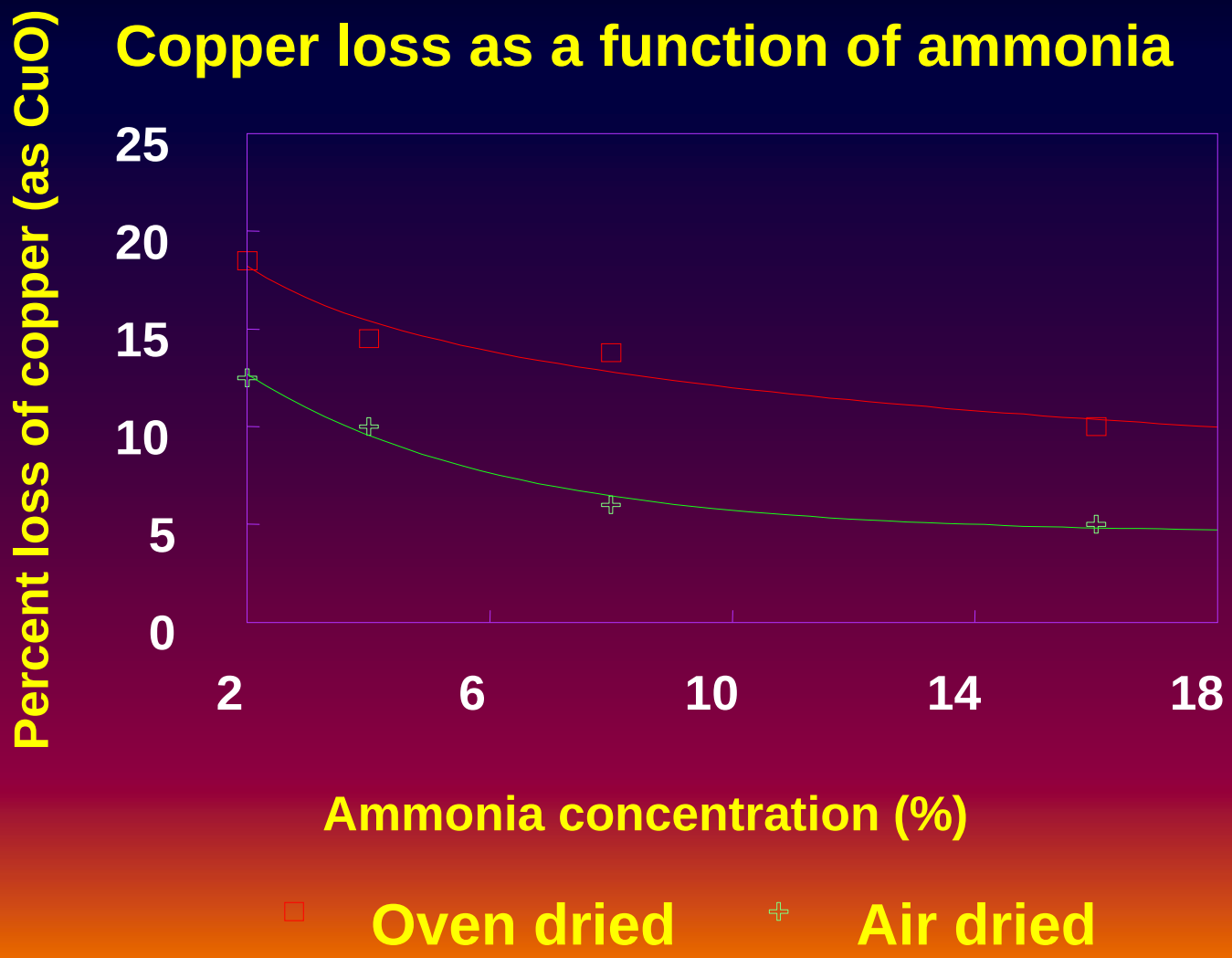
Fixation of Copper Amine and Ammonia Systems

Professor John N. R. Ruddick

Dept. of Wood Science
The University of British Columbia

Solvent	B.pt (°C)	pK_b	
NH_3	-33.3	4.75	
$HO(CH_2)_2NH_2$	171	4.17	MH
$NH_2(CH_2)_2NH_2$	117	~4.3	en

Effect of heat on fixation



Fixation of ammoniacal copper systems

$$[Cu(NH_3)_4\,(H_2O)_2]^{2+}$$

$$\Updownarrow$$

$$[Cu(NH_3)_{4-n}(H_2O)_{2+n}]^{2+} + nNH_3\uparrow$$

Fixation of amine copper systems

$$\text{Wood-OH} + \text{R-NH}_2 \Leftrightarrow \text{Wood-O}^- + \text{R-NH}_3^+$$

pH decreases

Fixation of amine copper systems

$[Cu(MH)_2]^{2+} \Leftrightarrow [Cu(MH)(M)]^{+} \Leftrightarrow [Cu(M)_2]$

pH	5-7	7-10	>10

Fixation of amine copper systems

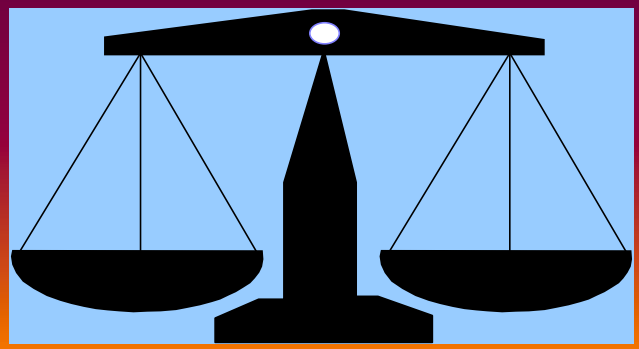
$[Cu(MH)_2]^{2+} + Wood\text{-}O^- \rightleftharpoons [Cu(MH)(M)\cdot OWood]$

$[Cu(MH)_2]^{2+} + 2Wood\text{-}O^- \rightleftharpoons [Cu(MH)_2(O\text{-}Wood)_2]$

$[Cu(MH)_2]^{2+} + 2Wood\text{-}O^- \rightleftharpoons [Cu(O\text{-}Wood)_2] + 2MH$

Fixation of amine copper preservatives

When copper amine preservatives fix in wood, a balance is required between the copper to amine bonding, and that formed between copper and the wood components.



Comparing the leaching resistance of copper 2-ethanolamine and copper ethylenediamine

Copper 2-ethanolamine (Cu-MH)

Copper ethylenediamine (Cu-en)

CuO% 1% N:Cu 4:1

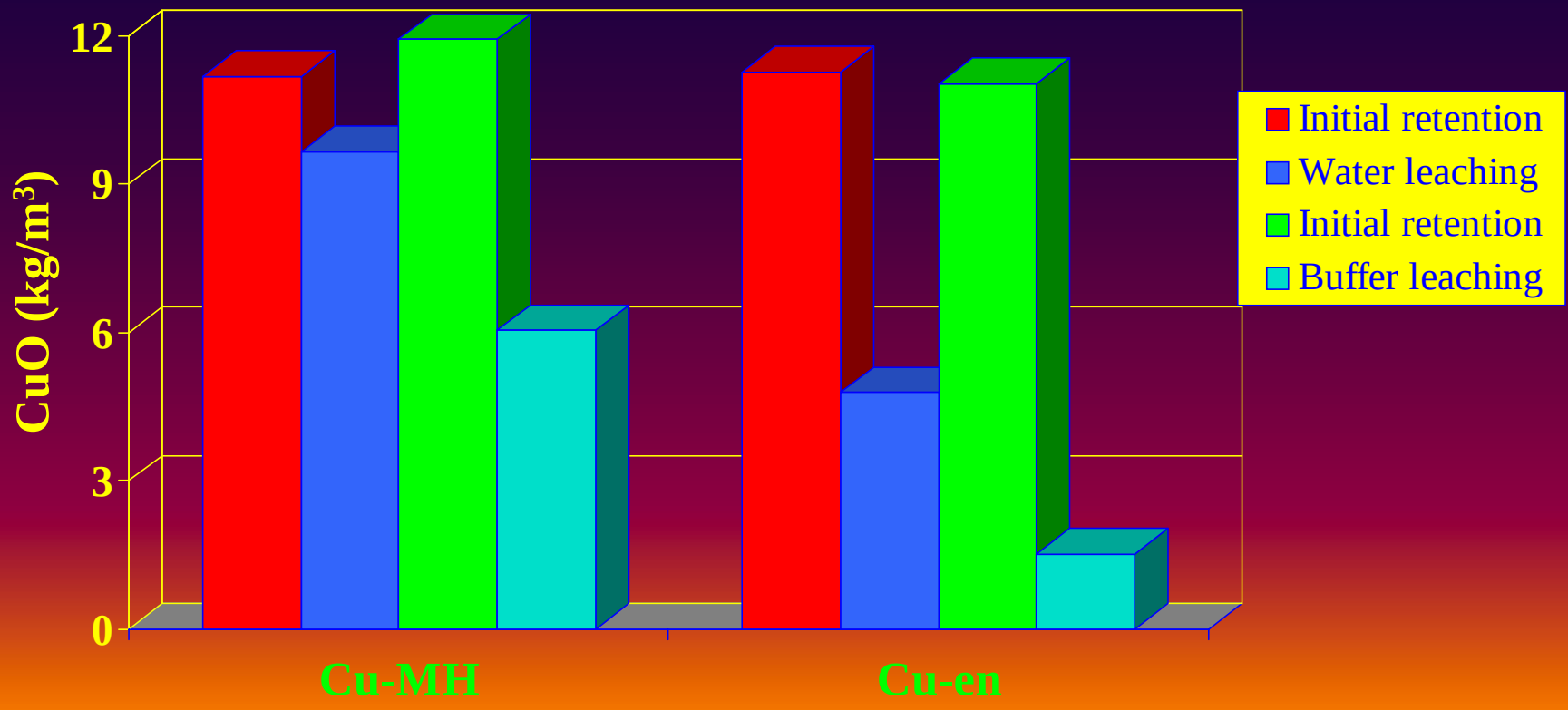
2-ethanolamine (MH) 5%

ethylenediamine (en) 5%

Materials and methods

Leaching process

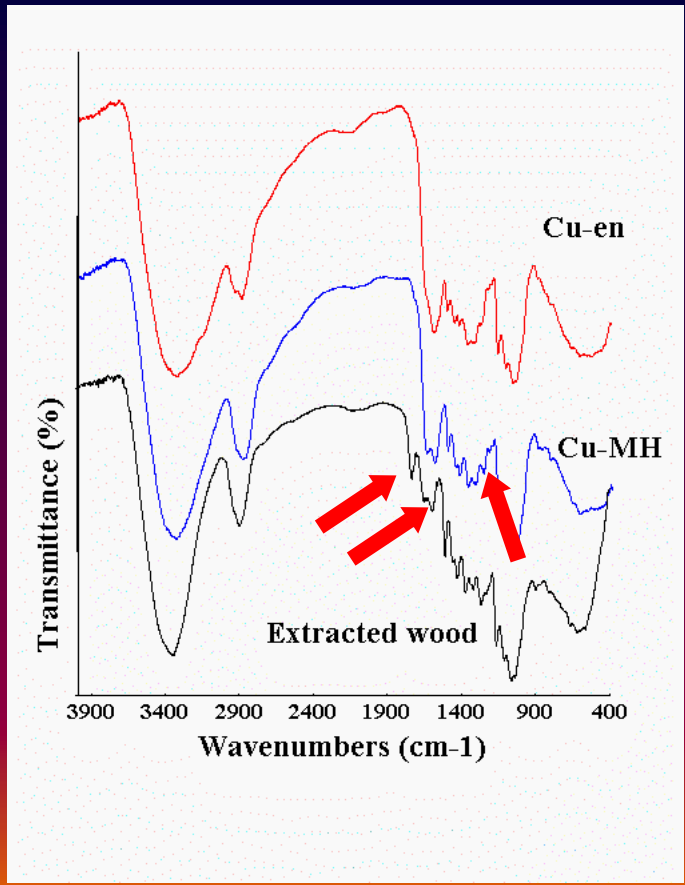
Copper content in copper amine treated wood before and after leaching



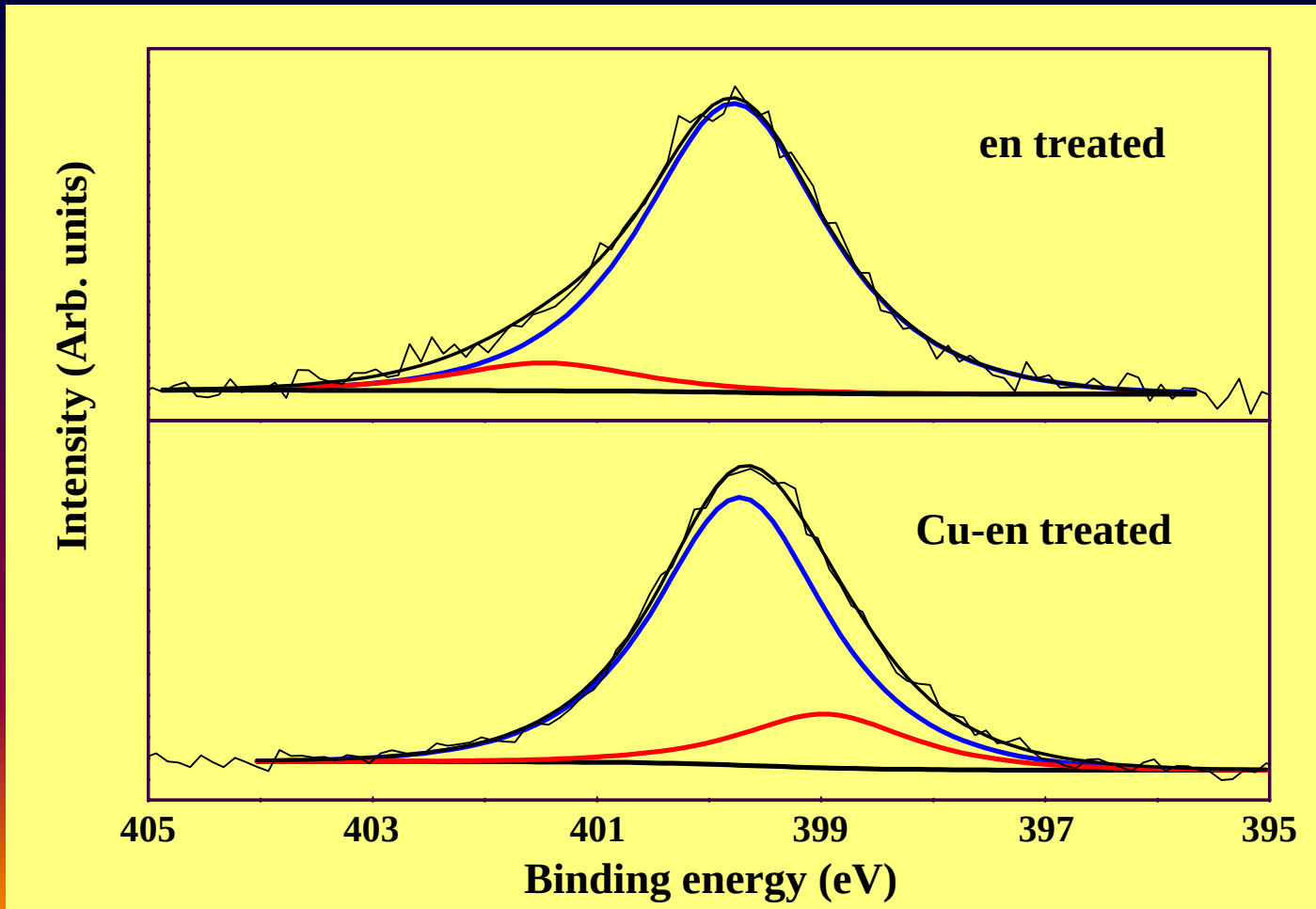
The nitrogen content in leached amine and copper amine treated wood

Treatment	N in the block (mmol/g wood)	
	Water leaching	Buffer leaching
MH	0.282	0.207
en	0.260	0.232
Cu-MH	0.299	0.196
Cu-en	0.171	0.241

Copper-amine treated wood



XPS N1s spectra of en and Cu-en treated wood

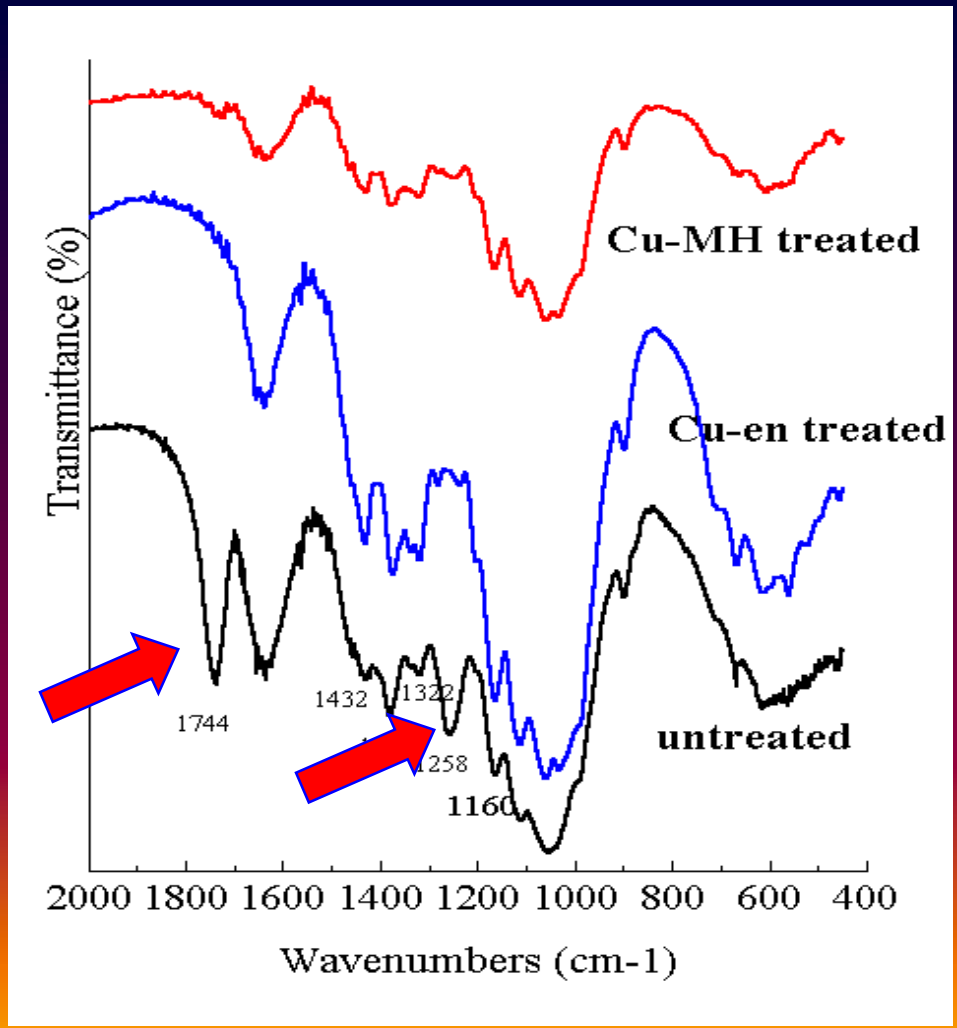


Fixation of amine copper systems

Does copper fix to:

- **CELLULOSE?** ✓
- **HOLLOCELLULOSE?**
- **LIGNIN?**
- **EXTRACTIVES?**

HOLLOCELLULOSE

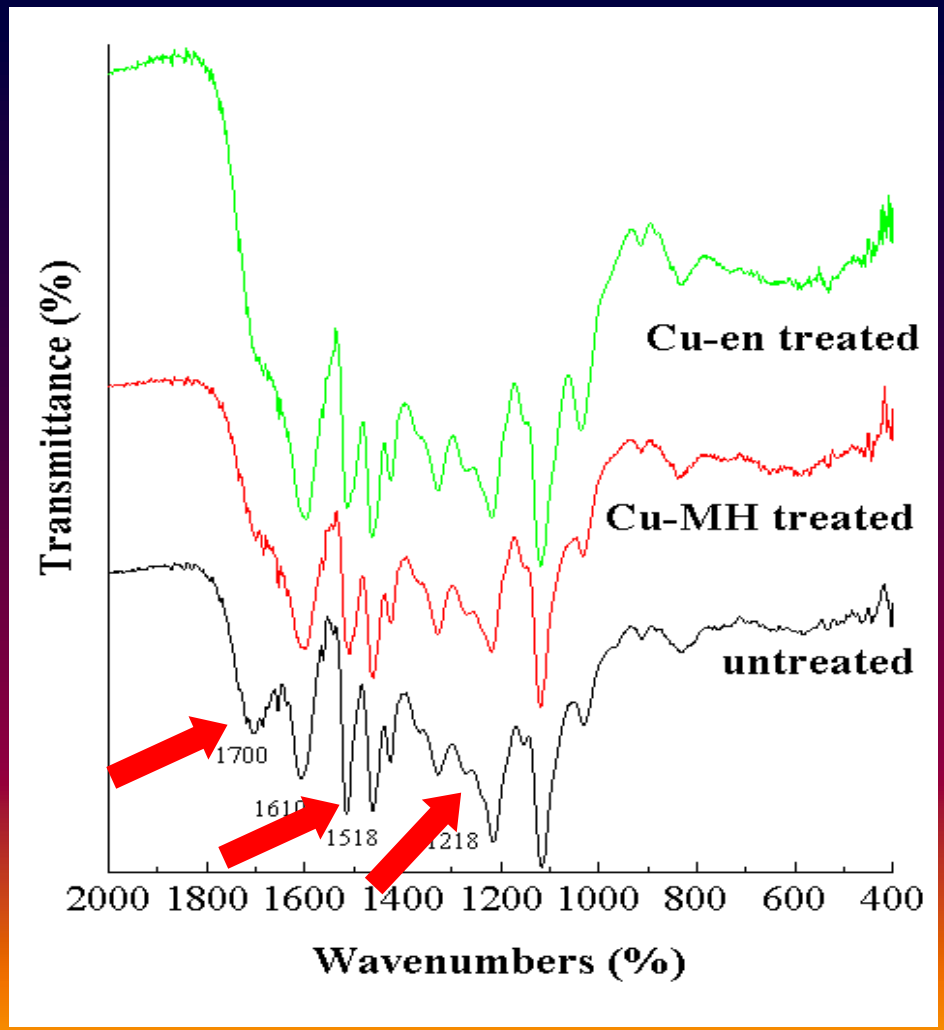


Fixation of amine copper systems

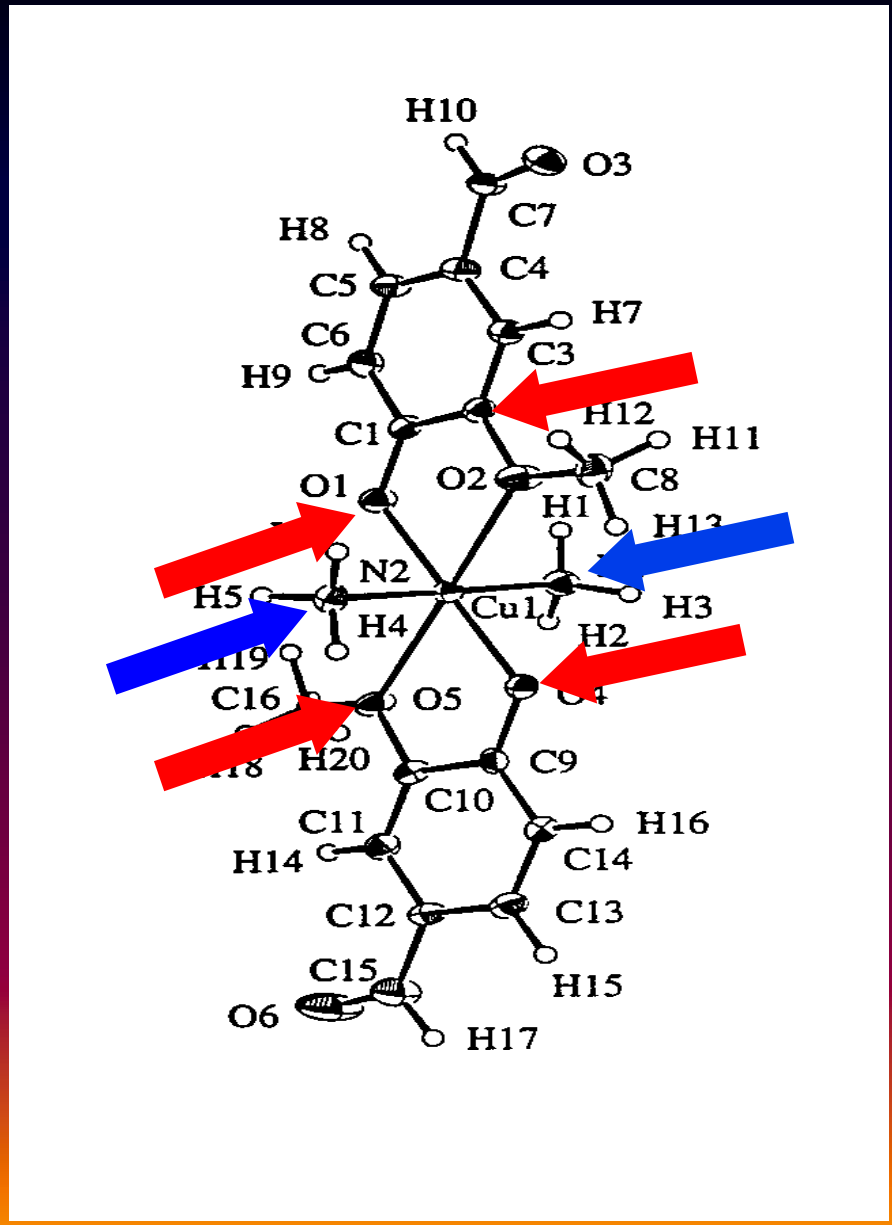
Does copper fix to:

- **CELLULOSE?** ✓
- **HOLLOCELLULOSE?** ✓
- **LIGNIN?**
- **EXTRACTIVES?**

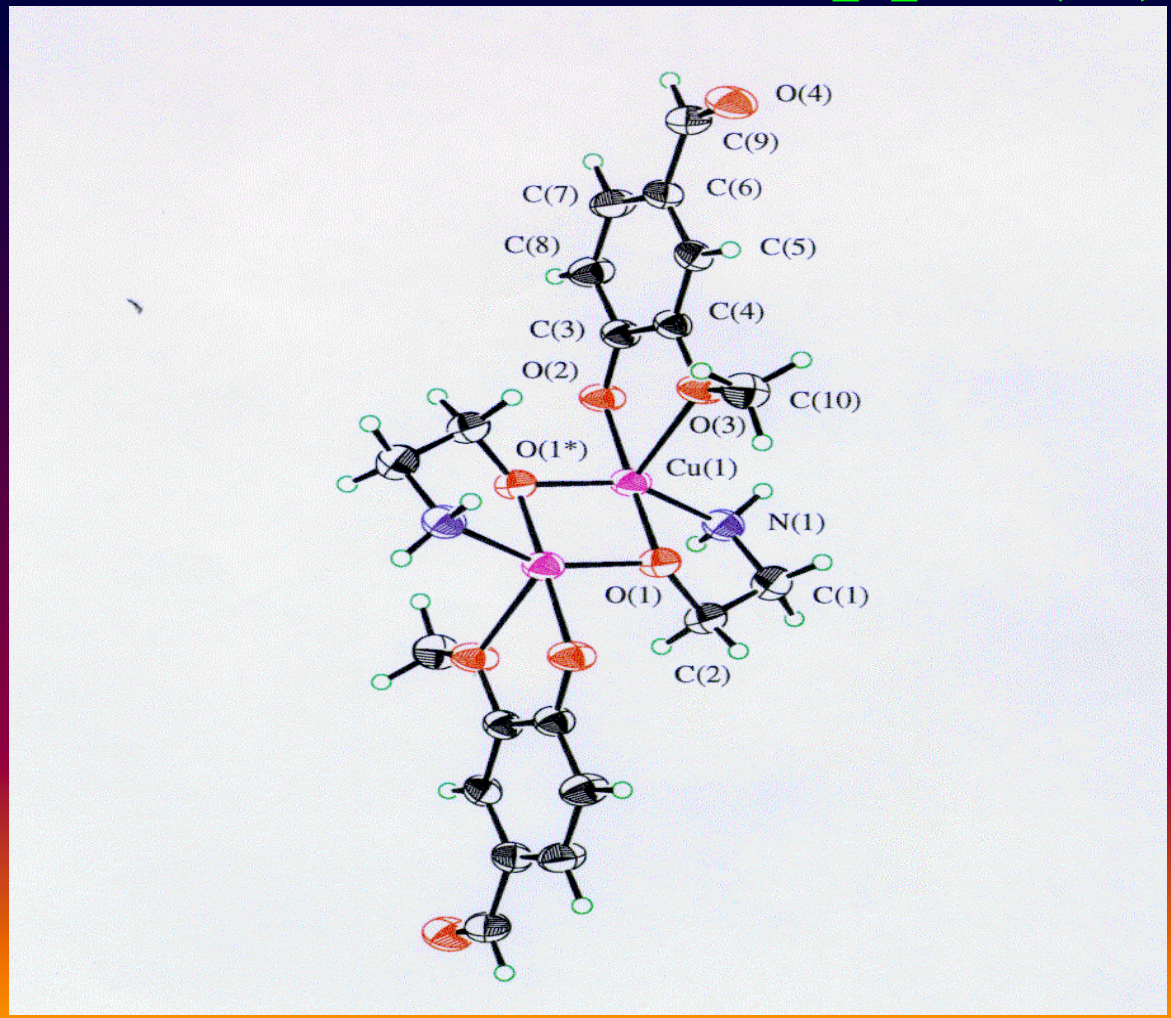
LIGNIN (ORGANOSOLV)



Crystal structure of di(ammine). bis(vanillato). copper(II)



Crystal structure of ethanolamine.vanillato.copper(II)

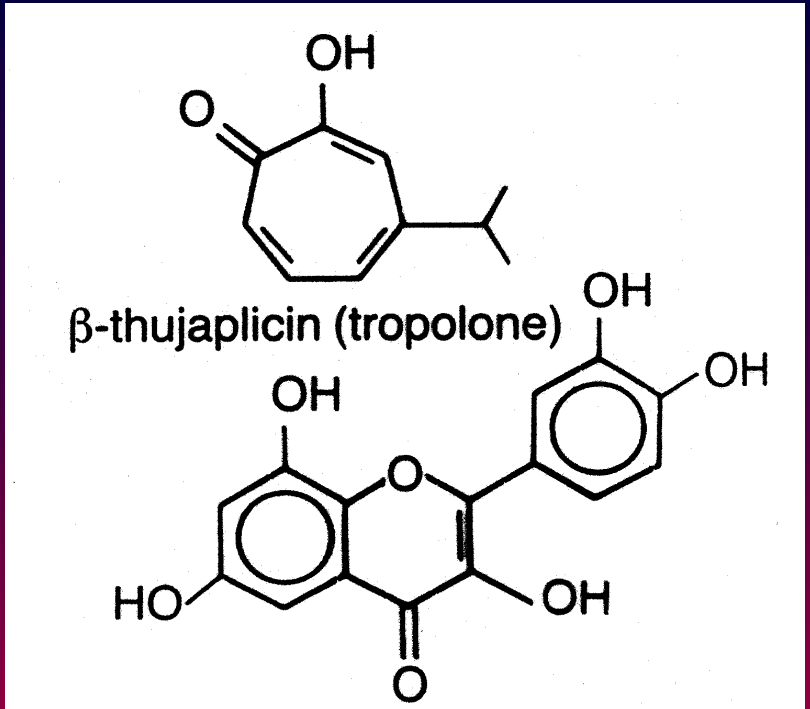


Fixation of amine copper systems

Does copper fix to:

- **CELLULOSE?** ✓
- **HOLLOCELLULOSE?** ✓
- **LIGNIN?** ✓
- **EXTRACTIVES?**

Extractive reactions



Complexes with extractives

Ammoniacal copper complex with taxafolin

$$[\text{Taxifolin}]_2.Cu_3(NH_3)_4.2H_2O$$

Calc. C: 38.96; H: 3.35; N: 6.26; Cu: 21.12

Found C: 38.29; H: 3.48; N: 6.74; Cu: 21.04

So what do we know?

- Amine treatment of wood resulted in the formation of stable products.
- Wood treated with Cu-MH leached much less than that treated with Cu-en.
- Citrate buffered leaching removed much more Cu than distilled water leaching.

and…….

- Amine reacts with wood irreversibly removing carboxylic functional groups
- Both amine and Cu-amine react primarily with hemicellulose, lignin, and extractives but not with cellulose

and lastly

- Copper amine-wood complexes are formed during fixation, although some copper wood complexes are also formed.