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UV-VIS SPECTRA OF LIGNIN MODEL COMPOUNDS IN THE PRESENCE OF METAL IONS AND CHELANTS

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ABSTRACT

The presence of transition metal ions, such as iron, in lignin rich pulp fibers has negative consequences on pulp brightness and brightness stability. Earlier studies showed that impregnation of lignin-rich pulps with chelants, such as DTPA and EDTA, is very effective in recovering the brightness loss and reducing both the photo-yellowing and thermal yellowing of mechanical pulps. In this study, the fundamentals associated with such a process are further studied with lignin model compounds in combination with UV-Vis spectroscopy. Four lignin model compounds, guaiacol, veratrole, vanillin and creosol, were tested. It was found that transition metal ions and lignin model compounds by themselves did not exhibit significant absorbance in the visible light range. However, when the two components were combined, a significant visible absorbance was observed. This was explained by the formation of coloured complexes between the transition metal ion and lignin model compounds, and transition metal ion-induced coupling reactions. Among the transition metal ion species studied Fe(III), Fe(II), Cu(II),

Mn(II) and Al(III), Fe(III) showed the strongest effect. In most cases, addition of a chelant to solutions containing transition metal ions and a lignin model compound reduced absorbance in the visible light range and blocked the coupling reactions. Furthermore, the EDTA- and DTPA-metal ion complexes exhibited ultraviolet shielding properties, which could be partly responsible for reduced photo-yellowing, when lignin-rich pulps are chelated.

INTRODUCTION

Transition metal ions can affect the optical properties of pulp in two general ways. Metal ions can cause the formation of coloured compounds on the pulp fibres and can catalyze the decomposition of bleaching chemicals, thereby reducing their effectiveness. Coloured compounds can be either inorganic or organic and both can affect the reflectance of bleached pulp.¹ Lignin model compounds can be used to study the effect of various functional groups within the lignin polymer on visible light absorption when complexed with different metal ions. While the complexation and spectral characteristics of catechol-type compounds have been studied extensively,²⁻⁸ the light absorptive characteristics of complexes involving other lignin-like compounds are less well known. This is important in terms of the relative abundance of different combinations of functional groups in lignin, because catechol-type structures are much less common than guaiacol-type units.

For this reason, guaiacol, veratrole, vanillin and creosol were chosen as the lignin model compounds (LMC) to be studied. Their spectral properties, in terms of their reaction and complexation products with iron(II) and (III), copper(II), manganese(II) and aluminum(III) were determined following a procedure given in a previous publication.⁸

EXPERIMENTAL

The four lignin model compounds (LMCs) were purchased from Aldrich with their purities as follows: guaiacol; 98%; creosol: 99%; veratrole; 99% and vanillin; 99%. The metal ions tested were iron(III) ($\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$), iron(II) ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$), copper(II) ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$), manganese(II) ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) and aluminum(III) ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$), all from Fisher Scientific. DTPA (40% solution) was obtained from Irving Paper in Saint John, New Brunswick.



The DTPA stock solution was neutralized to pH 6–6.5, while the metal ion solutions and LMC solutions were at their natural pH without further adjustment. The metal ion solutions were freshly prepared prior to use. All solutions except creosol were prepared in deionized and distilled water.

For each experiment, suitable volumes of each component were mixed in a vial. The solution was then measured for light absorptive characteristics under the conditions specified in each figure. UV-visible spectra were recorded using a Milton Roy Spectronic 1001 + spectrophotometer interfaced to μ -Quant software, which was run on an IBM PC. The cuvette width was 1 cm.

RESULTS AND DISCUSSION

Study of the spectroscopic properties of lignin-metal complexes focussed primarily on iron(III). Although copper is generally present in small quantities in pulp fibres, it was also a major focus because of its unique catalytic and complexation properties. Aluminum, iron(II) and manganese were only touched upon as their contribution to discolouration was minimal.

Iron(III)-Guaiacol Interactions

The first step in analyzing these systems was to determine if there was an increase in absorbance in the lignin model compound-metal ion solution compared with each component by itself. The absorbance of iron(III)-guaiacol solutions in the visible light range was substantially increased when compared with the individual component, as shown in Figure 1. Addition of guaiacol to the iron(III) chloride solution resulted in two bands very close in energy ($\lambda_{\max} = 422 \text{ nm}$, $\epsilon = 2376 \text{ Lcm}^{-1} \text{ mol}^{-1}$ and $\lambda_{\max} = 461 \text{ nm}$, $\epsilon = 2333 \text{ Lcm}^{-1} \text{ mol}^{-1}$). Because of their similar intensity, these bands were attributed to charge transfer absorptions.⁹ Following earlier studies,⁸ we explained the increase in absorption when guaiacol was added to the iron(III) solution by the hypothesis that the iron(III)-guaiacol complexes are formed.

Various ligand-to-iron concentration ratios were analyzed in an attempt to determine the effect of different LMC-metal ion complex stoichiometry. Iron(III)-guaiacol solutions reached an absorption maximum at an LMC to iron(III) ratio of 7:1 (Figure 2). By itself, the addition of excess uncoordinated guaiacol would not have been expected to increase absorbance in the visible range as guaiacol is colourless (see Figure 1).



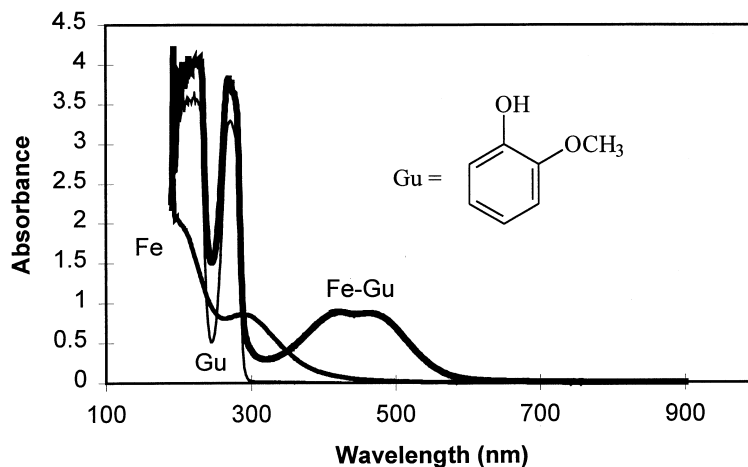


Figure 1. Comparison of the absorbance of an iron(III)-guaiacol (Fe-Gu) solution with that of iron(III)(Fe) and guaiacol (Gu) alone. $[\text{Fe}^{3+}] = 0.375 \text{ mM}$, $[\text{Gu}] = 2.25 \text{ mM}$, $T = 37^\circ\text{C}$, $t = 30 \text{ s}$.

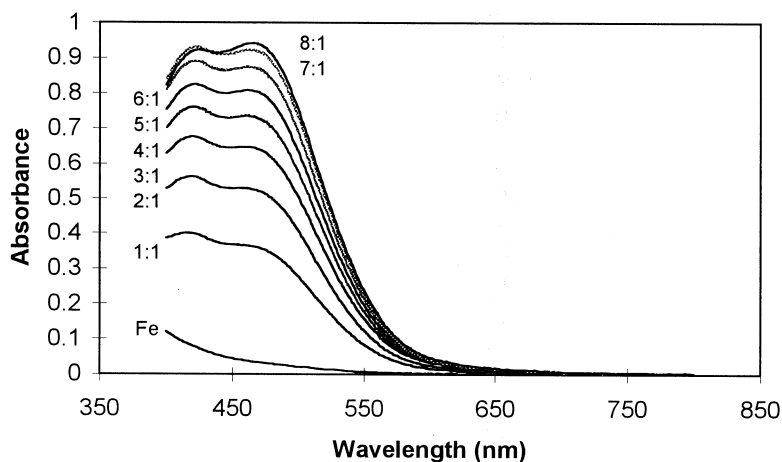
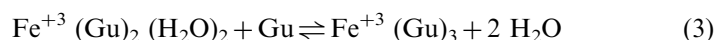
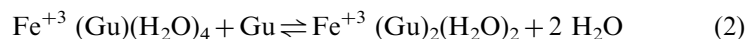
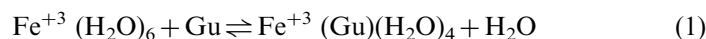


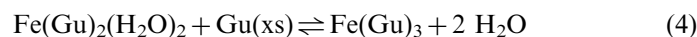
Figure 2. Comparison of the visible absorbance spectra of different guaiacol to iron(III)(FeCl_3) ratios in aqueous solution. $[\text{Fe}^{3+}] = 0.375 \text{ mM}$, $T = 37^\circ\text{C}$, $t = 30 \text{ s}$.

However, as the guaiacol to iron(III) concentration ratios increased, a series of stepwise complex formation equilibria may have been formed. (Equations 1 to 3).



where Gu = Guaiacol

As guaiacol was added in increasing concentrations, the applicable equilibrium would have progressed from Equation 1 to Equation 2 and absorption due to complex formation would have increased. Finally, at a concentration ratio of 7:1 (the absorption maximum) the excess guaiacol would have forced the equilibrium in Equation 3 to the right such that essentially all the iron(III) was coordinated by guaiacol:



The profile of the visible absorption spectrum of the iron(III)-guaiacol solution changed substantially over time and coincided with the appearance of a black solid. The reaction was allowed to continue until there was no longer a noticeable difference between the last two spectra. Over the 6-day total reaction period, the two absorptions described gradually became one fairly strong band and the intensity finally decreased and overspread to cover the complete visible spectrum (see Figure 3). The above experimental observation cannot be explained by the hydration of ferric ions and their subsequent polymerization because the product from the hydration of ferric ions and the subsequent polymerization are ferric oxides, which are rusty-red in colour, and it can be easily verified by leaving a ferric solution for an extended period of time. However, in our system, black precipitates, not rusty-red iron oxides, were formed. Alternatively, they may be explained by the formation of guaiacol oligomers/polymers. Previous research has shown that iron(III) catalyzes the formation of quinone structures and various guaiacol oligomers by an oxidative carbon-carbon coupling mechanism.¹⁰ Indeed, the oxidation of phenols by chemicals capable of one-electron abstraction, including iron(III), has been demonstrated.^{10,11-15} The disappearance of the λ_{422} band and the slight shift of the λ_{461} band to $\lambda_{\text{max}} = 470 \text{ nm}$ coincided with the appearance of several guaiacol oligomers reported by Schmalzl,¹⁰ suggesting that this was the occurrence that caused the spectral changes noted in Figure 3.

The data from the above section indicated that reduction of the iron(III) may have occurred over the reaction period. This assertion was easily tested



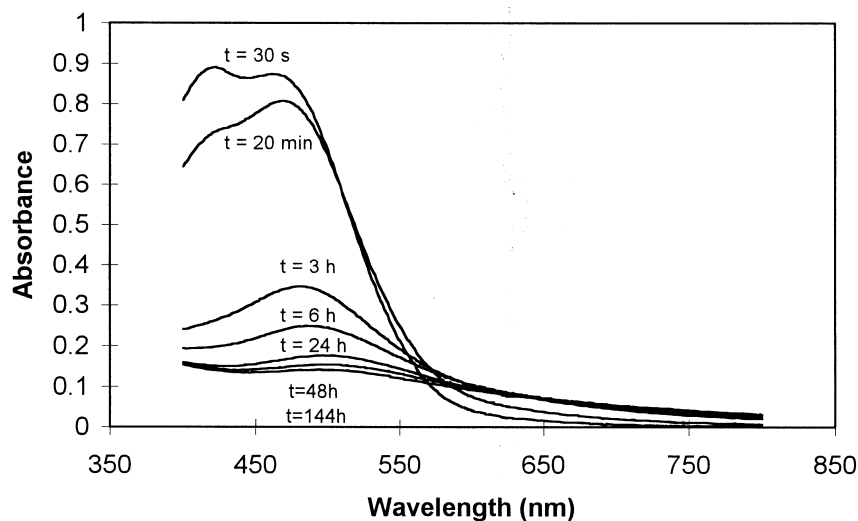


Figure 3. Change in the visible spectrum of an iron(III)-guaiacol solution with time. $[\text{Fe}] = 0.375 \text{ mM}$, $[\text{Gu}] = 2.25 \text{ mM}$, $T = 37^\circ \text{C}$.

qualitatively using thiocyanate (SCN^-), which is commonly used as a specific indicator for redox titrations of iron¹⁶ to differentiate between iron(II) and iron(III). When thiocyanate complexes with iron(III), an intense charge transfer peak (λ_{460}) is produced, resulting in a dark red solution. No visible absorption is present when thiocyanate coordinates iron(II). Potassium thiocyanate was added to iron(III)-guaiacol solutions such that it had a concentration ~ 60 times that of iron and ~ 10 times that of guaiacol. When thiocyanate was added after a 30 second reaction between guaiacol and iron(III), iron(III) was still present, while very little was present after a 3 day reaction.

The question then arose whether the original spectrum displayed by the iron(III)-guaiacol solution at $t = 30 \text{ s}$ (Figure 3) was attributable to a rapidly occurring oxidation reaction or to complexation as explained above.

The addition of DTPA to an iron(III)-guaiacol solution after colour formation ($t = 45 \text{ s}$) resulted in a complete erasure of the λ_{422} and λ_{461} bands and the appearance of a very intense absorption in the near ultraviolet. It was concluded that DTPA must have displaced the guaiacol as a ligand on iron and changed the spectrum in the process (Figure 4).

The effect of varying chelant-to-iron(III) ratios on the absorbance of iron(III)-guaiacol complexes was studied using DTPA. Figure 5



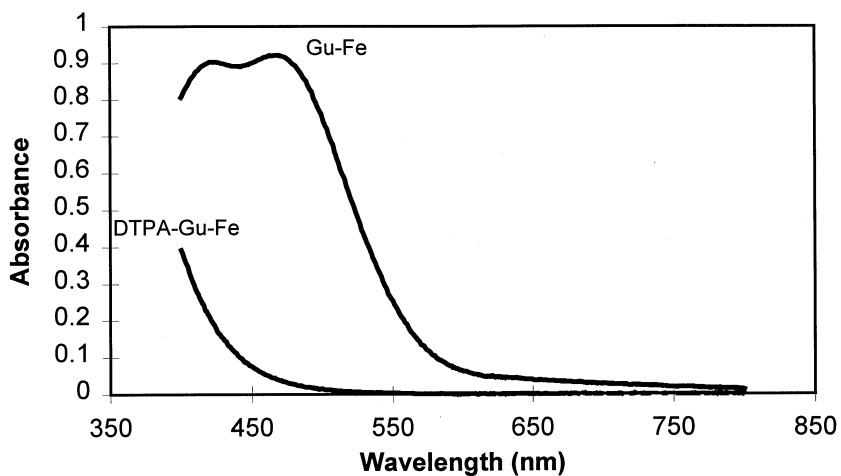


Figure 4. Change in the visible spectra of iron(III)-guaiacol solutions on addition of 0.375 mM DTPA. [Fe]=0.375 mM, [Gu]=2.25 mM, T = 37°C, t = 45 s.

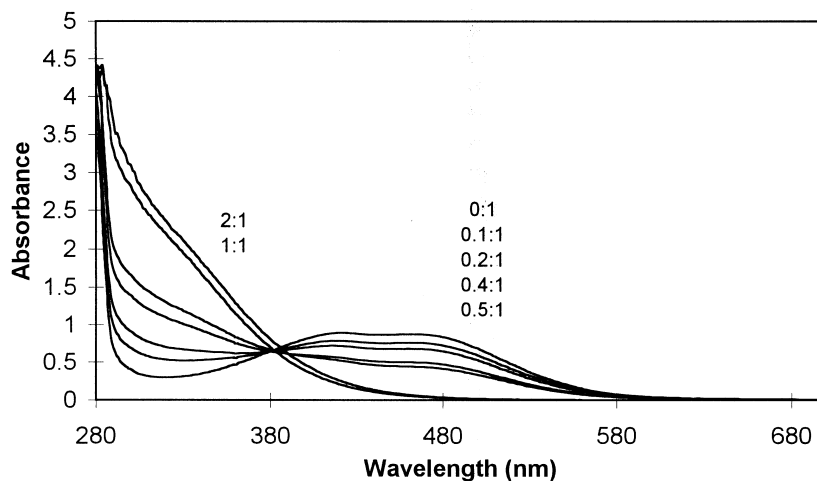


Figure 5. Effect of varying DTPA to iron(III) ratios on the absorbance of a solution of iron(III) and guaiacol. [Fe]=0.375 mM, [Gu]=2.25 mM, [DTPA] = ratio × [Fe], T = 37°C, t = 45 s.

demonstrates the capability of DTPA to reduce the colour of the iron(III)-guaiacol solutions. Ratios of DTPA to iron of less than one to one resulted in an additive spectral effect between DTPA-chelated iron and

the remaining iron that was still complexed by guaiacol. The gradual shift of the charge transfer band into the ultraviolet region as higher DTPA ratios were added is readily apparent. The visible spectrum of the iron(III)-guaiacol solution with DTPA added in a ratio of one to one is almost exactly coincident with the visible spectrum of DTPA-iron(III) alone, indicating complete ligand replacement (Figure 6).

The ability of DTPA to block the catalytic-oxidative reaction was also investigated. The iron(III)-guaiacol solutions having varying ratios of DTPA to iron were also analyzed after a 6-day reaction period to determine the catalytic effect of DTPA-complexed iron(III). We found that the addition of DTPA to an Iron(III)-guaiacol solution with a DTPA-to-iron(III) ratio of one to one produced a spectrum that was unchanged from that of DTPA and iron(III) alone, suggesting that DTPA-complexed iron(III) was inert in catalyzing/oxidizing guaiacol reactions. This could be important in the pulping industry, where metals complexed by DTPA may have their catalytic properties inhibited, resulting in less chromophore formation.

A comparison of the absorbance-reducing effects of two of the most common industrial chelants, DTPA and EDTA, was also performed. Treatments of iron(III)-guaiacol solutions with either chelant significantly reduced the absorbance (Figure 7). As in the case of DTPA, the spectrum of the EDTA-iron(III)-guaiacol solution was coincident with the

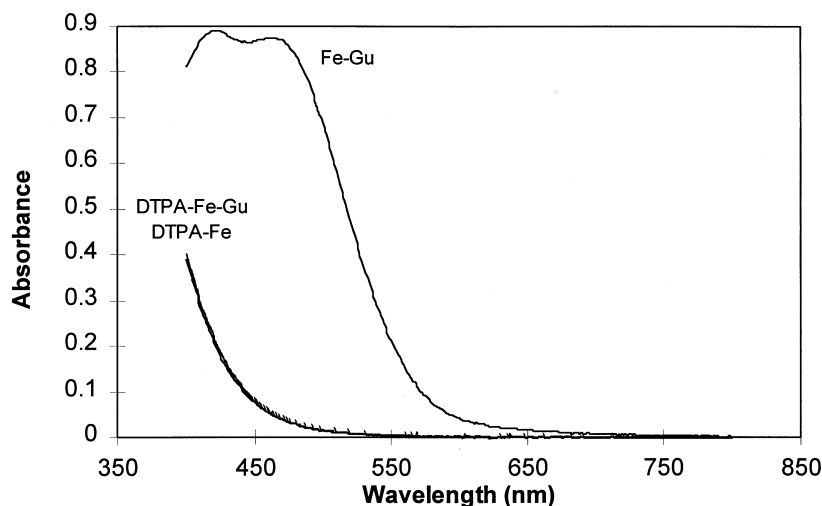


Figure 6. Replacement of guaiacol by DTPA in the iron(III)-guaiacol complex. $[Fe] = 0.375 \text{ mM}$, $[Gu] = 2.25 \text{ mM}$, $[DTPA] = 0.375 \text{ mM}$, $T = 37^\circ\text{C}$, $t = 45 \text{ s}$.

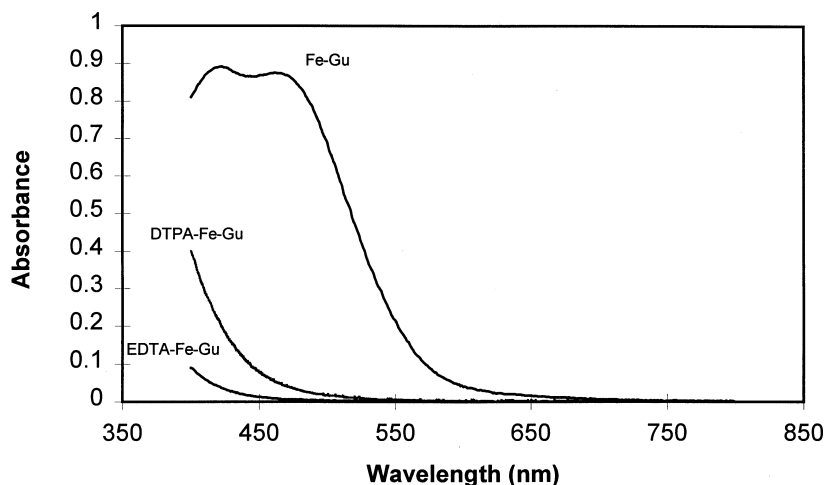


Figure 7. Comparison of the effects of EDTA and DTPA on the absorbance of an iron(III)-guaiacol solution. Spectra for EDTA-Fe and DTPA-Fe solutions were exactly coincident with EDTA-Fe-Gu and DTPA-Fe-Gu curves. Chelant was added at $t = 45$ s. $[\text{Fe}] = 0.375$ mM, $[\text{Gu}] = 2.25$ mM, $[\text{Chelant}] = 0.375$ mM, $T = 37^\circ\text{C}$.

EDTA-iron(III) spectrum. The EDTA-iron(III) complex had a much lower absorbance than the DTPA-iron(III) complex and the light absorptive characteristics are not changing as the reaction time increases. EDTA displayed the same protective effect as DTPA with respect to inhibiting the iron(III)-guaiacol reaction.

An important aspect of the spectra for the chelant-iron(III) complexes was their strong absorbance in the ultraviolet. In addition to metal removal, DTPA and EDTA complexes that remain on pulp fibres could provide a shield against photoyellowing.

We further found that the iron(III)-veratrole and -vanillin displayed similar absorptive properties, while iron(III)-creosol was more closely related to guaiacol. The four LMC solutions have negligible absorbance at 457 nm wavelength. In all cases, the addition of an LMC to an iron(III) solution resulted in an increase in absorbance. However, once again DTPA or EDTA was able to reduce the absorbance resulting from the metallic LMC complexes. The results are summarized in Figure 8. For all the four lignin model compounds studied, it appears that EDTA lowered the absorbance more effectively than DTPA.

Unlike guaiacol, the catalytic oxidation of veratrole and vanillin by iron(III), was negligible as evidenced by the fact that the UV-vis spectra



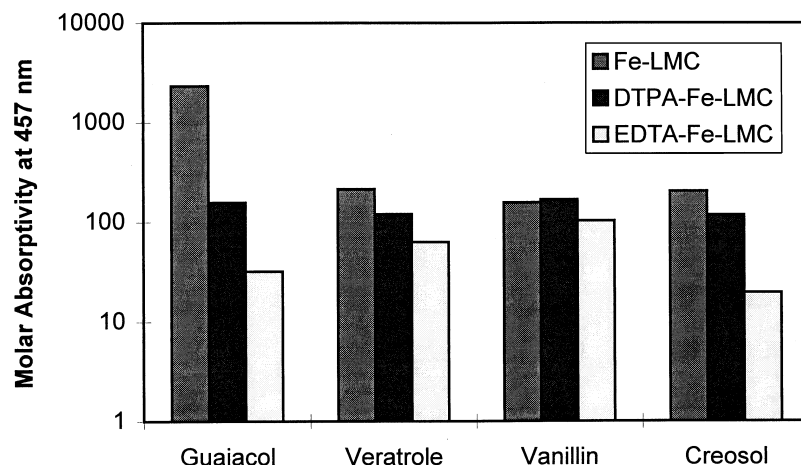


Figure 8. Comparison of the effectiveness of DTPA and EDTA at reducing absorbance at 457 nm for iron(III)-LMC solutions. All creosol solutions were 20% (v/v) alcohol/water solution. Ratio of LMC to iron(III) was 6:1, except creosol, which was 1:1 (highest absorbance). $T_{Ve,Va} = 37^{\circ}\text{C}$, $T_{Cre} = 23^{\circ}\text{C}$, $t = 45\text{ s}$.

underwent only a small change over time. This change was likely the sole result of the exchange of LMC ligands for water coordinated to iron(III), rather than of catalytic oxidation, since the basic shape of the spectra did not change over time. For the creosol-iron(III) system, the catalytic oxidation of creosol by iron(III) occurred to some extent, however significantly less than in the guaiacol-iron(III) system.

Copper(II)-LMC Interactions

The copper-LMC solutions took much longer to display a noticeable change in their spectra as the reaction progressed with the exception of copper-vanillin. Despite reaction periods ranging from 24 days to 1 month, significant absorption was not necessarily attained (Figure 9). As with the iron(III) complexes, most of the ligand field absorptions occurred in the visible range with the exception of some ultraviolet bands that tailed into the visible in the guaiacol, vanillin and creosol solutions. The exact location of these bands was camouflaged by the intense ultraviolet ligand spectra. Copper also exhibited significant catalytic properties, particularly in the case of guaiacol.



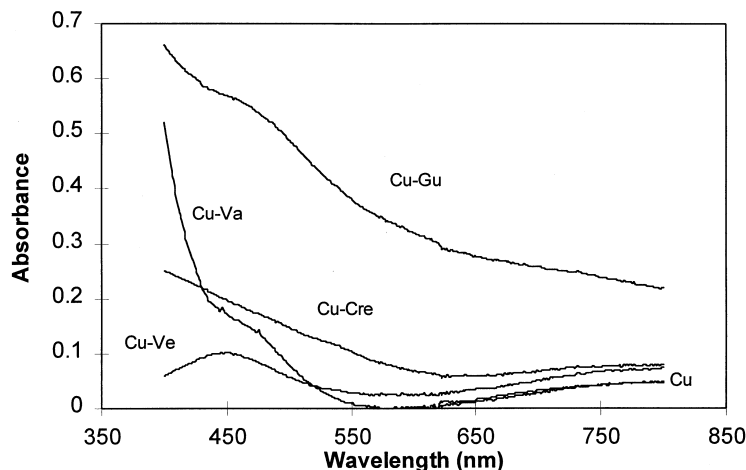


Figure 9. Visible absorption spectra of copper-LMC solutions. The spectrum for copper(II) sulfate ($[Cu]=4.0$ mM) was included as a reference and was coincident with the Cu-Va curve from 800 to 560 nm after which it exhibited no absorbance. $[Cu]_{Gu}=5.75$ mM, $[Cu]_{Ve}=4.0$ mM, $[Cu]_{Va}=1.5$ mM, $[Cu]_{Cre}=3.0$ mM, $[LMC]=4 \times [Cu]$, $T_{Gu, Ve, Va}=37^\circ C$, $T_{Cre}=23^\circ C$, $t_{Gu, Ve, Cre}=30$ days, $t_{Va}=30$ s, $t_{Cu}=30$ s.

Iron(II)-, Manganese(II)- and Aluminum(III)-LMC Interactions

Owing to their electronic structures, the complexes of these three metals were not expected to have significant visible absorbance as a result of ligand field electron transitions. In all cases, the absorbance when adding these three metal ions to solutions of the lignin model compounds was substantially lower than iron(III) and copper(II) an observation consistent with results obtained from the M^{n+} -catechol system.⁸ Generally, guaiacol and vanillin exhibited stronger absorbance in comparison with veratrole. For the same ligand, the absorbance decreased in the order Fe^{2+} , Al^{3+} and Mn^{2+} . Addition of either DTPA or EDTA to the metallic-LMC system reduced the absorbance.

It is noted that Mn(II) and Fe(II) appeared to have catalyzed reaction in the phenolic lignin model compound system.

CONCLUSIONS

The addition of iron(III) to a solution of guaiacol led to an increase in the absorbance of the solution within the visible range of wavelengths,



owing to the shift of a charge transfer band. Also, it is most likely that Iron(III) participated in a redox reaction with guaiacol that resulted in the formation of coloured products. Addition of the chelants DTPA and EDTA to iron(III)-guaiacol solutions led to a general reduction of absorbance within the visible spectrum. EDTA was more effective at reducing solution colour than was DTPA. Both industrial chelants were found to protect guaiacol against the chromophore-forming reaction involving iron(III). EDTA- and DTPA-iron(III) complexes exhibited intense ultra-violet absorption, suggesting that they may possess shielding effects against pulp and paper photoyellowing reactions.

Other metal ions such as Cu(II), Mn(II), Fe(II) and Al(II) were studied for their UV-vis spectrum when added to these four lignin model compounds. Generally, their absorbance was much less than that of Fe(III)-LMC. In all cases, addition of DTPA or EDTA reduced the absorbance.

REFERENCES

1. J. Polcin and W.H. Rapson, *Pulp Paper Canada*, 73(1):86 (1972).
2. E. Mentasti and E. Pelizetti, *J. Chem. Soc. Dalton Trans.*, 23, 2605 (1973).
3. E. Mentasti and E. Pelizetti, *J. Chem. Soc. Dalton Trans.*, 23, 2609 (1973).
4. R.F. Jameson and M.F. Wilson, *J. Chem. Soc. Dalton Trans.*, 22, 2614 (1972).
5. R.F. Jameson and M.F. Wilson, *J. Chem. Soc. Dalton Trans.*, 22, 2617 (1972).
6. C.A. Tyson and A.E. Martell, *J. Am. Chem. Soc.*, 90(13), 3379 (1968).
7. D.A. Davlatshoeva, A.N. Glebov, V.V. Ginzburg, A.R. Budanov and R.Sh. Safin, *Sh. Russian Journal of Inorganic Chemistry*, 40(2), 256 (1995).
8. A. Ghosh and Y. Ni, *J. Pulp Paper Sci.*, 24(1), 26 (1998).
9. D. Nichols, *Complexes and First Row Transition Elements*, MacMillan Press, Hong Kong, 1981.
10. K.J. Schmalzl, C.M. Forsyth and P.D. Evans, *Wood Sci. Tech.*, 29, 307 (1995).
11. H. Musso, *Angew. Chem.*, 75, 965 (1963).
12. H. Musso, *Angew. Chem., Int. Ed. Engl.*, 2, 723 (1963).
13. E.R. Altwicker, *Chem. Rev.*, 67, 475 (1967).
14. W.A. Waters, *Progr. Org. Chem.*, 5, 26 (1961).





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15. M. Mihailovic and Z. Cekovic, Oxidation and Reduction of Phenols. In: Patai, (Ed.): *The Chemistry of the Hydroxyl Group Part 1.*, Interscience, London, 1971.
16. D.A. Skoog, D.M. West and F.J. Holler, *Fundamentals of Analytical Chemistry*, 6th ed., Saunders College Publ., Toronto, 1992.



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