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A note on Mössbauer analysis of white oak surfaces colored with aqueous iron salt solutions

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ABSTRACT

Aqueous solutions of iron salts can be applied to a wood surface to modify its color. When applied on wood, iron ions are chelated by the wood's natural phenolic compounds. The resulting color of the wood surface is due to the type of reaction products formed, such as mono-, bis- and tris- complexes of polyphenols with iron cations. In order to identify the different complexes formed on *Quercus alba* L. wood's surface and the oxidation state of iron after application of different iron salts on the same wood species which influence the resulting color of wood's surface, Mössbauer spectroscopy was performed directly on iron-stained wood samples. Colors of the stained wood samples, measured by a spectrophotometer, were analyzed in relation to the differences between the reaction products. The results showed that for a given wood species, the oxidation and reduction behavior of the iron depended on both the type of counterion and the oxidation state of the chosen iron salt.

KEYWORDS
Color measurements; Mössbauer spectroscopy; white oak staining; wood polyphenols

Introduction

In Canada, local wood resources are abundant and can be incorporated in buildings to make them greener. Wood is a bio-sourced material that can be used either for structural components of the building or for the fabrication of floorings and furniture for interiors. Several types of phenolic compounds are present in wood as "extractives", which since they are present as free molecules, are easily available to form stable-colored complexes with metal ions.[1] Therefore, the application of metal salt solutions on wood surface is available as a method to modify wood color in order to increase the variety of wood product appearances found on the market. Polyphenols are capable of chelating different metal ions,[2,3] however iron salts are mostly used due to the intense colors produced and lower toxicity. Iron based stains can be used to give a weathered appearance of wood's surface. To color wood species that do not contain phenolic extractives that are capable of producing intense colors by reaction with iron salts, a prestain (e.g., tannic acid, pyrogallol, pyrocatechol) can be applied as a first step followed by the application of a metal salt (e.g., iron salts).[4] Hundhausen et al. (2020)[5] have shown that the application of ferrous sulfate solution to *Picea abies* wood samples from which the extractives had been removed, resulted also in color development after exposure to sunlight. Therefore, it has been postulated that in the absence of extractives, products of lignin degradation can cause color modification on wood's surface treated with ferrous sulfate by oxidation of iron (II).

Colors of complexes formed depend both on the oxidation state of the metal ion[6] as well as on the number of polyphenol ligands surrounding the metal ion.[7,8] Formation of complexes between polyphenols and iron salts depend also on other factors such as the pH of the solution and iron/polyphenol ratio.[1] Complexes of polyphenols with iron have been analyzed in multiple studies in the literature by mixing aqueous or solvent solutions containing a specific polyphenol with an iron salt to form colored complexes.[7,9] However, different types of phenolic extractives are present in wood and their types and quantities vary between different wood species and even within the same species.[10–15] Therefore, in order to determine the final oxidation state and type of complexes formed on a wood surface, it is necessary to perform analysis with minimal variation of the aforementioned conditions.

Mössbauer spectroscopy is a technique based on the recoilless emission and resonant absorption of γ rays by

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atomic nuclei.[16] This analytical technique permits the measurement of nuclear energy levels and the detection of small variations caused by interactions between the electrons and the nucleus.[17] Mössbauer spectra of the studied atom depend on the oxidation state, the coordination number, the symmetry of the complex and the presence or absence of magnetic ordering.[18] Multiple elements possess Mössbauer-active isotopes, however iron is the most studied since it is the most abundant multivalent element in geological environments among the Mössbauer active elements.[17,18] The importance of Mössbauer spectroscopy comes mainly from the possibility of determining the oxidation state and ferric/ferrous ratio with high accuracy.[17] This method is more reliable for ferric/ferrous ratio determination than wet chemical analysis since the preparation of Mössbauer samples does not affect their oxidation state.[17] Analysis of stained wood samples by Mössbauer spectroscopy is possible since this analysis can be performed on samples in solid state. The potential of applying this technique to wood analysis was shown in the study of Yamauchi et al. (2011) in which ancient buried wood samples of Japanese cedar (*Cryptomeria japonica* D. Don) and Japanese cypress (*Chamaecyparis obtusa* Endlicher) containing iron from rusted nails were analyzed by Mössbauer spectroscopy.[19] Yamauchi et al. (2017)[20] and Kurimoto et al. (2020)[21] investigated iron in *umoregi* wood obtained from trees excavated from the foothills of Mt. Chokai. It was suggested that the molecular structures of iron complexes significantly affect the *umoregi* wood color tone.[20] Yamagishi et al. (2020) used Mössbauer spectroscopy to characterize iron species in iron-impregnated Japanese cypress (*Chamaecyparis obtusa*) charcoal.[22] In this study, Mössbauer spectroscopy was used to analyze reaction products on the surface of white oak wood (*Quercus alba* L.) treated with different iron salts. Colors of stained wood surfaces were measured by a spectrophotometer and the results obtained by Mössbauer analysis were compared to better understand the differences in colors obtained by staining white oak wood surfaces with divalent and trivalent iron salts and with different counterions.

Materials and methods

Chemicals

Two ferrous salts which contain different counterions were selected for analysis in this study: ferrous acetate (95%) which was purchased from Fisher Scientific (Ottawa, Canada) and ferrous sulfate heptahydrate (> 99%) which was purchased from Sigma Aldrich (Oakville, Canada). In order to compare two iron salts with different oxidation state, ferric sulfate pentahydrate (97%) was selected for analysis and purchased from Fisher scientific (Ottawa, Canada).

Sample preparation

The steps involved in the preparation of the wood samples for Mössbauer analysis are presented on Figure 1. White oak (*Quercus alba* L.) wood samples were provided by Boa-Franc S.E.N.C (Saint-Georges, Canada) and stored in conditioning rooms at 20 °C and 42% relative humidity prior to further processing. In the first step, the heartwood and the sapwood of wood samples were separated. The heartwood only was used in the subsequent steps since phenolic extractives are present in higher quantities in heartwood compared to sapwood[15] which results in higher color development with iron salts. Wood samples were then milled using a Pulverisette 19 model cutting mill from FRITSCH company (Germany). The wood powder was sieved to a particle size less than 250 μm then stored in a freezer in the dark at −5 °C. Aqueous solutions of ferric sulfate, ferrous sulfate and ferrous acetate were prepared at 2% w/v in distilled water which was sufficient concentration to produce a good spectrum from Mössbauer analysis. Four mL of each iron salt solution was added to 500 mg of wood powder and then dried in a vacuum oven at 40 °C. Samples were stored at room temperature during fifteen days prior to Mössbauer measurements.

Mössbauer spectroscopy

Mössbauer spectroscopy measurements were recorded using a source of cobalt-57 in rhodium (50 mCi) at McGill University (Montréal, Canada). The isomer shift (IS) and Doppler velocity scale were calibrated using the sextet of pure iron foil (α-form). The Mössbauer measurements were performed at room temperature. The products percentages were determined from the integrated area of each fitted component.

Color measurements

Wood boards were conditioned at 20 °C, at 42% relative humidity until 8% moisture content was attained. Wood surfaces were sanded using a Costa Levigatrici 36CCK 1150 model wide-belt sanding machine (Schio, Italy) with TopTec sandpapers from Sia Abrasives Industries AG (Frauenfeld, Switzerland) of P120, P150 and P180 grit sizes. Aqueous solutions of iron salt solutions were prepared at 1% w/v in distilled water and

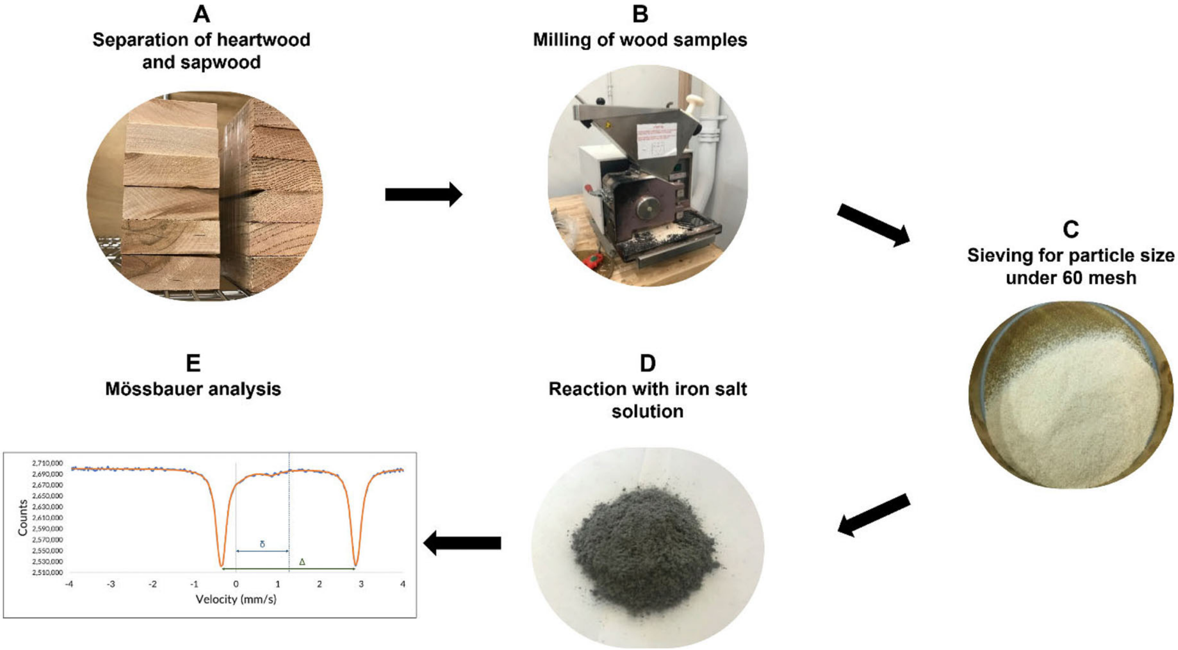

Figure 1. Steps involved in wood sample preparation for analysis by Mössbauer spectroscopy.

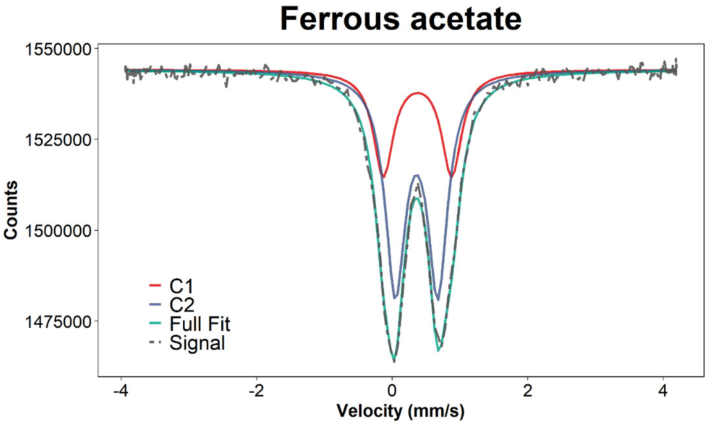

Figure 2. Mössbauer spectra of white oak wood powder stained with ferrous acetate aqueous solution showing the signal, the fitting curves of the different components as well as the overall fitting curve.

applied manually by using a high-density foam roller applicator and dried at room temperature. Color measurements were recorded with a Ci64 model X-rite spectrophotometer (Grand Rapids, United States) with a D65 standard illuminant and 10° angle of observation. Specular component included (SPIN) mode and CIEL*a*b* color system were chosen for the measurements.

Results and discussion

Mössbauer spectra of wood samples stained with aqueous solutions of ferrous acetate, ferrous sulfate and ferric acetate aqueous solutions are presented in Figures 2–4, respectively. Mössbauer spectra show the counts of transmitted γ rays as a function of the Doppler velocity.[16] The percentages of the fitted components and their corresponding values of quadrupole splitting, and isomer shift are presented in Table 1. The isomer shift (δ) corresponds to the offset from zero velocity of the spectrum which results from the Coulombic interaction between nuclear and electronic charge distributions (Figure 1).[18] The quadrupole splitting (Δ) is proportional to the peak separation of the corresponding quadrupole doublet in the Mössbauer spectrum and is due to the splitting of the nuclear energy levels caused by inhomogeneous electric fields from the valence electrons and neighboring ligands.[17]

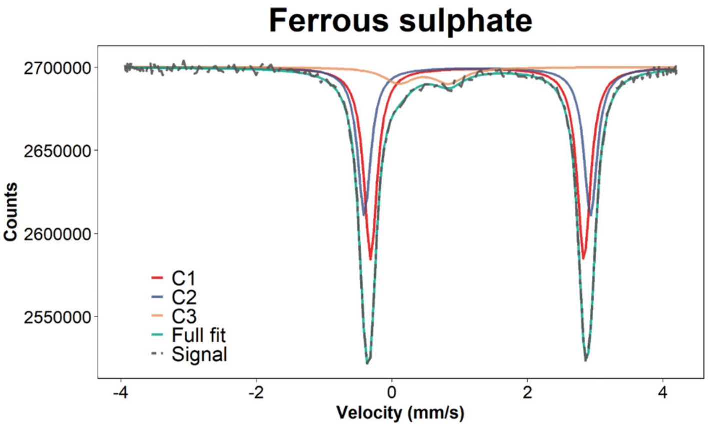

Figure 3. Mössbauer spectra of white oak wood powder stained with ferrous sulfate aqueous solution showing the signal, the fitting curves of the different components as well as the overall fitting curve.

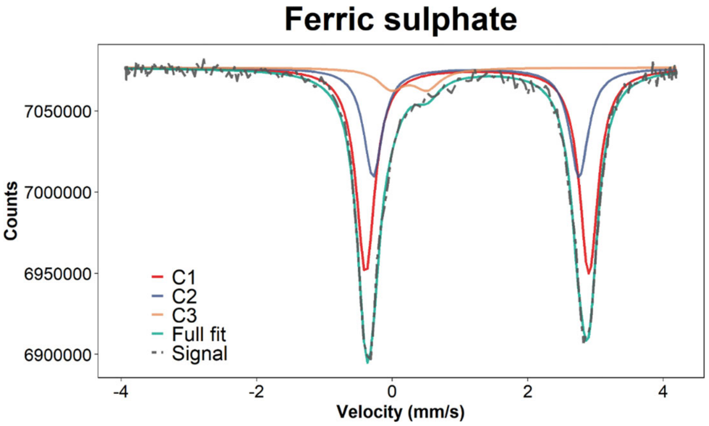

Figure 4. Mössbauer spectra of white oak wood powder stained with ferric sulfate aqueous solution showing the signal, the fitting curves of the different components as well as the overall fitting curve.

Table 1. Values of quadrupole splitting (Δ) and isomer shift (δ) obtained from Mössbauer spectra of white oak wood colored with ferrous acetate, ferrous sulfate, ferric sulfate and their respective percentages and corresponding oxidation state.

Iron salt applied on wood	Components	Percentages	Δ (mm/s)	δ (mm/s)	Oxidation state of iron in wood
Ferrous acetate	C1	33(2)	1,010(1)	0,372(4)	+ 3
	C2	67(2)	0,626(8)	0,358(2)	+ 3
Ferrous sulfate	C1	52(2)	3,146(5)	1,257(1)	+ 2
	C2	41(2)	3,338(7)	1,258(1)	+ 2
	C3	8(1)	0,74(3)	0,47(2)	+ 3
Ferric sulfate	C1	61(4)	3,29(1)	1,252(2)	+ 2
	C2	32(4)	3,04(2)	1,235(4)	+ 2
	C3	7(1)	0,52(4)	0,25(3)	+ 3

Oxidation state and structures of iron products

Results of Mössbauer analysis show that the iron in treated wood samples occurs in more than one chemical environment. Spectra of both ferrous sulfate (Figure 3) and ferric sulfate treated wood samples (Figure 4) were dominated by doublets corresponding to divalent iron oxidation state, however, for ferrous acetate treated wood, the spectrum was dominated by a doublet corresponding to trivalent iron (Figure 2). These results suggest that trivalent iron was reduced to divalent after application of ferric sulfate on wood surface. For ferrous acetate treated wood, the results suggest that divalent iron was oxidized to trivalent iron. After chelation of metal ions to polyphenols such as catechol, intramolecular electron transfer reactions may occur.[9] For example, when bound to polyphenol ligands, the reduction potential of iron is lowered and therefore the oxidation of divalent iron occurs faster to yield trivalent iron complexes with polyphenols. This phenomenon is commonly called "auto-oxidation".[7] The rate of the ferrous iron auto-oxidation depends on the type of counterion of the iron salt[7] which could explain differences obtained between the ferrous acetate and ferrous sulfate treated wood. The chelation of iron ions by polyphenol ligands can lead to the reduction of ferric ion or oxidation of ferrous ion with simultaneous oxidation of polyphenols to quinoid compounds. In the study of Mellican et al. (2003), the authors found that ferric sulfate was reduced by polyphenols in solution.[9] The authors also found that the color development was slower with ferrous sulfate compared to ferric sulfate and suggested that ferrous sulfate was oxidized to ferric state then reduced again. In our study, oxidation state of ferrous sulfate treated wood was mostly divalent, however, we cannot determine if after application of the ferrous sulfate solution on wood surface, divalent iron is oxidized then further reduced.

In order to obtain further information about the types of possible complexes formed on the wood surface, values of quadrupole splitting and isomer shift obtained in this study were compared to the values reported for polyphenol/iron complexes in the literature.[23,24] The chemical environment of iron present in majority (67%) for ferrous acetate treated wood could be attributed to bis-complexes of ferric polyphenolate complexes and the second type of product (33%) could be attributed to mono-complexes of ferric polyphenolate complexes. For samples treated with ferrous sulfate and ferric sulfate, minor products in ferric state could be attributed to mono-complexes of polyphenols. For divalent iron complexes, no reference values were found in the literature for comparison. Wood polyphenols can also form multinuclear complexes with iron as shown by Yamauchi et al. (2017) in *umoregi* wood analysis,[20] however, Mössbauer analysis in this study is not sufficient to conclude if multinuclear complexes are also formed.

It was previously shown that the formation of mono-, bis- and tris- complexes of polyphenols with iron is dependent on the pH[7] and at pH less than 4, mono complexes are mostly formed. At pH between 5 and 6.5, both bis- and tris- complexes are formed and at higher pH values, tris complexes dominate.[7] White oak heartwood possess an acidic pH which was determined to be 3.51 ± 0.02 in previous study, by pH measurements performed on water/wood mixtures[15] and the pH of the iron salt solutions is also acidic. Therefore, acidic pH could explain the dominance of mono and bis complexes in stained wood. In the study of Jaén et al (2003), the reaction products of gallic acid, ellagic acid and pyrogallol solutions at their natural pH with metallic iron were analyzed by Mössbauer spectroscopy.[25] They found that the reaction products depended on the polyphenol concentration. At low concentrations of polyphenols (0.1%), oxyhydroxides were formed, however, at concentrations higher than 1%, sparingly soluble and amorphous ferric and ferrous polyphenolate complexes were found.[25] In our previous study,[15] spectrophotometric and phosphorus-31 NMR analysis were performed on the ethanolic extract of wood and the results showed that white oak wood extractives contained different types of phenolic compounds and that the quantities of phenolic extractives were higher in the heartwood compared to the sapwood of white oak. In this study, only the heartwood of white oak was used, which minimizes the influence of polyphenol types and quantities on the results obtained in this study.

Iglesias et al (2001) studied the interaction of tannic acid with metallic iron to form ferric tannates in the objective of using tannins as corrosion inhibitors.[26] The authors found that the reaction followed a first order reaction kinetics and at very early stages of the reaction, mono-complexes were formed, however, a mixture of mono- and bis-complexes were formed at further stages of the reaction. Therefore, in future studies, it would be interesting to follow the reaction products on wood samples through different periods of time as well as after the photodegradation of the colored samples which causes color changes of wood's surface.

Colors of wood surfaces stained with iron salts

L*, a* and b* coordinates obtained by color measurements of wood surfaces stained with different iron salts are shown in Figure 5.

The comparison of b* coordinate, which represent the yellow/blue axis, show that ferric sulfate has the lowest b* values indicating the most intense blue tone among the three types of stains used. The comparison of a* values, which represent the green/red axis, show that a* value is the highest for wood stained with ferrous acetate aqueous solution which is significantly higher than both ferrous sulfate and ferric sulfate treated wood surfaces according to Tukey HSD test. The slightly reddish color obtained on ferrous acetate treated wood could be explained by the final oxidation state of trivalent iron, which was determined by Mössbauer spectroscopy analysis. In the study of Hider et al (1981), it has been shown that frozen aqueous solutions of hydroxybenzene complexes with iron had green and blue colors at acid pH, containing divalent iron, and purple and red color, containing

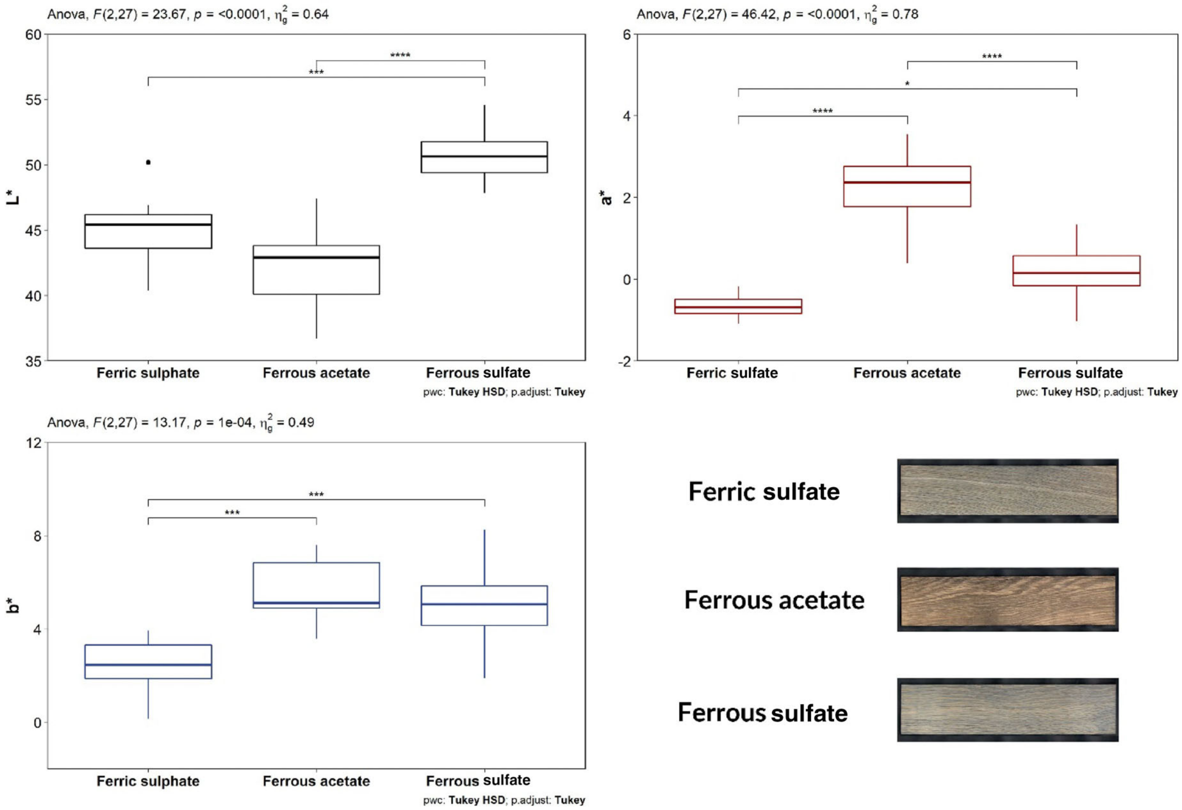

Figure 5. Graphs showing the L*, a* and b* coordinates representing the lightness, red/green and the yellow/blue scales, respectively for white oak wood colored with ferrous sulfate, ferrous acetate, and ferric sulfate.

trivalent iron.[6] The authors suggested that the color of the complex would be a good indication of the oxidation state of iron in polyphenolic complexes.[6] The comparison of L* coordinate, which represents the lightness axis, shows that the color of ferrous sulfate treated wood is significantly lighter than ferric sulfate and ferrous acetate treated wood. Results of Mössbauer analysis showed that the iron on both ferrous sulfate and ferric sulfate treated wood samples was mostly divalent iron. The lighter color obtained by ferrous sulfate treated wood is in accordance with the results obtained in the study of Mellican et al. (2003), in which they found that color development with catechol was more intense with ferric sulfate compared to ferrous sulfate. The authors suggested that ferrous sulfate was likely oxidized to ferric iron before reacting with catechol. Colors of complexes depend also on the number of ligands surrounding the iron ion. Colors of mono-, bis- and tris-complexes of catecholate with trivalent iron have been reported to have blue/green, blue/purple and red colors respectively.[7] In wood composition, different types of ligands could be speculated to interact and therefore, the color cannot be attributed to one type of coordination complex only. However, we speculate that the dominance of bis-complexes compared to mono complexes in ferrous acetate-stained wood, could be responsible of colors tending to reddish or gray compared to blue.

This study showed that different color shades can be obtained by staining white oak wood with aqueous solutions of iron salts depending on the oxidation state and the counterion of the chosen iron salt. A better understanding of the differences in formed products will allow the industries to develop new staining products depending on the desired final color. These staining systems could be suitable for indoor applications, however, problems due to leaching by rain and weathering could occur in outdoor applications.[27] Moreover, the addition of metal ions to wood can potentially influence the photostability of wood samples due to their chelation by wood's extractives and reactivity with lignin photodegradation products.

Conclusion

In this study, Mössbauer spectroscopy was used to analyze reaction products on white oak wood surface, treated with different iron salts, in order to compare the differences in products formed. Results of this study have shown that the oxidation state of the iron following the treatment with ferrous acetate was predominantly trivalent iron, while after the treatment with sulfates, both for ferric and ferrous sulfate, the Mössbauer analyses showed the prevalence of divalent iron oxidation state. The color measurements were in harmony with Mössbauer results for acetate treatment, according to literature results on complex formation studies with polyphenols. Mössbauer spectroscopy was shown to be a useful technique for determining the differences in reaction products formed on wood surfaces stained with iron salts which are responsible of the differences in resulting colors of white oak wood surfaces stained with aqueous solutions of iron salts. As the structures of polyphenols differ among different wood species, further research investigating the reaction products of iron salts on other wood species by Mössbauer spectroscopy should be conducted. The suitability and stability of wood surfaces stained with iron salts should be assessed for the desired application conditions.

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Conflict of interest

The authors declare that they have no conflict of interest.

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