

XRF ANALYSIS OF PRESERVATIVE DISTRIBUTION IN DIFFERENT SPECIES WOOD SAMPLES AFTER MODEL LOW-PRESSURE TREATMENT PROCESS

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ABSTRACT

Four wood species (pine - *Pinus sylvestris* L., spruce - *Picea abies* L., ash - *Fraxinus excelsior* L., oak - *Quercus robur* L.) were submitted for model low-pressure preservative treatment process. Distribution of the copper based active substance in the structure of wood samples was analyzed after treatment using XRF technique. Measurements were performed on surfaces parallel and perpendicular to annual rings. The most regular copper concentration gradient was obtained for spruce (regular concentration decrease in the direction from sample front to centre). Penetration into oak samples is not observable at all. Copper concentration gradient in ash samples is very irregular but the penetration degree is quite high. Results for pine samples are quite similar to spruce but the concentration gradient is less regular. Higher concentration of copper was detected on surfaces parallel to annual rings in relation to perpendicular ones.

KEYWORDS: Copper, preservative, penetration, X-ray spectrometry.

INTRODUCTION

Different instrumental techniques are widely used for analysis of preserved wood. Identification of preservative kind is one of common applications (Martin et al. 2005). Instrumental techniques are also useful for verifications of elaborated methods of previously preserved wood decontamination, in order to utilize (Goto et al. 2007). Other authors (Dhamodaran and Gnanaharan 2001) applied ICP and AAS techniques to determine interactions between preservative treatment process and different parameters of wood. X-ray spectrometry was applied to analyze penetration and distribution of preservatives: copper based (Zawadzki et al. 2010a), model solutions of chlorine (Zielenkiewicz et al. 2009), chromium (Zawadzki et al. 2010b) in wood samples. Authors emphasize basic advantages of XRF technique: No need

of laborious sample preparation procedure, non-degrading and non-time consuming character of measurements with relatively big number of results. The possibility of “mapping option” application which allow for concentration gradient analysis on specified sample surface, makes this technique the perfect tool for the analysis of penetration and distribution of preservative after treatment. Such an analysis gives many informations about the treatment quality, the degree of preservation, preservative retention or the suitability of different wood species for penetration.

Excluding above mentioned papers (Zawadzki et al. 2010a, Zielenkiewicz et al. 2009, Zawadzki et al. 2010b), there are not many references concerning instrumental analysis of preservative penetration quality. XRF was used to examine how the dipping time influences the depth of copper based preservative penetration (Humar and Lesar 2009). Authors often apply modern microscopes for penetration analysis (Rijckaert et al. 2001, Nussbaum et al. 1998, Wallström and Lindberg 1999). AAS technique was used (Mazela et al. 2007) to determine the dependence of boron compound concentration in samples of pine and aspen wood on the distance from the sample edges. In other paper Schoknecht and Bergmann (2000) examined substances such as tebuconazole and cypermethrin on the cross-section of pine wood (*Pinus sylvestris* L.), Islam et al. (2009) analyzed the distribution of copper azole in the structure of douglas fir (*Pseudotsuga menziesii* Franco), but only classic chemical analysis techniques were applied.

The aim of this paper is to determine differences in retention of copper based preservative into the structure of wood samples of four species. Mapping option of XRF spectrometer was used to realize this task. Presentation of XRF abilities to analyze preservative penetration into wood structure is the additional target.

MATERIAL AND METHODS

Four species were chosen for examination: Pine (*Pinus sylvestris* L.), spruce (*Picea abies* L.), ash (*Fraxinus excelsior* L.) and oak (*Quercus robur* L.). Sapwood of pine, spruce and ash and heartwood of oak were examined. That is because heartwood of oak is more often used in practice. Tab. 1 presents density and relative humidity of analyzed wood.

Tab. 1: Mean density and relative humidity of examined wood.

Species	Density (kg.m ⁻³)	Relative humidity (%)
pine	510	9.7
spruce	460	9.4
ash	680	9.8
oak	680	9.5

Two samples of each species with dimensions 30x30x60 mm (correspondingly: radial, tangential and longitudinal dimensions) were submitted for model, low-pressure preservative treatment process. Eight samples were placed in beakers with copper-based preservative (ACQ-kind, containing about 10 % of copper) solution, which was made by dissolving 10 g of preservative in 1000 g of water. Beakers were located in Shel Lab vacuum dryer, and then the pressure was reduced to 10 kPa. After 20 min pressure was equalized with atmospheric and samples were left in the solution for consecutive 20 min. After removing them from the solution they were placed on a paper for 72 h. According to other paper concerning preservative distribution in wood structure

(Zawadzki et al. 2009), excess water evaporates after this time and preservative migration stops.

Each sample was cut into four pieces (slices) parallel to the grain. One sample from each species was cut parallel to annual rings, other was cut perpendicular. It is presented in the Fig. 1.

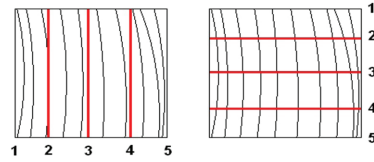


Fig. 1: Scheme of samples cutting (analyzed surfaces are marked with numbers).

Surfaces marked with numbers were then analyzed with Spectro Midex M XRF spectrometer, using “mapping option”. Each surface was scan “point by point” using collimator with 2x2 mm screen. Each point was exposed for X-rays during 30 s. So called “impulse counts” for each point were the result of measurements. This value can be treated only in qualitative way (comparison), because no proper calibration for wooden matrix is available. Element concentration is increasingly dependent on “impulse counts”. Fig. 1 - Scheme of samples cutting (analyzed surfaces are marked with numbers), a – parallel and b – perpendicular to annual rings.

RESULTS AND DISCUSSION

Fig. 2 – 5 present maps of copper presence (“impulse counts”) on all examined crosssections, both parallel and perpendicular to annual rings. Results for pine wood samples are presented in the Fig. 2.

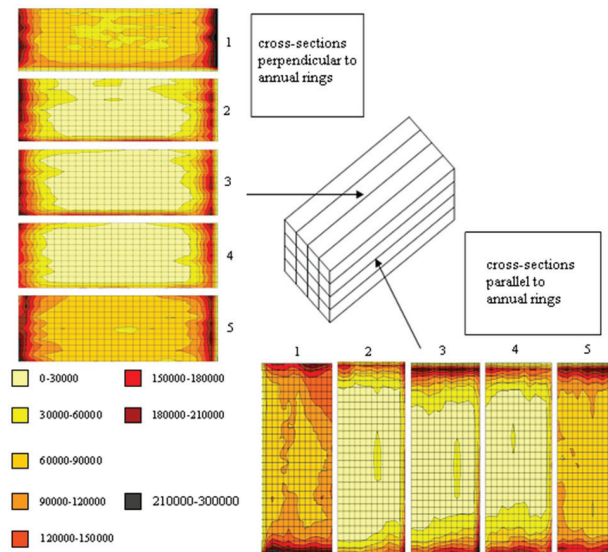


Fig. 2: Copper “impulse counts” on analyzed surfaces of pine wood samples.

Copper content on internal surfaces of pine samples (both parallel and perpendicular) decreases parallel to the grain in the direction from sample front to centre. Thin areas of raised copper content on edges is visible in most cases. On surfaces parallel to annual rings areas of raised copper content seem to reach deeper into the samples.

Differences between external cross-sections (1 and 5) parallel and perpendicular to annual rings are observable. Copper content is higher on surfaces parallel to annual rings (especially in case of the no. 1). Most of the surface is covered with colors which mean range of impulse counts from 60000 to 90000 and from 90000 to 120000. External cross-sections perpendicular to annual rings are mostly filled with color meaning 60000-90000 range, but on the surface no. 1 there is a big inclusion of 30000-60000 range. This area fragments are mainly long and thin, while areas of high copper content on parallel surfaces are rather wide (for about half of the sample width).

Similar observations can be made for spruce wood samples (Fig. 3). Distribution of the active substances is more regular than in pine wood samples. Higher copper content of external layers parallel to annual rings is significantly visible (for both sides of the sample). Most of these surfaces areas are covered with color corresponding to range of impulse counts of 80000-120000, while external layers perpendicular to annual rings are filled with the area 40000-80000.

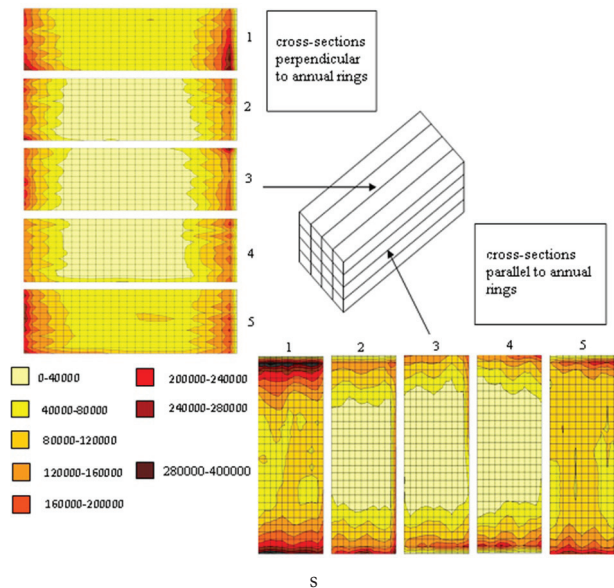


Fig. 3: Copper "impulse counts" on analyzed surfaces of spruce wood samples.

Extremely different distribution was obtained for ash samples (Fig. 4). Areas with high copper concentration near sample fronts are much smaller in relation to coniferous species samples. Gradient of copper concentration is very irregular on internal as well as on external cross-sections. Differences in concentration level between parallel and perpendicular (to annual rings) surfaces are clearly observable for internal ones. "Impulse counts" range of 15000-30000 is dominant one on both parallel and perpendicular cross-sections, but on perpendicular ones there are many thin and long areas with the range of 0-15000, while on parallel surfaces there are many

areas with the range of 30000-45000 and different width.

Also on external surfaces areas of raised concentration are long and thin for perpendicular ones and wider for parallel.

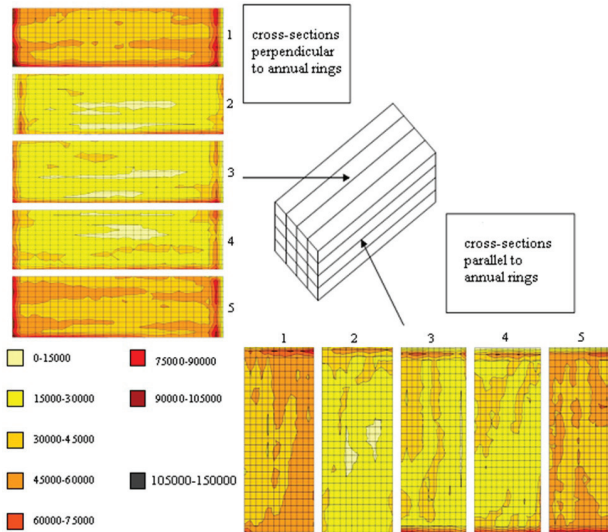


Fig. 4: Copper "impulse counts" on analyzed surfaces of ash wood samples.

Fig. 5 presents results obtained for oak wood samples. Copper concentration gradient on external surfaces is extremely random. Penetration of the active substance into samples is hardly observable, both on surfaces parallel and perpendicular to annual rings.

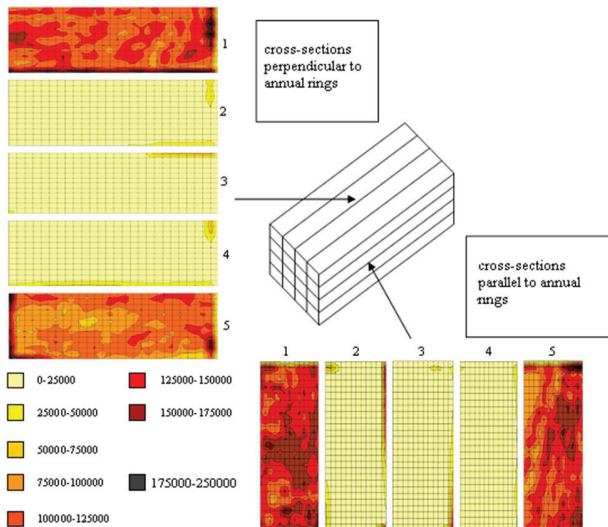


Fig. 5: Copper "impulse counts" on analyzed surfaces of oak wood samples.

Our results show that distribution of the active substance in pine and spruce wood samples is similar after preservative treatment in the same conditions. It is consistent with the results of Wytwer (1966, 1971) which showed that the penetration depth after preservation in water soluble salts is almost the same. However the same author stated that the amount of absorbed preservative is many times higher for pine wood. It cannot be confirmed in present paper because of qualitative character of measurements. Spruce sapwood is in the 3rd class of saturation ability - hard to saturate (EN 350-2 1997) but the penetration parallel to the grain is possible. One visible difference is that copper concentration gradient for spruce samples is more regular.

Presented results for pine wood are not exactly consistent with previous analyses of other authors (Zawadzki et al. 2010b), where relatively deeper penetration from both sides (perpendicular to the grain) was detected. Areas with higher copper content along samples sides are wider (even 30 % of sample width), especially in the distance up till $\frac{1}{4}$ of sample length from both fronts. It can be explained by other (smaller) dimensions of samples which they examined. Differences in penetration parallel and perpendicular to the grain are significantly more visible in case of larger samples – in smaller samples these two directions of penetration overlay on relative larger area of the cross-section. The surface is smaller but absolute depth of penetration (from both sides) is comparable.

Observed differences between cross-sections parallel and perpendicular to annual rings in pine wood may be caused by the structure of early- and late wood. Pores in early wood, which density is lower in relation to late wood, are much more available. Empty spaces can be easily filled with the preservative. Areas of early wood on cross-sections parallel to annual rings are wide, as areas with raised impulse counts range. On the other hand, thin and long areas with decreased impulse counts range on surfaces perpendicular to annual rings, may correspond to thin late wood layers with high density and low volume of empty spaces.

Even these empty spaces in early wood are not enough available to fill the pine samples interior.

Comparing the results obtained for pine wood with experiments performed by Schoknecht and Bergmann (2000) it can be stated that they are compatible. Authors analyzed the depth of different preservatives penetration and they denoted that the effective depth of penetration perpendicular to the grain in most cases does not exceed 2-3 mm. Observed differences between parallel and perpendicular surfaces are much smaller in spruce wood. Pores in wood of this species are hard to penetrate - 3rd class of saturation ability - hard to saturate (EN 350-2 1997). However, differences on surfaces 1 and 5 parallel to annual rings are clearly observable. It may be caused by partially opening of pores as a result of pressure changes during preservation process.

Penetration of copper based preservative into spruce wood was examined by Humar and Lesar (2009). Their results show that the effective depth of penetration may also (like in case of pine wood) reach 3 mm, but essential dipping time is too long to be accepted. 1000 min of dipping leads only up to 1 mm of penetration depth. Also Nussbaum et al. (1998) stated that even wood coatings (different types) penetrate pine better than spruce. Samples interior is much better penetrated in common ash samples, in spite its density is higher in relation to coniferous species. It is caused by good permeability of ash which is ring-porous species.

Oak samples are not penetrated at all despite their density is similar to ash. It is commonly known that oak heartwood is very hard to saturate (4th class of the saturation ability according to EN 350-2 1997).

CONCLUSIONS

Differences in the distribution of copper based preservative in the structure of different wood species using XRF technique are exactly observable. Then XRF seems to be the perfect tool to analyze the quality of preservative treatment or the influence of different factors on preservative retention and distribution. Application of correct calibration for each species will allow for exact determination of the absorbed agent amount. Presented method could be also used to examine the influence of environmental pollution on wood chemical composition (heavy metals) or other processes containing wood saturation (e. g. wood coloring). Presented results show that, excluding oak, all examined species are liable for preservative penetration. Density seems to not influence the penetration liability.

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