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Influence of moisture content on EPR parameters of copper in impregnated wood

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Subject Influence of moisture content on Electron Paramagnetic Resonance (EPR) spectra of spruce wood impregnated with different, water-based copper solutions.

Introduction Copper is one of the most important and efficient ingredients in wood preservatives. Copper fixation in wood is thought to operate by several different complex reactions, depending on the type of formulation and in most cases it is still not well understood. One of the possible techniques to study surroundings of copper, which provide information on fixation mechanism, is electron paramagnetic resonance spectroscopy (EPR) (Pohleven et al. 1994, Dagarin et al. 1996). Therefore, the influence of moisture content on EPR parameters of copper in impregnated wood is significant information for further interpretation of EPR spectra and for interpretation of fixation mechanisms.

Materials and methods The samples were made of Norway spruce sapwood (*Picea abies* Karst). Dimensions of the samples were 3.0 (longitudinal direction) × 1.0 × 0.5 cm. They were vacuum impregnated (according to the standard EN 113 (1989)) with three different aqueous copper based solutions; copper(II) octanoate with ethanolamine ($c_{EA} = 2\%$) or copper(II) sulfate or copper(II) sulfate with ethanolamine. The concentration of copper was 1.0×10^{-2} mol/l, being equal in all solutions. After impregnation, the samples were dried according to the standard EN 84 (1996). Dry impregnated and unimpregnated wood was then stored for three weeks in closed chambers above saturated salt solutions, to reach the equilibrium moisture content. We used the following saturated salts solutions: $MgCl_2 \times 6H_2O$ (32.9% RH), $NaNO_2$ (64.8% RH) and $ZnSO_4 \times 7H_2O$ (90.0% RH) (Schneider 1960; Browning 1967). Additionally, some samples were soaked in water for two days. After three weeks of conditioning, three samples were used for electron paramagnetic resonance (EPR) measurements and the other three samples were used for determination of moisture content in wood. Moisture content was determined gravimetrically (Table 1). EPR measurements were performed at room temperature on Bruker ESP-300 X-band spectrometer. (Microwave Frequency = 9.62 GHz, Microwave Power = 20 mW, Modulation Frequency = 100 kHz, Modulation Amplitude = 0.1 mT). Four corners of each sample were cut off and inserted into a resonator. Measurements did not show any significant differences between parallels.

Results and discussion From the data in Table 2 it can be seen that moisture content in wood significantly influenced the EPR spectroscopic parameter $g_\perp$ of copper(II) in wood treated with copper(II) sulfate. Noticed was the shift of $g_\perp$ value from 2.076 at 32.9% RH to 2,081 at 90.0 RH, respectively (Table 2). The shift was even more pronounced for samples soaked in water ($g_\perp = 2{,}086$) (Fig. 1) (Table 2). It is presumed that this shift occurred as copper(II) sulfate is not chemically fixed to wood (Richardson 1997). It is assumed that in such case copper(II) is adsorbed to wood just through coordinated water with hydrogen bonds. It is known that the density of water in wood is well correlated with moisture content (MC). Density of bound water at 5% MC is almost 1.25 kg/l, which is much more than mean density of bound water at fiber saturation point (FSP) (1.15 kg/l) or mean density at maximum MC (1.018 kg/l) (Stamm 1964; Walker 1993). Water molecules coordinated around copper(II) enter the above described "water environment" in wood which influences the surroundings of copper(II) ions, and consequently the g values of Cu^{2+} ion in $CuSO_4$ treated wood. Thus, water must have an important influence on copper EPR values.

Table 1. Moisture content of the samples impregnated with three different aqueous copper based solutions after conditioning. (CuS – copper(II) sulfate, CuS EA – copper(II) sulfate with ethanolamine, CuE – copper(II) octanoate with ethanolamine)
Tabelle 1. Feuchte der Holzproben nach Imprägnierung mit drei verschiedenen wasserlöslichen Kupferlösungen (nach Konditionierung): CuS – Kupfer(II)-sulfat, CuS EA – Kupfer(II)-sulfat mit Ethanolamin, CuE – Kupfer(II)-octanoat mit Ethanolamin

Treatment	Relative air humidity %	Moisture content			
		Control %	CuS	CuS EA	CuE
$MgCl_2 \times 6H_2O$	32.9	6	7	9	9
$NaNO_2$	64.8	11	13	14	14
$ZnSO_4 \times 7H_2O$	90.0	22	22	22	23
Soaked in water		37	38	39	37

Table 2. $g_\perp$ of copper in wood impregnated with the aqueous solution of copper(II) sulfate, after conditioning at different relative air humidities
Tabelle 2. $g_\perp$ von Kupfer in Holzproben die mit wässrigen Kupfersulfat-Lösungen imprägniert waren, nach Konditionierung bei verschiedenen Luftfeuchten

Treatment	Relative air humidity %	$g_\perp$ of copper(II)
$MgCl_2 \times 6H_2O$	32.9	2.076
$NaNO_2$	64.8	2.078
$ZnSO_4 \times 7H_2O$	90.0	2.081
Soaked in water		2.086

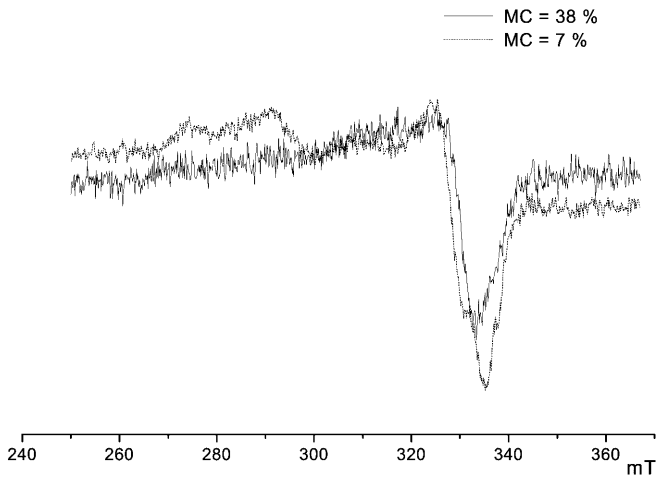

Fig. 1. EPR spectra of wood impregnated with the aqueous solution of copper(II) sulfate, at two different moisture contents (MC)
Bild 1. EPR-Spektren von Holzproben nach Imprägnierung mit wässrigen Kupfersulfat-Lösungen bei zwei verschiedenen Holzfeuchten

On the other hand, in wood impregnated with copper(II)/ethanolamine preparations, the moisture content did not have any influence on the g values of copper. It was assumed that the first coordination sphere around copper(II) in wood in this case consists of ethanolamine molecules and because of that, MC cannot influence the g values of copper(II). This presumption is supported by some of the recent results (Humar and Petriè 2000). It was noticed that in copper(II)/ethanolamine-impregnated wood, significant amounts of ethanolamine remained in wood after drying. In unimpregnated samples, no significant changes of the EPR spectra, caused by MC, were observed.

Conclusions Moisture content has an important influence on copper(II) EPR parameters in wood impregnated with the aqueous solution of copper(II) sulfate. Therefore, care has to be exercised at interpretations of these spectra. On the other hand, in wood impregnated with aqueous solutions of copper(II) octanoate or copper(II) sulfate with ethanolamine, moisture content did not influence the spectroscopic parameters of Cu(II). The reason for this is supposed to be in a different mode of adsorption/fixation of Cu(II) to wood components of these two solutions in comparison to the aqueous solution of $CuSO_4$.

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