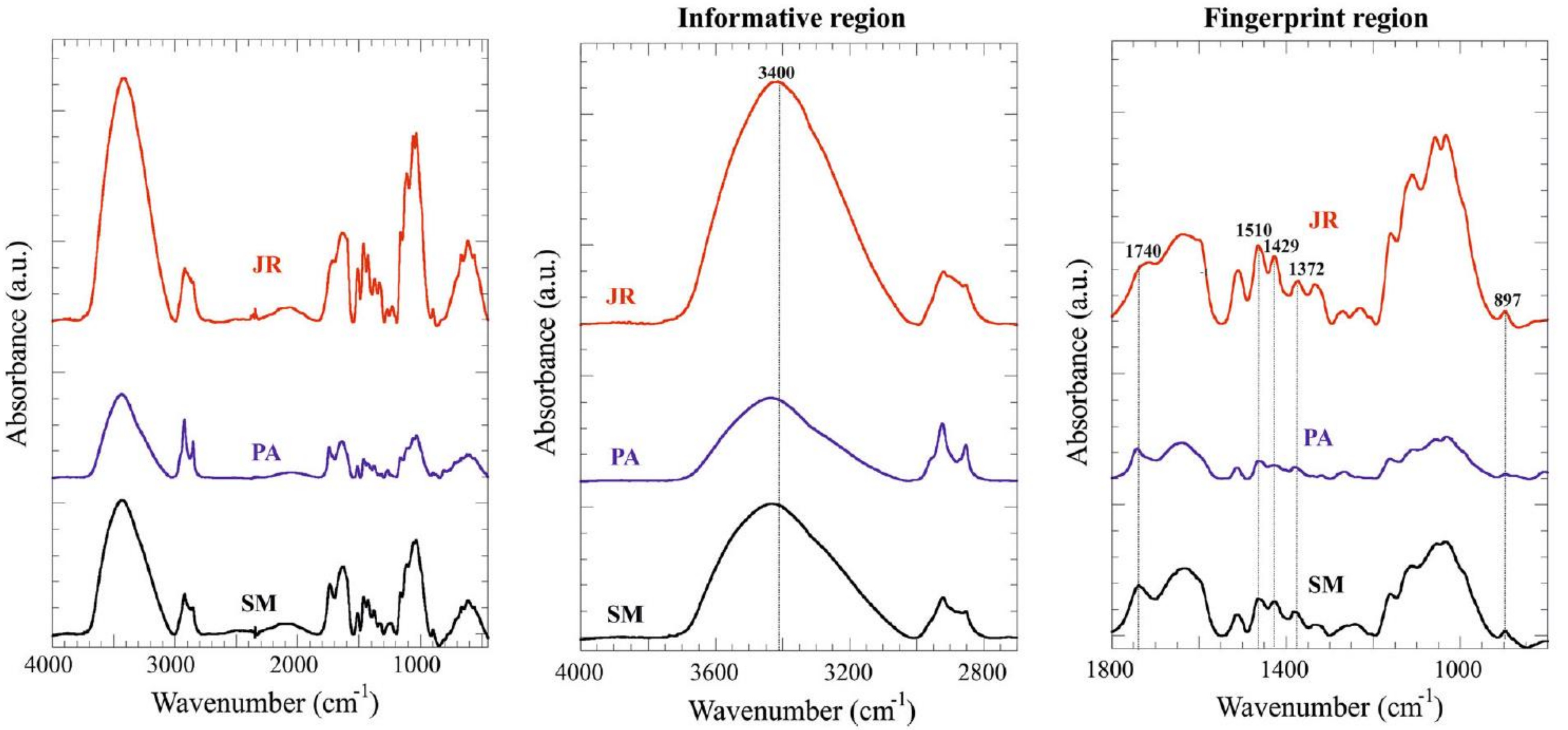

Fig. 2 FTIR spectra for the investigated wood samples. The wavenumbers for the bands employed in the calculation of the FTIR indexes are marked in the Figure

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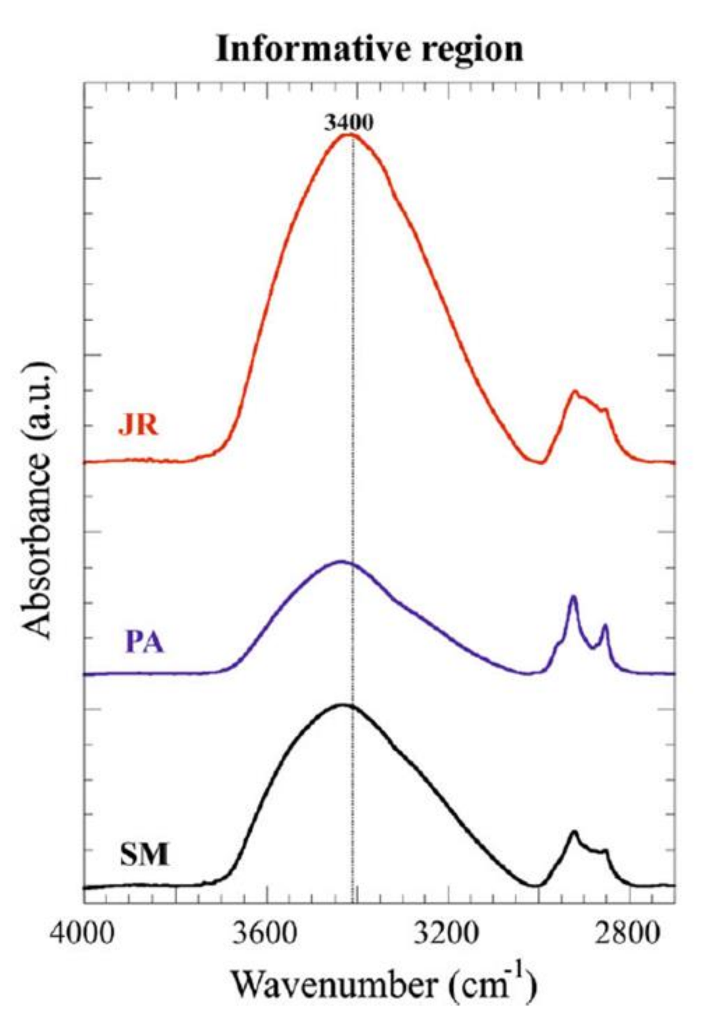
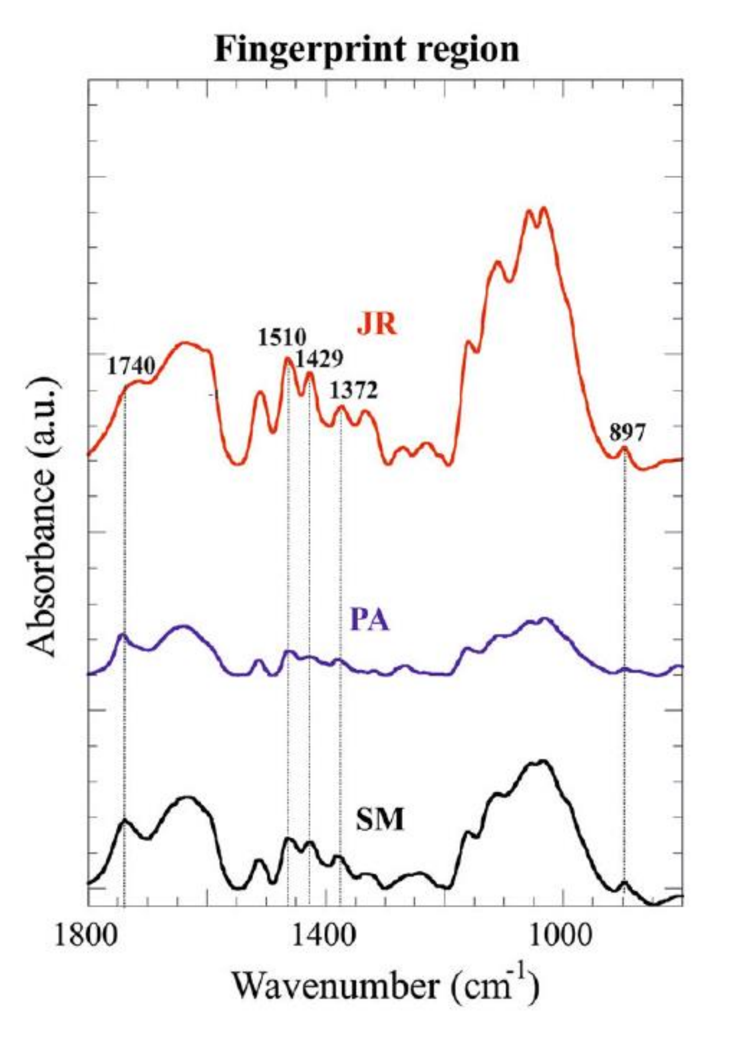
Analysis of the FTIR Spectra: the Informative Region



We detect a peak centered at ca. 3400 cm^{-1}, which can be attributed to **OH stretching vibrations.** Consequently, this signal can be related to the degree of hydrogen bonding between hydroxyl groups in wood components (cellulose, hemicellulose, lignin and water).

We also detected a band at ca. 2900 cm^{-1}, which is due to asymmetric and symmetric **CH stretching vibrations**. Generally, the absorption intensity at 2900 cm^{-1} is used as internal standard for determination of **the cellulose structural degree** in wood samples.

Analysis of the FTIR Spectra: the Fingerprint Region



In the **fingerprint region** (wavelength range between 1800 and 800 cm^{-1}), we focused on the following signals characteristic of wood:

- C=O stretching vibrations of carboxyl and acetyl groups in hemicellulose (peak centered at 1740 cm^{-1});
- C=C stretching of the aromatic ring in lignin (band at 1510 cm^{-1});
- CH_2 bending of cellulose (band at 1430 cm^{-1});
- CH bending in cellulose and hemicellulose (band at 1372 cm^{-1});
- C–H vibrational mode in cellulose (peak centered at 897 cm^{-1}).

The quantitative analysis of the FTIR spectra allowed us to determine specific indexes related to both the cellulose crystallinity and the composition of the wooden samples.

ANALYSIS OF THE FTIR SPECTRA (II)

Total Crystalline Index (TCI) = $(I_{1372\ cm^{-1}})/(I_{2900\ cm^{-1}})$

Lateral Order Index (LOI) = $(I_{1729\ cm^{-1}})/(I_{897\ cm^{-1}})$

Lignin index (LI) = $(I_{1510\ cm^{-1}})/(I_{1372\ cm^{-1}})$

Carbonyl index (CI) = $(I_{1740\ cm^{-1}})/(I_{1372\ cm^{-1}})$

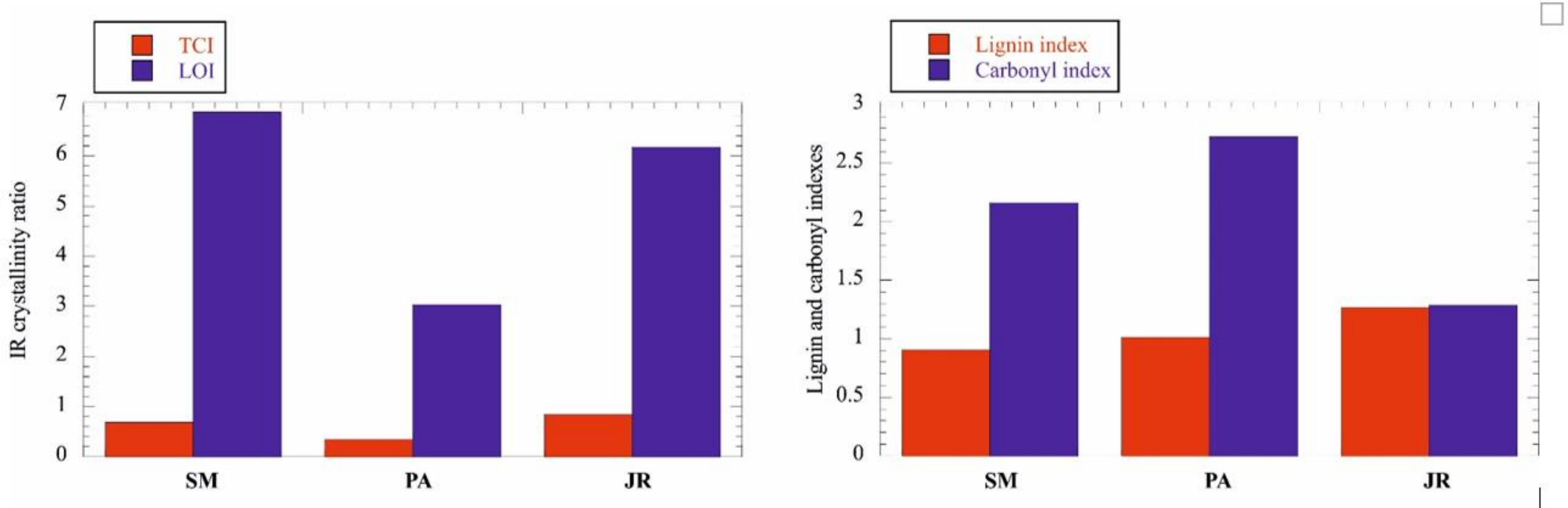


Figure. Relative crystallinity (TCI and LOI) and lignin/carbonyl indexes determined from the FTIR spectra analysis of the investigated wood samples.

Thermogravimetric Curves, TG and DTG

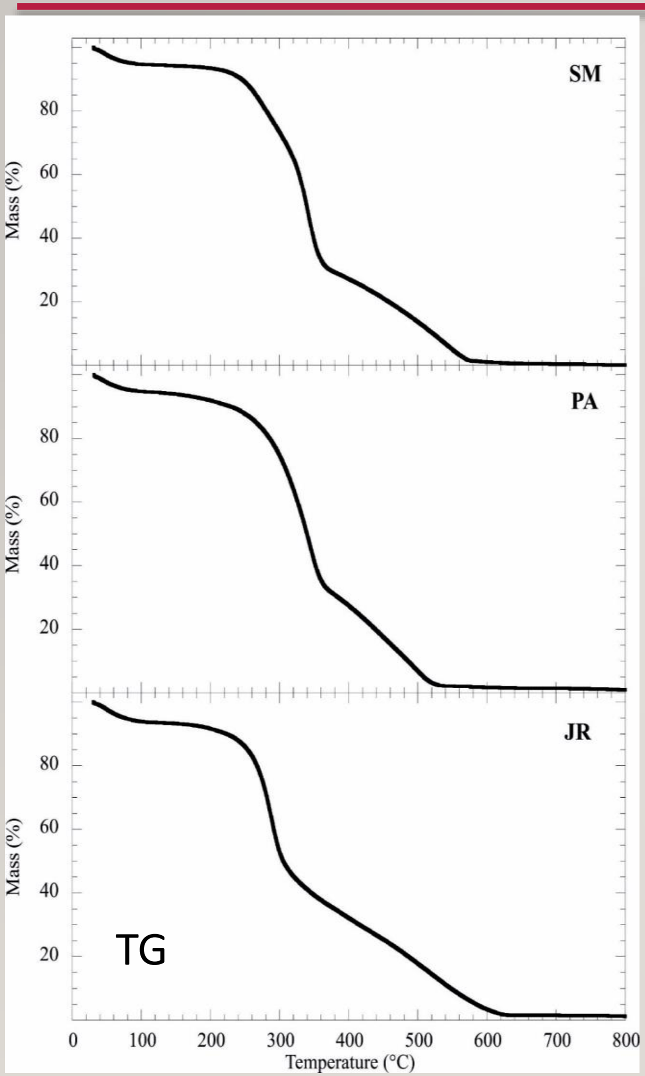
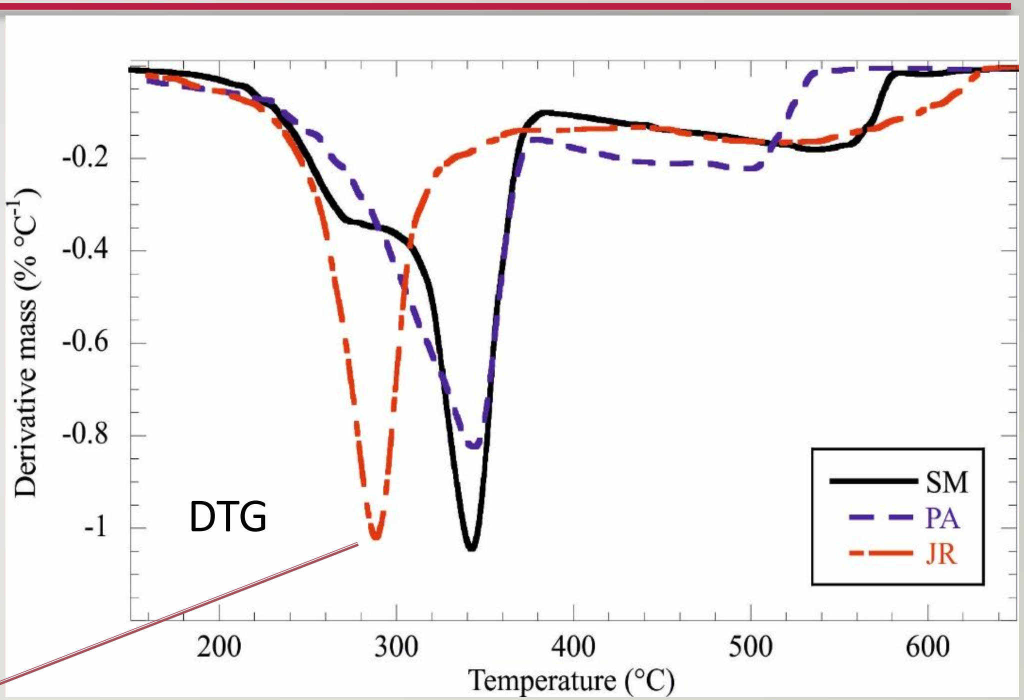


Figure. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of mass as a function of temperature of the three wood samples, $\beta = 10$ °C min^{-1}.



DTG peak ⇒ cellulose degradation

We observe three different mass losses (ML) due to specific degradation processes of historical woods.

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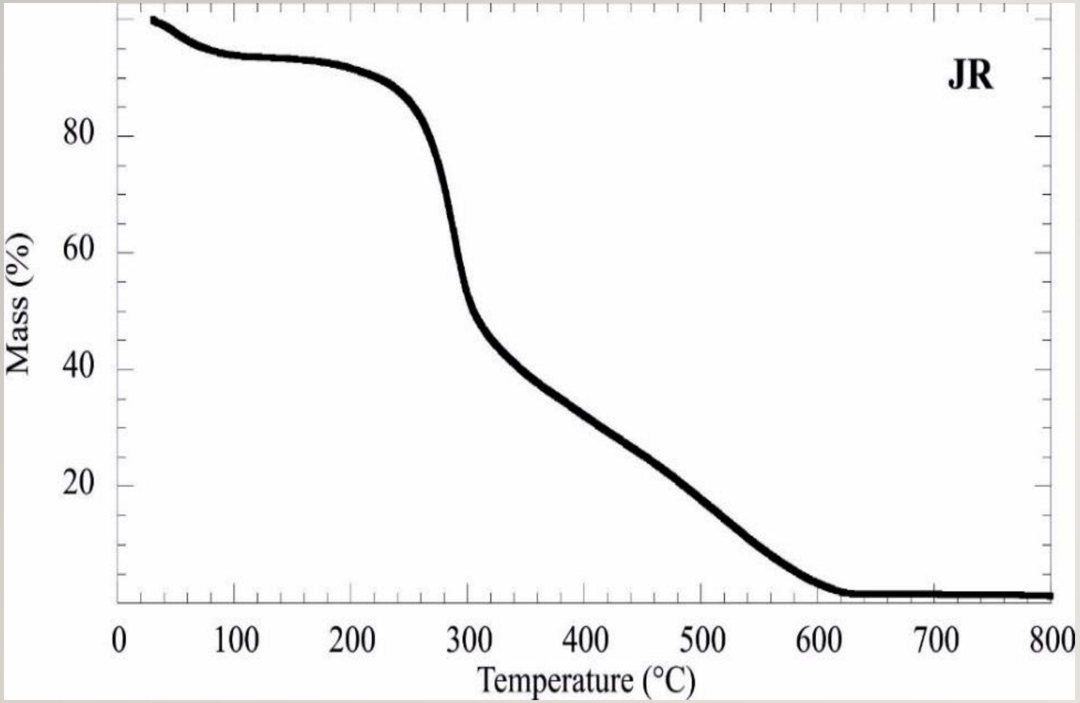
Thermogravimetric Curves



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- $\mathbf{ML_{25\text{-}150}}$ can be correlated to the moisture content of the sample. The largest $\mathbf{ML_{25\text{-}150}}$ was detected for **JR**, which is the wood with the strongest hygroscopic degree.
- We observe two separated mass losses at 180-380°C and 380-600°C respectively, highlighting that the wood pyrolysis represents a multistep degradation mechanism. $\mathbf{ML_{180\text{-}380}}$ and $\mathbf{ML_{380\text{-}600}}$ can be associated to the pyrolysis processes of the wood components, which are hemicellulose, cellulose and lignin.
- The $\mathbf{(ML_{180\text{-}380})/(ML_{380\text{-}600})}$ **ratio** could be correlated to the specific composition of the historical wood. The largest $(ML_{180\text{-}300})/(ML_{380\text{-}600})$ ratio is estimated for **JR**, while **SM** exhibits the lowest value.

THERMOGRAVIMETRIC CURVES: TG AND DTG RESULTS

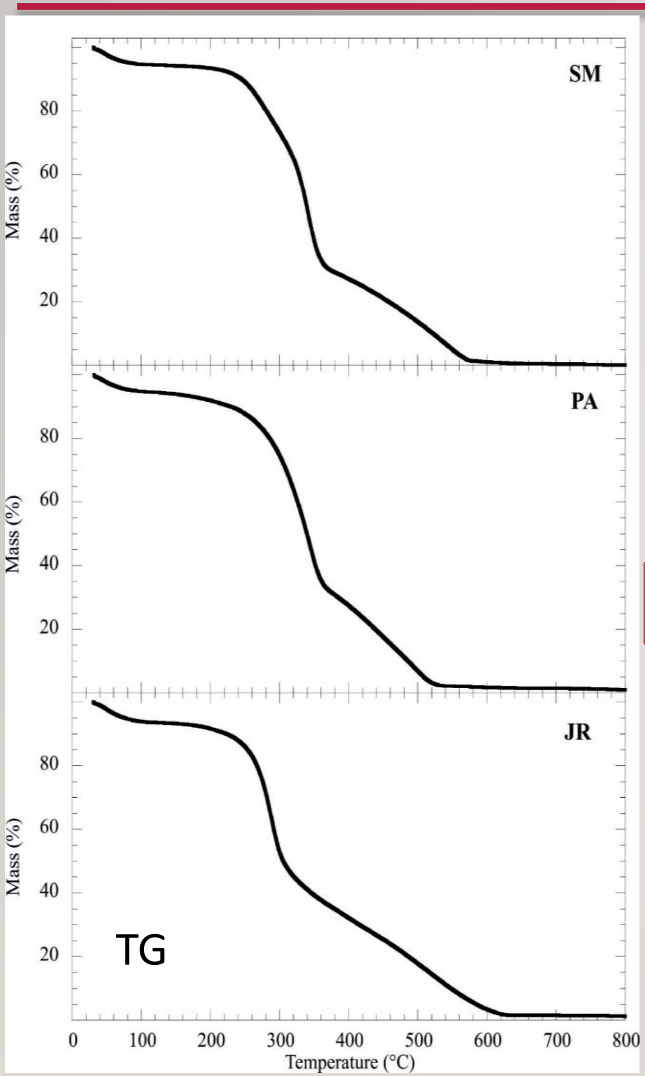
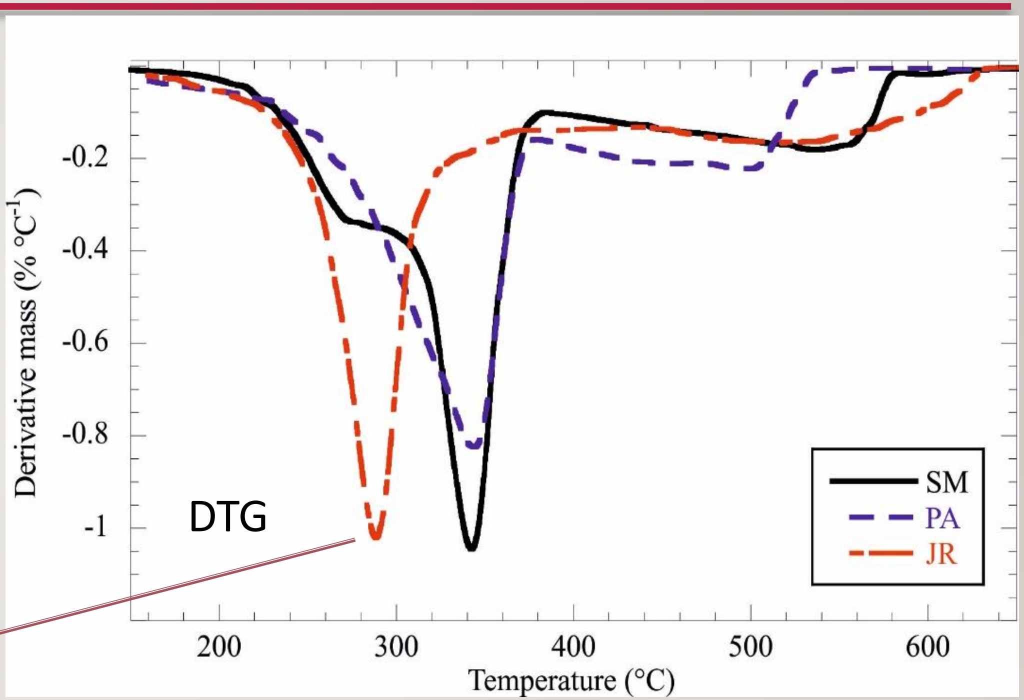


Figure. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of mass as a function of temperature of the three wood samples, $\beta = 10$ °C min^{-1}.

Three different mass losses (ML) due to specific degradation processes of wooden materials.

DTG peak ⇒ cellulose degradation



Wood	ML_{25-150} (wt%)	$ML_{180-380}$ (wt%)	$ML_{380-600}$ (wt%)	$(ML_{180-380})/(ML_{380-600})$	DTG peak (°C)
Swietenia mahagoni (SM)	5.65 ± 0.06	64.6 ± 0.7	28.1 ± 0.3	0.435 ± 0.009	342 ± 3
Picea abies (PA)	5.93 ± 0.06	62.0 ± 0.7	28.9 ± 0.3	0.46 ± 0.01	341 ± 3
Juglans regia (JR)	6.67 ± 0.07	57.6 ± 0.6	31.5 ± 0.3	0.54 ± 0.01	288 ± 3

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The Activation Energy

- ✓ By the Kissinger−Akahira−Sunose (KAS) method, a model free isoconversional methods, for the kinetic of the wood pyrolysis process, one can calculated that the average E_a values for **SM**, **PA** and **JR**, which result 203, 156 and 43 kJ mol^{-1}, respectively.
- ✓ We can state that **JR** possesses the lowest energetic barrier to the pyrolysis. These results agree with the DTG peak data, which revealed that **JR** is the worst wood in terms of thermal stability under inert atmosphere. According to the TG data, we can assert that **JR is the most sensitive wood to the decay and structural deterioration**. Therefore, **JR** needs more accurate protocols for its preservation.
- ✓ **Thermogravimetric results can be univocally interpreted by the analysis of the FTIR spectra of the woods. The combination of TGA and FTIR spectroscopy analyses might be useful to investigate the conservation state of wooden artworks.**

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Conclusions

The investigated wood samples exhibit variable lignin and carbonyl indexes as well peculiar cellulose crystallinity degree: **we observe that cellulose in *Picea abies* possesses the highest degree of disorder**.

The analysis of both thermogravimetric (TG) and differential thermogravimetric curves (DTG), under inert atmosphere, evidenced that the historical woods present different thermal stability depending on their structural and compositional characteristics. Compared to the other woods, we observed that ***Juglans regia* exhibits a strong reduction (ca. 60 °C) of the cellulose degradation temperature**. This result was supported by the non-isothermal thermogravimetric studies, which evidenced that **the activation energy of the wood pyrolysis for *Juglans regia* is ca. 4-5 times lower than those of the other wood samples**. On this basis, we can state that ***Juglans regia* is the most sensitive wood to the structural deterioration**.

Thermal properties of the historical woods were correlated to the specific indexes estimated from FTIR spectra. Interestingly, we observed that the activation energy of the pyrolysis process linearly decreases with the lignin index of the wood.

This work evidences that the combination of FTIR spectroscopy and thermogravimetric analysis can provide a robust protocol to predict the conservation state of historical woods.

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Acknowledgment

- Work financially supported by the Department of Physics and Chemistry - Emilio Segrè by the Project: *Manufatti lignei: dalla diagnostica alla fruizione*

THANK YOU!