Infrared spectroscopy as a tool to estimate the age of wood

How we can use the molecular decay of wood for dating purposes

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Keywords: *molecular decay—wood dating—FTIR spectroscopy—Random forest model—dendrochronology*

CHNT Reference: Reiter, Franziska; Tintner, Johannes; Spangl, Bernhard; Smidt, Ena and Grabner, Michael. 2021. Infrared spectroscopy as a tool to estimate the age of wood. How we can use the molecular decay of wood for dating purposes. Börner, Wolfgang; Kral-Börner, Christina, and Rohland, Hendrik (eds.), Monumental Computations: Digital Archaeology of Large Urban and Underground Infrastructures. Proceedings of the 24th International Conference on Cultural Heritage and New Technologies, held in Vienna, Austria, November 2019. Heidelberg: Propylaeum.
doi: 10.11588/propylaeum.747.

Motivation and Background

The dating of wooden objects is of high relevance, as wood is preserved comparably well under various preservation conditions. Among these, waterlogged wood is especially often found in large quantities. Dry storage results either in situations of constructions sites as well as the Arctic region and desert zones. Another advantageous condition preserving wood is found in salt mines or other toxic environments (Rowell and Barbour, 1990).

Currently, wood is dated by means of either dendrochronology or radiocarbon dating. However, both methods have weaknesses and drawbacks, as samples might not be dateable or the costs might be rather high. The purpose of this master thesis was to use the molecular decay measured by means of infrared spectroscopy to establish a prediction tool for the age of a sample.

Fourier Transform Infrared (FTIR) spectroscopy is a common tool to evaluate the chemical composition of materials, especially organic matter. The method measures the vibrational signals of molecules or molecular groups induced by infrared light. It has been successfully applied in studies on the aging of wood, paper and charcoal (Trafela et al., 2007; Smidt et al., 2017). For statistical modelling of the spectra, an approach coming from the field of machine learning was applied—random forest models.

The aim of our work was to establish dating tools for wood based on the molecular decay measured by means of FTIR spectroscopy.

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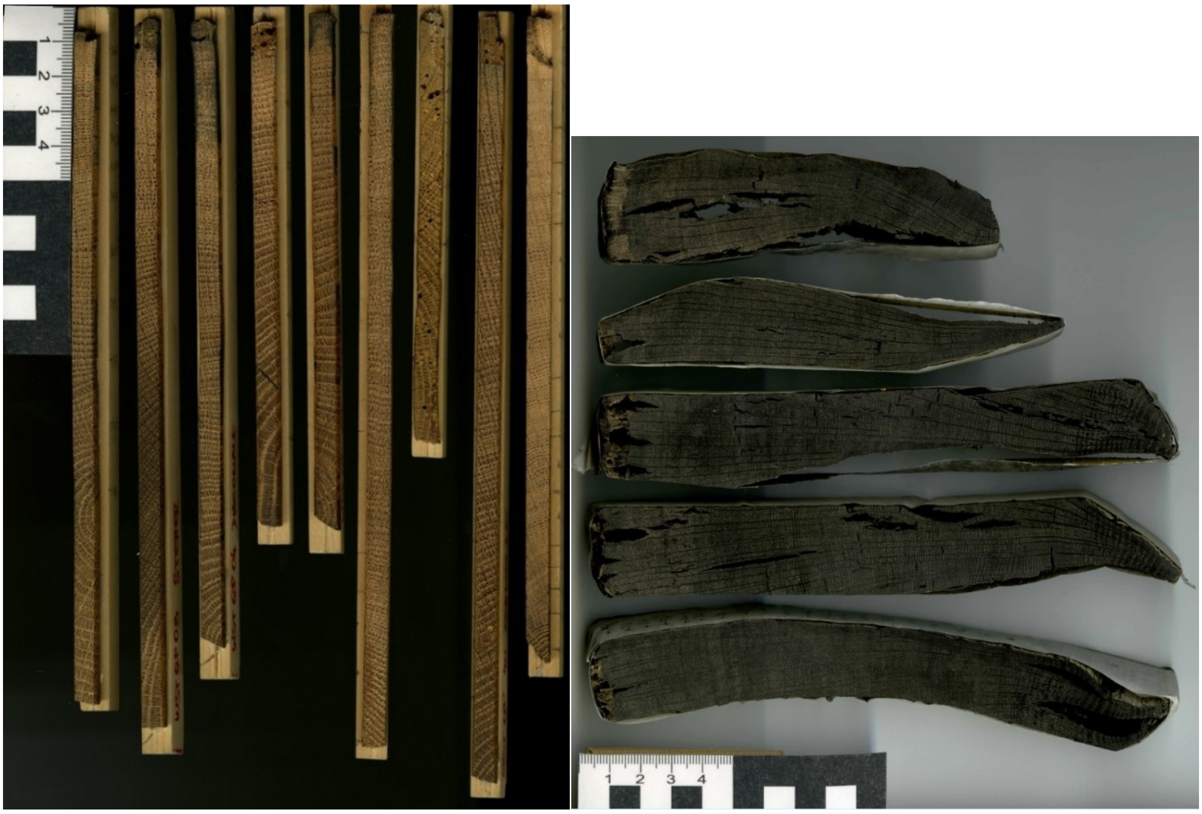
Materials, preservation conditions, and methods

The sample set was comprised of wooden samples of different origins. Construction wood came from buildings in the cities of Hallein and Salzburg, St. Stephans Cathedral in Vienna and Heidenreichstein castle in Lower Austria. Waterlogged wood originated from a cold lake in the mountains of Dachstein massif in Upper Austria and the Roman Harbour in Weyregg, Upper Austria (Fig. 1). Salty environment was covered by samples from the prehistoric salt mine in Hallstatt, Upper Austria. Additionally, living trees were sampled to prove the aging effects were already measurable at the earliest stages. The storage conditions of construction wood can be described as dry and relatively moderate temperatures (usually protected against outdoor weather). Waterlogged samples were stored at mean water temperatures of 11 °C and below. Wood from a salt environment can be described as densely packed in a mixture of salt and clay (Tintner et al., 2018).



a b

Fig. 1. a) Wooden cores from St. Stephans Cathedral, Vienna. b) cuts from the Roman harbor at Weyregg, Upper Austria (© F. Reiter).

Wood of four different species/ genera was tested: spruce (*Picea abies*), larch (*Larix decidua*), oak (*Quercus* spp.), and fir (*Abies alba*), totalling 190 wooden pieces with 3533 performed measurements. Dendrochronology served as a reference method delivering the age for the calibration set. The ages of the samples covered around 3000 years for spruce, 2000 years for oak, 3500 years for larch, and 700 years for fir. Infrared spectroscopy was carried out in the mid infrared range in ATR (Attenuated Total Reflectance) mode. The polished solid surface of the wood samples was measured. A single measurement was (as far as possible) performed on a single tree ring. Thereby, the FTIR spectra could be assigned to a distinct year reference. Several regions in the spectra were selected to be included into further analyses. These areas can be assigned to different molecular groups originating from different chemical compounds of the wood. Dating tool were performed for each species/ genus separately.

Results and Discussion

The band regions most relevant for the prediction varied among the species. For spruce and fir a region around 1730 cm^{-1} was the most significant one. Fig. 2 displays the systematic decrease of this band region at exemplarily chosen spectra of different age. The band region can be assigned to acetyl groups in hemicelluloses (Schwanninger et al., 2004). This group had previously already been identified to be highly relevant in the wood aging processes of archaeological wood (Tintner et al., 2016). The molecular decay of oak wood was visible in, the acetyl groups, as well as characteristic bands of molecular groups in cellulose. For the larch model, a further region assigned to a resin band had to be included. The environmental aging conditions in living trees, waterlogged wood and construction wood led to comparable aging processes. Therefore, these conditions were combined in one prediction model. Salt environment led to slightly, but clearly different aging conditions and thereby diverging readings. Separate models for salt environment are necessary and already in preparation.

The prediction error for a single measurement varied from 367 years in the larch model, 274 years in the spruce model, 113 years in oak, to 97 years in the fir model. As FTIR spectroscopy can be performed easily on a high number of measurement points on a wooden artefact, the prediction quality of an artefact will increase depending on the number of measurements. It can be assumed that a prediction quality for artefacts between 50 to 100 years can be achieved for all species.

Drawbacks of the method are brittle parts of wood, where microbial decay led to stronger degradation processes. Also, the outer surface of construction wood facing compartment air displays an accelerated degradation rate of the significant band region around 1730 cm^{-1}. Furthermore, it has to be stressed that the models are restricted to selected environmental conditions (wood stored in a salt environment cannot be predicted properly).

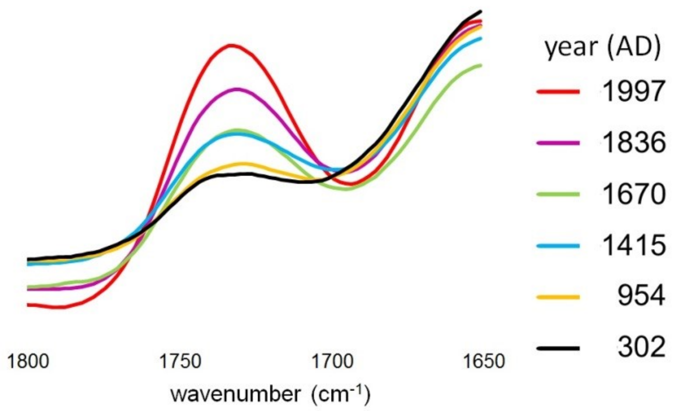


Fig. 2. Molecular decay of acetyl groups in hemicelluloses of resulting in a band decrease around 1730 cm-1 in FTIR spectra. The year (AD) has been determined by means of dendrochronology. Measurements are randomly selected from spruce samples with different age.

Conclusion and Outlook

Within the master thesis, the potential of FTIR spectroscopy to detect the molecular decay of wood and its use for dating purposes was demonstrated. The established models are adapted for four common European tree species /genera (spruce, larch, oak, fir) covering between 3500 and 700 years. Prediction quality for a single measurement ranges from 367 to 97 years. As the quantity of measurements does not affect the costs of testing as much as in other procedures, artefacts can be predicted more precisely for the same price. Further models for different species and different storage conditions will be established in the near future.

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