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RAMAN SPECTRA OF DECAYED WOOD SAMPLES

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abstract: The purpose of the research was to identify the characteristic frequencies of decayed wood samples by NIR FT-Raman spectroscopy. The guaiacyl and syringil marker bands of 1594 cm^{-1} and 1599 cm^{-1} were used to distinguish between hardwood and softwood species. Comparison between spectra acquired in the Raman compartment and with a sonde, using various laser powers and number of scans emphasized only small differences.

keywords: decayed wood, NIR-FT-Raman spectra, syringyl and guaiacyl markers, softwood, hardwood

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1. Introduction

Continuing our previous FTIR study on wood samples used in traditional village constructions, in order to obtain the full image of the vibrational activity of lignocellusic mateials the FT-Raman spectralanalysis was done [1]. Biological deterioration of wood results in an increased lignin content. The possibility to evaluate the decayed samples is necessary in order to establish the best conservation procedure.

Raman technique is widely used to characterize wood products and in general lignocelulosic materials [2-5].

To characterize lignin of wood, the Raman bands for C=C stretching derived from 4-hydroxy-3-methoxyphenyl (guaiacyl) nuclei and from 3,5-dimethoxy-hydroxyphenyl (syringyl) nuclei (Fig. 1) were analyzed [6].

The syringyl band was shifted to a lower frequency compared to a guaiacyl band. Syringyl nuclei exhibited a C=C stretching band at 1594 cm^{-1}, while guaiacyl nuclei exhibited the band at 1599 cm^{-1}. These bands were designated as syringyl and guaiacyl marker bands, respectively. Hardwood and softwood exhibit different physical-chemical characteristics. One of the reasons is the chemical structure of lignin. Softwood mainly contains only guaiacyl lignin, while hardwood contains both guaiacyl and syringyl lignin, and the syringyl/guaiacyl (S/G) ratio varies among species.

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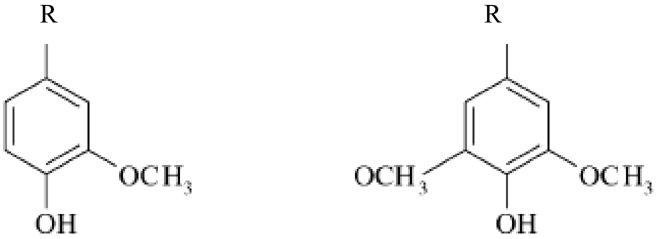

Fig. 1 *Molecular formula for model compounds of lignin: left guaiacyl nuclei; right syringyl nuclei*

Experimental

FT-Raman spectra of all samples were recorded with a Bruker FT-Raman instrument between 0 and 4000 cm^{-1}. A Nd:YAG laser with an exciting power between 1 mW – 500 mW at a wavelength of 1064 nm was used. For each spectrum, minimum 50 scans were accumulated at a resolution of 4 cm^{-1}. The detector and integral preamplifier were cooled to 77 K by liquid nitrogen for all measurements. The Raman holder containing about 2 mg of milled sample was placed directly in the instrument without the need for position optimization between samples. Also the Raman system coupled with an optical fiber to the mobile head, which makes the system very versatile and readily applicable *in situ* measurements, was used directly on the wood samples surface. To our knowledge this spectrometer has an unique configuration, being a very versatile and performant research instrument in our country.

Results and discussion

Figs. 2, 3 and 4 show FT-Raman spectra obtained in various conditions for different types of wood.

Important acquisition parametrs are the Raman laser source power and the number of scans. Using a laser power too strong (above 200 mW, depending on the probe) produce a peak at 3500 cm^{-1} due to termic effect, that is why the power should be reduced until this peak dissapear.

Sensitivity (signal to noise ratio) for mobile sonde is lower than for the sample compartment acquired spectra but the fluorescence is also lower in the first case which is an advantage of this technique.

Very degraded wood samples (100 years oak, outdoor exposed, 50 years acacia)which present a dark color are difficult to analyze due to fluorescence peak. Flourescence effect cover the vibration bands.

Assignment of lignin bands for *F. crenata* is given in the Table 1 [6].

The assignment of guaiacyl and syringil bands markers is used in the literature [6] to distinguish between softwood and hardwood samples. For pine tree, a softwood the guaiacyl band is positioned at 1600 cm^{-1} in conformity with reported data but for all the hardwood samples we have obtained the syringyl band at 1605 cm^{-1} instead of 1594 cm^{-1}. For this reason our next goal is to realize Density Functional Theory (DFT) calculations to obtain the vibrational frequencies for monomer units of lignin.

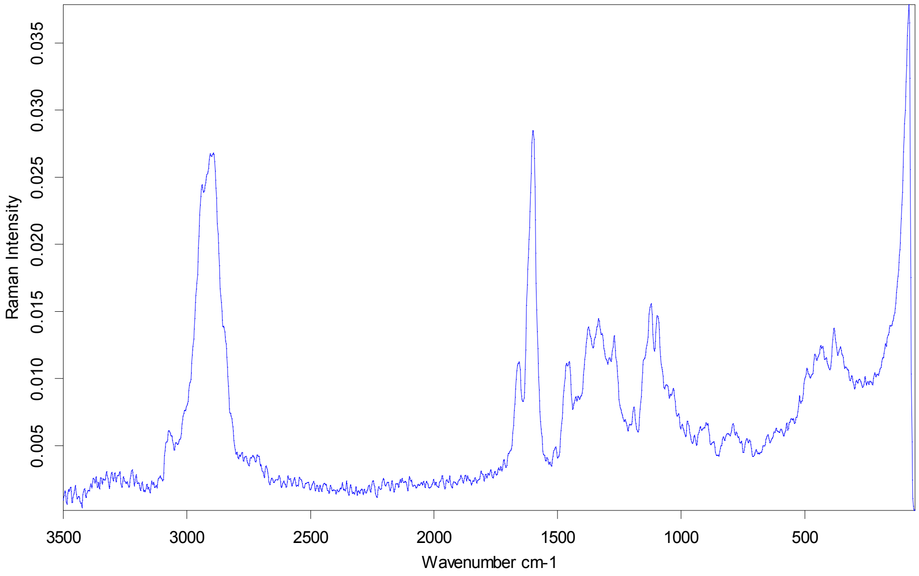

Fig. 2 *Raman spectrum at sample surface (*in situ*) of 70 years pine sample at 500 mW.*

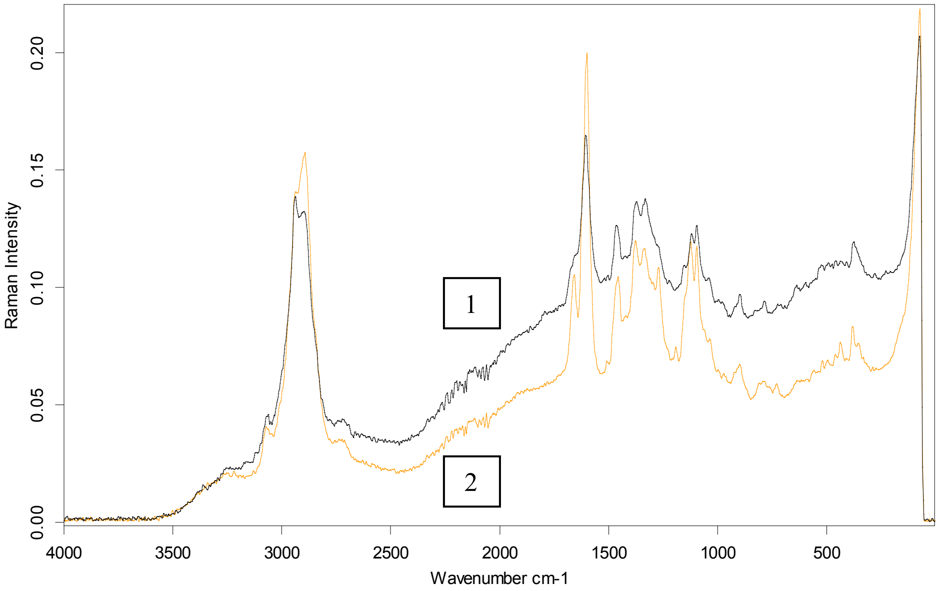

Fig. 3 *Raman spectra of hornbean (1) and pine (2) milled samples.*

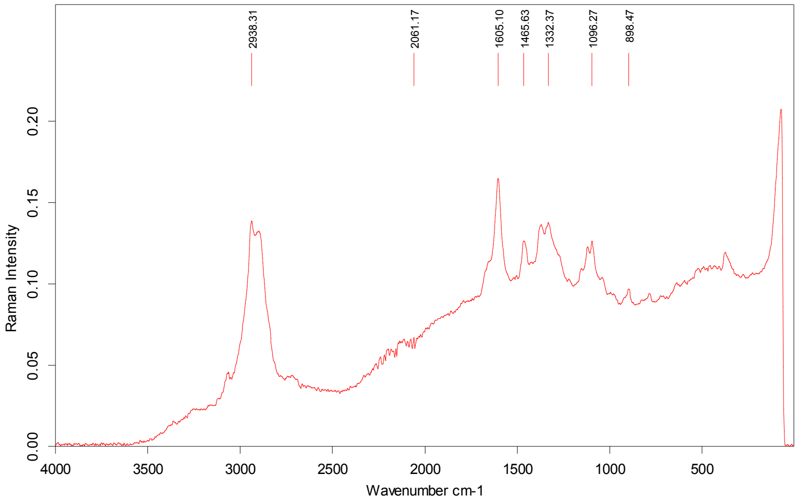

Fig. 4 *Raman spectra of plum tree milled sample*

Table 1 Lignin-derived Raman bands found in the NIR-FTR spectra [6].

No	Frequency (cm^{-1})	Assignment
1	3320	ν(O-H)
2	3070	ν (=CH)
3	2983	ν (C-H)
4	1668	ν (C=O)
5	1602	ν (C=C)
6	1332	δ (CH)
7	1189	δ (CH_2)
8	379	ν and breathing (aromatics)

Conclusions

Raman spectra of different decayed wood using two types of Raman techniques were aquired and analyzed.

Acquisition parameters are very sensitive and must be optimized for each sample. Utilization of the mobile sonde it is a great advantage for *in situ* experiments but the sensitivity is lower than the traditional acquistion mode.

Characteristic frequencies of guaiacyl and syringyl components of lignin polymer permits to distinguish between hard and softwood samples.

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REFERENCES

1. Dobrică, I., Bugheanu, P., Stănculescu, I. and Ponta, C. (2008) *Ann. Univ. Buc. Chim.*, anul XVII vol. **I**, 33.
2. Shen, Q., Rahiala, H. and Rosenholm, J.B. (1998) Evaluation of the Structure and Acid–Base Properties of Bulk Wood by FT-Raman Spectroscopy, *J. COLL. INTERFACE SCIENCE* **206,** 558-68.
3. Kihara, M., Takayama, M., Wariishi, H. and Tanaka, H. (2002) *Spectroch Acta Part* A **58**, 2213-21.
4. Saariaho, A.-M., Argyropoulos, D.S, Jaaskelainen, A.-S. and Vuorinen, T. (2005) *Vibrational Spectroscopy* **37**, 111-21.
5. Ibrahim, A., Oldham, P.B., Conners, T.E. and Schultz, T.P. (1997) *MICROCHEMICAL J.* **56**, 393-402.
6. Takayama, M., Johjima, T., Yamanaka, T., Wariishi, H. and Tanaka, H. (1997) *Spectrochimica Acta Part A* **53**, 1621-28.