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Different pretreatment methods for ^{14}C dating of Younger Dryas and Allerød pine wood (*Pinus sylvestris* L.)

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ABSTRACT

An analysis was performed on samples from a series of well-preserved tree trunks and in situ stumps of Allerød/Younger Dryas age found in Koźmin and Kwiatków, Kolska Basin, Central Poland. Five different types of wood preparation methods were investigated in three Polish radiocarbon laboratories (Gliwice, Poznań and Krakow) in order to find the most stable, repeatable and reliable procedure. Their effect was tested on the stable carbon isotope ratio ($\delta^{13}C$) and ^{14}C age. Additionally, FTIR spectroscopy was used as a simple technique for obtaining rapid information on the structure of wood constituents and chemical changes taking place in wood due to various chemical treatments.

The results of AMS measurements did not show statistically significant differences in radiocarbon ages of samples prepared according to the tested methods. On the other hand, $\delta^{13}C$ measurements showed that the smallest scattering results gave α-cellulose obtained by the method BABA + Bleaching (with $NaClO_2$ and HCl) + strong base. Moreover, the mean $\delta^{13}C$ values for holo-cellulose samples are higher than those for α-cellulose samples.

Studies evidenced that the methods of preparation leading to holo- or α-cellulose gave the same FTIR spectra, while the standard method of the chemical pretreatment of samples for ^{14}C measurements (ABA) preceded by mercerization is insufficient for removing compounds containing aromatic rings.

1. Introduction

The sequences of annual growth rings of trees enable the construction of absolute chronologies including the Holocene and the Late Glacial. It is difficult to overestimate the scientific importance of the dendrochronologically and ^{14}C dated sequence of annual growths. The sequence enables the reconstruction of changes in the concentration of ^{14}C in the biosphere and atmosphere. It is particularly significant for the Late Glacial part of the radiocarbon calibration curve which had been constructed using a floating conifer chronology (12700–14300 cal BP, (Adolphi et al., 2017; Kaiser et al., 2012; Krąpiec et al., 2018a)) and the preceding part (up to 12594 cal BP) with an absolutely dated oak and pine tree chronology. Our project intend to supplementation of the two mentioned accurately replicated dendrochronological records (Krąpiec et al., 2018a).

The choice of wood preparation method for high resolution ^{14}C measurements is often a compromise between minimizing material loss and separation of the least-mobile wood component which best reflects the initial state (content of ^{14}C isotope) at the moment of ring formation. A number of studies have been carried out on wood preparation for ^{14}C measurements (Anchukaitis et al., 2008; Bird et al., 1999; Hajdas et al., 2016; Hoper et al., 1998; Nemec et al., 2010b; Santos

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et al., 2001; Santos and Ormsby, 2013; Sookdeo et al., 2016; Southon and Magana, 2010). In this study the authors decided to test different types of wood preparation methods. Five methods of the chemical pretreatment of wood were employed in three Polish radiocarbon laboratories (Gliwice, Poznań and Krakow). The aim was to find the most stable, repeatable and reliable one and to assay their effect on carbon isotope composition: the stable isotope ratio ($\delta^{13}C$) determined by IRMS and ^{14}C age derived from AMS measurements. Additionally, FTIR spectroscopy was used to investigate the structure of wood components. This simple and rapid technique allows the tracking of chemical changes taking place in wood due to various chemical treatments.

2. Materials

Three samples of wood from subfossil Scots pine (*Pinus sylvestris* L.) were used for this study. Two wood samples: K-11X and 2 KOZ 80Z represented subfossil trunks from the Koźmin site (52° 5′24.12″N, 18°38′38.12″E; Kolska Basin, Central Poland), where within the Late Vistulian low terrace of the Warta River a horizon of organic sediments with a so called "fossil forest" had been discovered (Dzieduszyńska et al., 2014). In a 0.5 m thick peat layer, numerous tree trunks and roots from the uppermost Allerod and Younger Dryas occurred. Two tree trunks, differing in their state of preservation (wood density), were selected for the tests. The K-11X wood sample was worse preserved than sample 2 KOZ 80Z, however, both preservation state was still sufficient enough for dendrochronological analysis and the precise division of the samples into particular growth rings. The sample K-11X, which consist of 10 equal width rings, was used only for first tests. The sample 2 KOZ 80Z, which consists of 2 relative wide rings, was used for $\delta^{13}C$, FTIR and ^{14}C measurements.

A third sample, 2 KXX2, was taken from a subfossil pine trunk at the Kwiatków site (52° 5′54.85″N, 18°39′9.02″E), located 2.2 km to the northeast (NNE) of the Koźmin site, where the same horizon of organic rich sediments occurred. From this sample, five successive annual growth rings from the external part of the trunk (rings 185 to 189) were taken.

The wood was sampled as fine shavings cut from wood blocks with an Olfa® knife. Samples were cut in such a way as to ensure uniform representativity of each annual growth ring. Subsequently, samples were homogenized by mixing and subsequent splitting into subsamples for different laboratories and different methods of chemical pre-treatment.

3. Methods

3.1. Chemical pretreatment

The first tests were carried out on samples of wood K-11X (Kwiatków) and 2 KOZ 80Z from the Koźmin site. The main tests of chemical pretreatment were performed on the sample of wood K_XX2 185–189.

Five different cellulose preparation methods as presented in Table 1 were tested.

Except for method OZ, the first step (BABA = base-acid-base-acid) in the remaining methods is a modified standard acid-base-acid (ABA) procedure, used from the beginning of the radiocarbon dating method. A preceding ABA sodium base (called mercerization) treatment was suggested by Nemec et al., 2010b as the main wood components (and more precisely the alcoholic, phenolic, and carboxylic groups of the main wood components) are more dissociated at high pH. This mercerization process is a standard procedure in the paper and textile industry for years.

The second step, bleaching, was tested in two variants - using acetic or hydrochloric acid. Both methods are used as standard in numerous laboratories. The product of bleaching is holo-celulose.

The third step leads to α-cellulose and includes a sequence of

Table 1
Tested chemical pretreatment methods on wood samples K-11X and 2KOZ 80Z. Samples were rinsed in deionized water (Hydrolab HLP 30) to pH = 6 before using another reagent. No rinses were used between repetitions in step 2.

No.	Method code	1st step BABA	2nd step Bleaching	3rd step Strong base	Final product	References/comments
1	OZ	–	$NaClO_2$ + CH_3COOH 75 °C, 1h (first ½ h in ultrasonic bath) repeated 7 times	10% NaOH, 75 °C, 45′; 17% NaOH, room temp., 45′; 1% HCl, room temp., 2′	α-cellulose	Loader et al., 1997/ – standard method used in Gliwice Lab. – possible acetylation
2	MOZ	Mercerization (4% NaOH, 12 h) + classic ABA method (4% HCl, 75 °C, 1h) 4% NaOH, 75 °C, 1h 4% HCl, 75 °C, 1h	as above	as above	α-cellulose	This study/ – modified method 1 – possible acetylation
3	MO	as above	as above	–	holo-cellulose	This study/ – modified method 1 – possible acetylation
4	MS	as above	$NaClO_2$ + HCl (pH = 2) 75 °C, 2h + 15′ in ultrasonic bath repeated 2 times	–	holo-cellulose	Nemec et al., 2010a; Nemec et al., 2010b/ – standard method used in Poznań Lab. – HCl used to avoid acetylation
5	MSZ	as above	as above	10% NaOH, 75 °C, 45′; 17% NaOH, room temp., 45′; 1% HCl, room temp., 2′	α-cellulose	This study/ – modified method 4 – HCl used to avoid acetylation