THE FIXATION CHEMISTRY OF COPPER BASED WOOD PRESERVATIVES

John N.R. Ruddick,
Department of Wood Science, Faculty of Forestry, University of British Columbia,
Vancouver, B.C. V6T 1Z4

Summary

X-ray photoelectron spectroscopy (XPS) and electron spin resonance spectroscopy (ESR) have become useful techniques for studying the chemistry of the fixation reactions of copper and chromium wood preservatives. Recent XPS results on chromated-copper-arsenate (CCA) treated pine are reviewed which highlight the influence of extractive movement on the spectral parameters. The CCA fixation resulted in slight changes in the C1 and C2 components of the C(1s) spectra of CCA treatment of extractive-free, sapwood. Analysis of the chromium ESR spectra in CCA-treated wood, indicated that a relatively stable chromium(V) species was formed, which decreasing in concentration over several months. A nitrogen analysis of two year old ammoniacal copper arsenate (ACA) treated spruce poles revealed enhanced nitrogen levels, which corresponded to the preservative content. This showed that some nitrogen was retained during fixation of ACA, complexed in the treated wood. An ESR analysis of ammoniacal copper sulphate and acetate treated wood confirmed that copper-nitrogen complexes were formed in the wood. The number of copper-nitrogen bonds in the complex appeared to be related to the ammonia content in the solution. The fixation of ammoniacal copper carbonate in wood was monitored as a function of the ammonia concentration in the treating solution. The resistance of the copper to leaching, improved at high ammonia concentration. A technique was presented which could be used to monitor the fixation of ammoniacal copper preservatives in wood. The pH of the leachate from freshly treated blocks was measured, together with the copper and arsenic concentration in the leachate and the leached blocks. The results confirmed that fixation of ammoniacal copper preservatives could be monitored using the pH of the leachate. The chemistry of the reaction of sodium nitrite and copper sulphate was investigated using ESR and XPS. The results showed that during the nitrite fixation of the copper, the N(1s) binding energy was reduced. In addition, leaching experiments demonstrated that in order to achieve the desired effect, both the copper chemical and the sodium nitrite had to be present in the treating solution.

1. Introduction

The fixation of preservatives to the wood substrate is extremely important, since it impacts greatly both on the performance and the environmental impact of the treated product. It is known, that for the most widely used copper based preservative in North America chromated-copper-arsenate (CCA), that the components are rendered insoluble through a series of chemical reactions involving the chromium . Considerable research has been carried out in an attempt to understand this reaction sequence (Dahlgren 1974, and 1975; Dahlgren and Hartford 1972a, b, and c; Pizzi 1982a, b, and c, 1983, 1990a and b), but key elements still remain either unknown or confused. Recently, sophisticated instrumental techniques have been applied to try to identify the reaction steps in the fixation process (Hughes *et. al.*, 1992; Ostermeyer *et al.*, 1988 and 1989; Ruddick *et. al.*, 1992a and b; Williams and Feist, 1984; Yamamoto and Ruddick, 1992a and b).

Even less is known about the mechanism of fixation of ammoniacal copper preservatives, such as ammoniacal copper arsenate (ACA) or ammoniacal copper quaternary chloride (ACQ). It had been suggested that during the fixation of ACA, the ammonia in the solvent was lost leading to precipitation of copper arsenate in the wood, (Hartford, 1972). However, early research on ACA treated spruce wood revealed an enhanced nitrogen content even two years after treatment. Clearly, a reaction between the ammonia and the copper in the preservative or the wood substrate has resulted in a complex formation which leads to bound nitrogen.

The objective of the current paper is to review recent x-ray photoelectron spectroscopic (XPS) and electron spin resonance (ESR) research on the fixation of CCA and ACA in softwoods.

2. CCA Fixation

2.1 Interpretation of XPS C(1s) spectra in chromic acid and CCA-treated wood

XPS is a surface analysis technique which can provide information on both the oxidation state and type of bonding present for a chemical element. In general chemical is applied to microtomed sections or alternatively the sections are removed from treated wood. Of interest in the fixation of CCA is the composition of the various oxidation states of the carbon present in the wood components. Assignments have been made on the basis of the interpretation of the C(1s) spectra proposed by Dorris and Gray (1978), in which C1 type carbons correspond to C-C, C-H or C=C type bonding, C2 corresponds to C-O bonding, and C3 corresponds to C=O bonding. Thus the XPS spectra reflect the carbons present in lignin, holocellulose and extractives. The XPS C(1s) spectra of unextracted, untreated ponderosa pine (*Pinus ponderosa* Laws.) sapwood, showed equivalent amounts of the C1 and C2 components at *ca.* 45% with the balance being C3 type carbon (Table 1) while extraction with an ethanol-toluene solution resulted in a dramatic reduction in the C1 type carbon and an increase in the C2 carbon. The C3 type carbon remained unchanged. Thus extractives contribute primarily to the C1 and C2 oxidation states of the C(1s) spectra. Even aqueous treatment caused the movement of these extractives to the surface during drying, resulting in misleading spectra (Yamamoto and Ruddick 1992a).

If the extractives are removed prior to application of CCA, the XPS spectra show hardly any change in composition of the C(1s) components, although the reaction O/C is increased. This increase in the oxygen can arise both from the formation of C-O bonding and also from the formation of chromium, copper and arsenic oxide type complexes in the wood. If C-O bonding is formed, the unchanged spectral components of C(1s) can only be explained by step wise oxidation of both C1 and C2 type carbons and the evolution of carbon dioxide with the creation of C1 type carbons. The evolution of carbon dioxide from wood treated with CCA has been reported by Williams and Feist (1984). The influence of accelerated fixation on the XPS spectra has also been examined (Ruddick *et al.*, 1992b). It revealed that the C1 and C2 components in the XPS spectra were slightly different when different fixation conditions were used (Figure 1). If the wood samples were extracted after treatment then the spectra became essentially the same. Differences in the original spectra could be therefore assigned to differences in the extractive migration.

2.2 Interpretation of XPS Cr(2p), Cu(2p) and As(3s) spectra in CCA-treated wood

The oxidation state of the chromium present in CCA-treated wood can be examined using the Cr($2p_{3/2}$) binding energy of the spectra. For hexavalent chromium the binding energy was found to be 580.9 eV while that of the trivalent form was 577.6 eV. In radiata pine, the chromium binding energy lowered to 579.1 eV one day after treatment, and then reduced very slowly to 578.5 eV some three months later (Yamamoto and Ruddick, 1992a). This suggested that a slow reaction was continuing for several months after treatment. Interestingly, the binding energy did not correspond to that anticipated for trivalent chromium. Examination of the spectrum showed that the envelope was quite broad and appeared to contain more than one peak. Further studies are needed to resolve the spectral changes.

The XPS spectra of Cu ($2p_{3/2}$) and Cu($2p_{1/2}$) each contained a satellite at higher binding energy, confirming the presence of copper(II). The arsenic spectra did not show any evidence of change in binding energy during fixation, so that it was concluded that neither the copper nor the arsenic undergo changes in oxidation during the fixation reaction (Yamamoto and Ruddick, 1992a).

2.3 ESR spectral analysis of chromic acid and CCA-treated wood.

Electron spin resonance has proved an extremely useful technique for examining chemical reactions in wood (Hon 1981 and references therein; Hughes *et al.*, 1992; Plackett, 1987; Yamamoto and Ruddick, 1992b). The technique has been widely employed for studying the formation of free radicals in wood during weathering. For CCA- or ACA-treated wood it is possible to observe the ESR spectrum, since the copper compounds are paramagnetic. This arises because in copper(II) compounds copper contains an unpaired electron in the d^9 electronic configuration, in which the unpaired electron is in the $d_{x^2-y^2}$ orbital and all other orbitals are doubly occupied. The majority of the copper(II) complexes have a distorted octahedral geometry with the two axial bonds being longer than those in the plane. The ESR spectra can display hyperfine structure as a result of interaction with the nucleus. Thus for copper and a nuclear spin value of $I = 3/2$, there will be $2I + 1$ (i.e. 4) equally spaced peaks. The magnitude of the hyperfine coupling constant, A, is proportional to the degree of interaction between the unpaired electron and the nucleus. There are three major contributions to A, the degree of s-character of the unpaired electron, coupling of the spin in the core s-orbitals and the nuclear spin through interaction with the core electrons, and coupling of the magnetic moments of the nucleus and the unpaired electron. The degree of delocalization of electrons from the nucleus also effects A, with increased covalency leading to smaller A values.

ESR spectra are usually collected as a graph of the first derivative dI/dB of absorption intensity against the applied magnetic field (B) to reduce noise. The two states produced as a result of the interaction of the spinning electron with the magnetic field are defined by: $\Delta E = g\mu B$. For a free electron $g = 2.0023$. In a molecule, the unpaired electron can occupy an orbital which is quite well localized on a single atom or it may be delocalised over several atoms. The magnitude of g is then related to the nature of the bonding to the ligand and can be quite different from 2.0.

a) Chromium trioxide treatment

Since hexavalent chromium contains no unpaired electrons, chromic acid does not produce an ESR spectrum. When Japanese cedar (*Chryptomaria japonica*) is treated with 2% CrO_3 solution, an ESR signal consisting of a set of three peaks at g-values of 1.987, 1.975 and 1.965 was observed (Figure 2). These values are similar to those found previously for the reaction products of humic acid with chromium(VI) and which were proposed to indicate chromium(V) (Goodgame *et al.* 1984). The three components in the chromium(V) signals soon merged into one sharp Cr(V) signal at g=1.980 (Figure 2). In addition to the chromium(V) signal, a very broad signal due to Cr(III) appeared one or two hours after the chromic acid treatment which gradually increased in intensity. The chromium(V) signal was still detectable several months after the treatment, suggesting the presence of a stable complex. This is unusual since most chromium(V) compounds produced in solution by reduction of chromium(VI) are relatively short-lived (Goodgame *et al.* 1984, Boyko and Goodgame 1986).

b) CCA treatment

The ESR spectrum of western hemlock treated with CCA gave a simple broad ESR spectrum, similar to that produced by $CuSO_4$ solution alone (Figure 3a). This was anticipated since the chromium (VI) does not give any signal. As the CCA fixation reaction progressed a single sharp signal of a Cr(V) species (g = 1.980) appeared which increased as the Cr(V) concentration increased (Figure 3b and c). The peak began to weaken one week after treatment, although it could be detected for several months in the specimens, suggesting a slow conversion of the chromium(V) complex. It is of interest to note that when McMahon *et al.* (1942) determined the chromium fixation by leaching, they found that the reaction proceeded for about six months. Similarly Häger (1969) has suggested that the insoluble complexes formed rapidly in CCA-treated wood by a chromium oxidation-reduction reaction slowly hydrolyze, and that it is these hydrolyzed complexes which provide CCA-treated wood with its performance. A broad ESR signal due to the Cr(III) was detected soon after CCA treatment. It became more noticeable (450G line width) as the fixation progressed. The relative heights of the Cr(III) and Cr(V) signals were measured and may be used to indicate the degree of the chromium reduction from Cr(V) to Cr(III) during fixation (Table 2).

The ESR parameters for copper(II) in CCA-treated wood are shown in Table 3. Softwoods and hardwoods gave almost the same ESR spectra. The ESR signal for Cu(II) became better resolved with increasing fixation, (Figure 3d), exhibiting four peaks at $g_{//}$ and a single peak at $g_{\perp}$. The ESR g-values were consistent with copper (II) in a $d_{x^2-y^2}$ ground state, bonded to four oxygen atoms arranged in a square planer (distorted octahedral) coordination. These oxygen atoms may belong to either functional groups on the wood or water molecules. The ESR g-value for Cu(II) in CCA-treated wood were similar to those obtained with $CuSO_4$, except for a slight increase in $A_{//}$, which may arise from an increased delocalization of the unpaired electron on the copper-oxygen ligand complex.

3. Fixation of ammoniacal copper preservatives

3.1 Nitrogen analysis of ACA-treated wood

The fixation of ammoniacal copper based wood preservatives, such as ACA has generally been considered to be based upon loss of ammonia and precipitation of insoluble copper arsenate (Hartford, 1972). This explanation was challenged when it was observed that ACA-treated spruce poles retained enhanced nitrogen levels more than two years after treatment (Ruddick, 1979). Analysis of four zones: at the surface (0 to 5 mm), at the limit of the copper penetration, the heartwood just beyond the limit of the copper penetration, and the center of the cross section. The results showed that the nitrogen level was greatly enhanced in the ACA treated wood and seemed to be related to the level of treatment, (Figure 4a and b). In addition, there was evidence that the ammonia had penetrated beyond the penetration by the copper, since a slight enhancement of the nitrogen in zone 3 (Figure 4a). Subsequent examination of this same pole material after almost ten years of field testing confirmed that the nitrogen remained enhanced (Ruddick and Kim, 1985).

3.2 ESR spectral analysis of wood treated with simple aqueous copper preservatives.

ESR spectra of copper sulphate treated, earlywood and latewood, of ponderosa pine sapwood and heartwood, were identical with $g_{//} = 2.387 \pm 0.002$ and $g_{\perp} = 2.086 \pm 0.002$ (Ruddick *et al.*, 1992a). The copper(II) ESR parameters for treated earlywood sapwood samples are shown in Table 4. Copper sulphate in wood exhibiting a hyperfine structure at lower field, the parameters of which suggested a $d_{x^2-y^2}$ ground state ,with copper bonded to four (or six) oxygen atoms in a square planar (or distorted octahedral) configuration.

Wood impregnated with copper acetate dissolved in either water or methanol gave similar spectra, which compared well to that of copper sulphate. Clearly, any interaction with the substrate was independent of the solvent. Ammoniacal copper carbonate treated wood gave ESR spectra in which the $A_{//}$ was slightly smaller and the $g_{//}$ values larger, than those in the original solution. It was concluded (Ruddick *et al.*, 1992a) that in treated wood, two of the ammonia ligands had been replaced by copper-oxygen bonding either from water or from the wood substrate leading to a distorted octahedral complex having two ammonia ligands bonded in the equatorial position. Hughes *et. al.*, (1992) recently published ESR spectral data for ammoniacal copper treated *Pinus sylvestris*, in which the ESR parameters were similar to those found in solution. This would suggest that the complexes formed in the wood during reaction with ammoniacal copper compounds, may depend to some extent on the ammonia concentration in the solvent at the time of treatment. A second interpretation for the reduction in $A_{//}$ and increase in $g_{//}$ could be molecular distortion from square-planar toward tetrahedral geometry. No ligand-nitrogen coupling was observed due to different symmetries around the ion.

Matchstick sized specimens treated with $Cu[(en)_2]SO_4$, and 1,2-diaminoethane treatment of copper sulphate-treated wood (Ruddick *et al.*, 1992a), gave spectral parameters typical of copper(II) complexes with four nitrogen ligands (Farkas and Kurzak, 1990). This confirmed the accessibility of the copper in the wood to further complex formation in agreement with an earlier observation (Plackett *et al.*, 1987). Motschi (1984) has described the negative relationship between $g_{//}$ and log K_{tot} (overall stability constant) represented by the equation $\log K_{tot} = 84(2.44 - g_{//})$. Thus copper(II) complexes lower in $g_{//}$ have better copper fixation. It is suggested that the complexes formed in wood impregnated with copper sulphate and copper acetate have a central copper ion bonded by solvent to form four equatorial Cu-oxygen bonds, while that for ammoniacal copper carbonate appears to have two copper-oxygen and two copper-nitrogen equatorial bonds, (although four copper-nitrogen bonds may also be formed). Wood treated with $Cu[(en)_2]SO_4$ or $Cu(en)_2^{2+}$ has four equatorial copper-nitrogen donor bonds. These assignments can be made from both literature data on other copper-amine spectra and the established linear relation between $g_{//}$ and $A_{//}$ for copper compounds possessing a square planar (elongated octahedral) geometry (Peisach and Blumberg, 1974).

3.3 Influence of ammonia concentration on the fixation of ammoniacal copper preservatives

The ESR examination of ammoniacal copper carbonate treated wood had suggested, that the copper complex formed in the wood may be influenced at least in the short term, by the ratio of the copper to ammonia. To investigate this, small blocks (19 mm x 19 mm x 19 mm) treated with ammoniacal copper carbonate were wrapped and allowed to fix for one week, before being either oven dried or air dried for one week and leached in distilled water for one week. The results showed that higher ammonia content in the treating solution did appear to improve the degree of copper fixation (Figure 4c). However, the ammonia levels required were too high to be of use in commercial practice.

3.4 Monitoring fixation in wood treated with ammoniacal copper preservatives

With the increased awareness of the environmental impact of industrial operations today, the wood preserving industry is keen to eliminate any potential for pollution, particularly from treated wood. This has lead to research on techniques for accelerating the fixation of CCA so that the conversion of chromium is completed before the wood leaves the treating cylinder area. However, recent industrial developments have re-emphasized the potential of ammoniacal copper based preservatives. Therefore, it will be important to address the fixation of ammoniacal copper based preservatives, both in terms of understanding the fixation mechanism and developing analytical methods for determining when fixation is complete. A recent investigation examined the relationship between the pH of the leachate from ACA-treated wood and the loss of copper and arsenic. Small ponderosa pine sapwood blocks (19 mm x 19 mm x 19 mm) were treated with ACA and at selected time intervals were leached ultrasonically for one hour. They were then oven dried and analyzed for copper and arsenic using x-ray spectrometry. The pH of the leachate was measured. The results are presented in Figure 5. There is a clear relationship between the pH of the leachate and the leaching of the preservative. Thus the monitoring of leacnate from borings removed from ammoniacal copper preservative treated wood could be used as a method of monitoring the fixation process. While the loss of copper relates very well to the change in pH of the leachate, the arsenic depletion is rapid at first and then reaches a more or less constant loss of about 12%. This may be interpreted as indicating that at least 12% of the arsenic will not be complexed by the copper in the wood and will be lost during service. An examination of ACA-treated western white spruce poles, ten years after treatment and exposed in a field test site, revealed that loss of arsenic had occurred, particularly at the lower retentions (Figure 6). The ratio of copper to arsenic (expressed as oxides) which in freshly treated wood was 1:1, became approximately 1.5:1.

4. Fixation of copper nitrite in wood

The fixation reaction of CCA in wood is driven by the reduction of chromium and the formation of chromium(III) copper and arsenic complexes. Recently, Hughes *et al.* (1992) reported that copper could be fixed in wood using sodium nitrite. This reaction has been extensively explored using ESR, XPS spectroscopic techniques as well as by leaching experiments (Ruddick and Johansson, 1992). In the investigation small quantities of either Avicel (microcrystalline cellulose) or ponderosa pine sapwood sawdust were soaked with the treating solution, oven dried and then leached ultrasonically for two hours. Measurement of the copper content before and after leaching allowed the depletion to be measured. Samples of the treated Avicel and sawdust were recorded using XPS to examine the changes in the C(1s), N(1s) and Cu(2p) spectra. Since the migration of extractives can confuse the interpretation of XPS spectra, the sawdust was first extracted with ethanol-toluene prior to treatment for the XPS analysis. ESR Spectra were used to determine the presence or absence of copper-nitrogen bonding. The results were most interesting. When Avicel or wood was treated with copper sulphate and sodium nitrite, the degree of copper fixation was excellent, being close to 100%. However, when the materials were treated sequentially, first sodium nitrite and then copper sulphate, the degree of fixation was hardly different than that found with copper sulphate or acetate alone (Table 5).

The XPS spectra of Avicel showed almost no change when treated with either sodium nitrite or sodium nitrite and copper sulphate (Figure 7). Thus the mechanism by which the copper was rendered insoluble, did not appear to involve the cellulose. The XPS spectra of the untreated, extracted sawdust and the same material after treatment with either sodium nitrite alone or a solution of copper sulphate and sodium nitrite are shown in Figure 8. They indicate that the C1 component in the C(1s) spectra was greatly increased as a consequence of the sodium nitrite treatment, confirming the reducing action of the nitrite. The C2 component was reduced. The XPS N(1s) spectrum of sodium nitrite showed one major peak at 404.5 eV with a minor peak at 408 eV. These were ascribed to the nitrogen present in nitrite and a nitrate impurity, respectively. In the wood treated with nitrite, there is a peak centered on 405 eV with a shoulder at 404 eV. A third peak is present at a much lower binding energy of 400.5 eV. These peaks may be assigned to residual sodium nitrite, nitrite reacted with wood and a reduced form of nitrogen produced by the reaction with wood, respectively. The XPS N(1s) spectra of the copper sulphate/sodium nitrite treated wood showed essentially two peaks, centered on 404 eV and 400.5 eV. These corresponded to a nitrite complexed with wood and a reduced form of nitrogen, respectively.

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Table 1. O/C ratio and fractional area percent of C(1s) peak in untreated and CCA-treated unextracted and extracted ponderosa pine sapwood.

Specimen	O/C	C1	C2	C3
Untreated				
Unextracted, section	0.453	44.2	46.6	9.2
Extracted, section	0.585	25.2	65.0	9.8
Water dipped and dried section	0.326	57.4	33.6	9.0
Ethanol-toluene extractives	0.290	96.6	3.4	-
CCA-treated - unextracted				
3% CCA then fixation at 20°C	0.458	63.1	27.5	9.4
3% CCA, accelerated fixation	0.514	53.8	36.6	9.6
3% CCA, fixation at 20°C, extraction*	0.451	46.8	42.1	11.1
3% CCA, accelerated fixation, extraction*	0.413	47.6	40.8	11.6
CCA-treated - pre-extracted				
3% CCA fixation at 20°C	0.671	25.8	63.6	10.6
3% CCA, accelerated fixation	0.659	28.0	62.7	9.3

* Following CCA-treatment and preservative fixation, the treated wood was extracted with ethanol-toluene.

Table 2. Time dependence of chromium reduction in wood treated with CCA as measured by relative heights of Cr(III) to Cr(V) signals

Species/Time	Signal height (arb. units) Cr(III)	 Cr(V)	Ratio
Western hemlock			
1 min	0	3	0.00
10 min	0	11	0.00
40 min	0	22	0.00
200 min	0	55	0.00
3 days	37	75	0.49
4 days	44	72	0.61
7 days	60	61	0.98

Table 3. ESR spectral parameters for copper(II) in CCA-treated wood, seven days after treatment

Species	$g_{//}$	$A_{//}$ (10^{-4} cm^{-1})	$g_{\perp}$
Western hemlock	2.400	146	2.083
Japanese cedar	2.405	146	2.082
Anthocephalus	2.403	151	2.087

Table 4. ESR Spectral Parameters for Copper(II) in Treated Wood.

Treatment	$g_{//}$	$A_{//}$	$g_{\perp}$ x $10^{-4}cm^{-1}$
$CuSO_4$ in water*	2.372	132	2.082
$CuSO_4$ in water**	2.388	150	2.080
$Cu(CH_3COO)_2$ in water*	2.357	139	2.077
in methanol*	2.353	141	2.074
$CuCO_3/NH_4OH$*	2.272	166	2.068
$CuCO_3/NH_4OH$**	2.282	177	2.069
$[Cu(en)_2]SO_4$ formed in wood*[1]	2.205	197	2.060
$[Cu(en)_2]SO_4$ in water*	2.204	190	2.064

* Measured at room temperature, and ** at 77K.

[1] 1,2-diaminoethane secondary treatment of $CuSO_4$ treated wood.

Table 5. Leaching of copper from treated Avicel

Treatment	Copper content before leaching % w/w	after leaching %w/w	Percent copper remaining
Avicel			
sodium nitrite, then copper sulphate	0.942	0.083	9.8
sodium nitrite + copper sulphate	1.009	1.109	100
Wood			
coppper acetate	1.742	0.799	45.9
sodium nitrite, then copper acetate	2.261	1.162	51.4
sodium nitrite + copper acetate	3.302	3.001	90.9

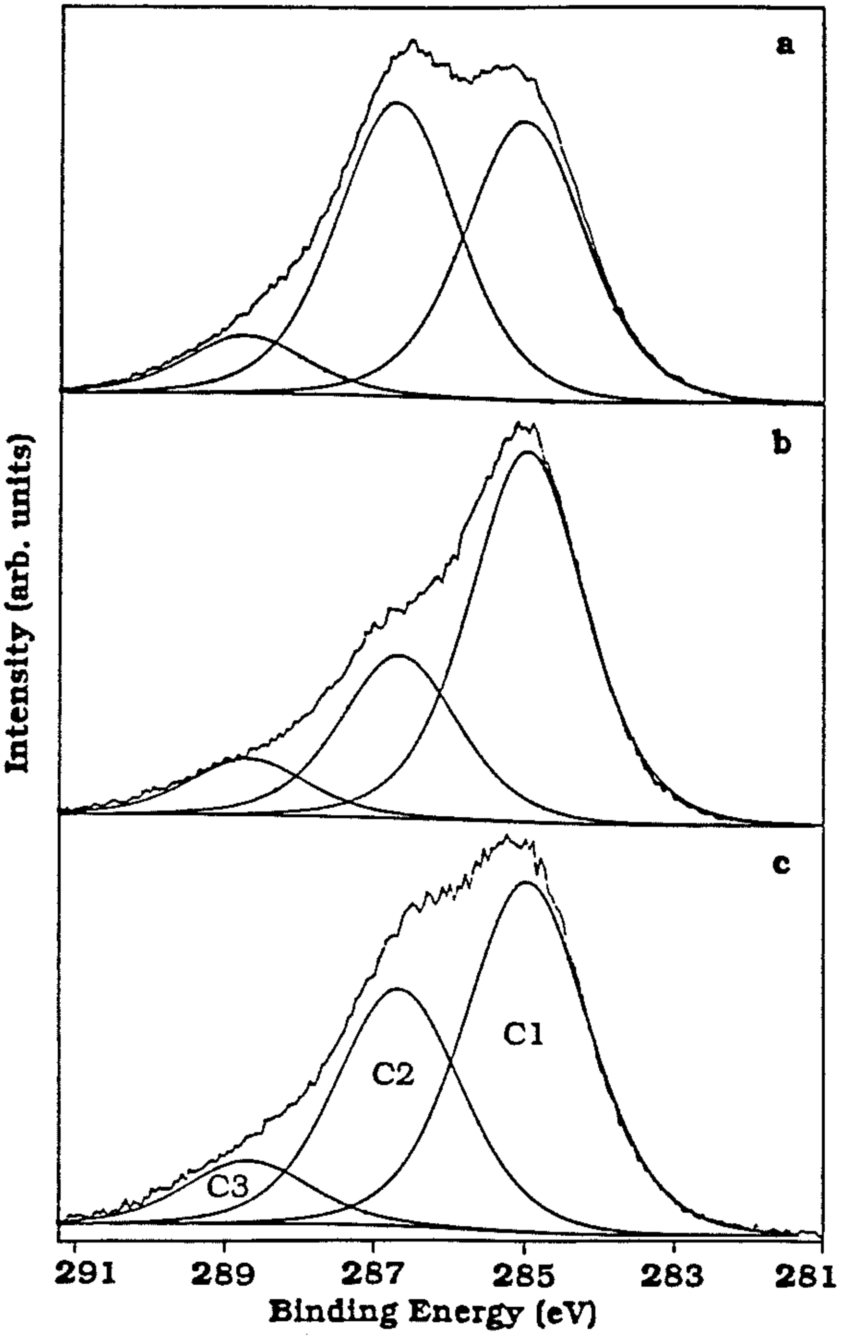

Figure 1. XPS C(1s) spectra of ponderosa pine; a) unextracted, b) unextracted section treated with 3%CCA and fixed at 20°C, c) unextracted section treated with 3% CCA followed by accelerated fixation.

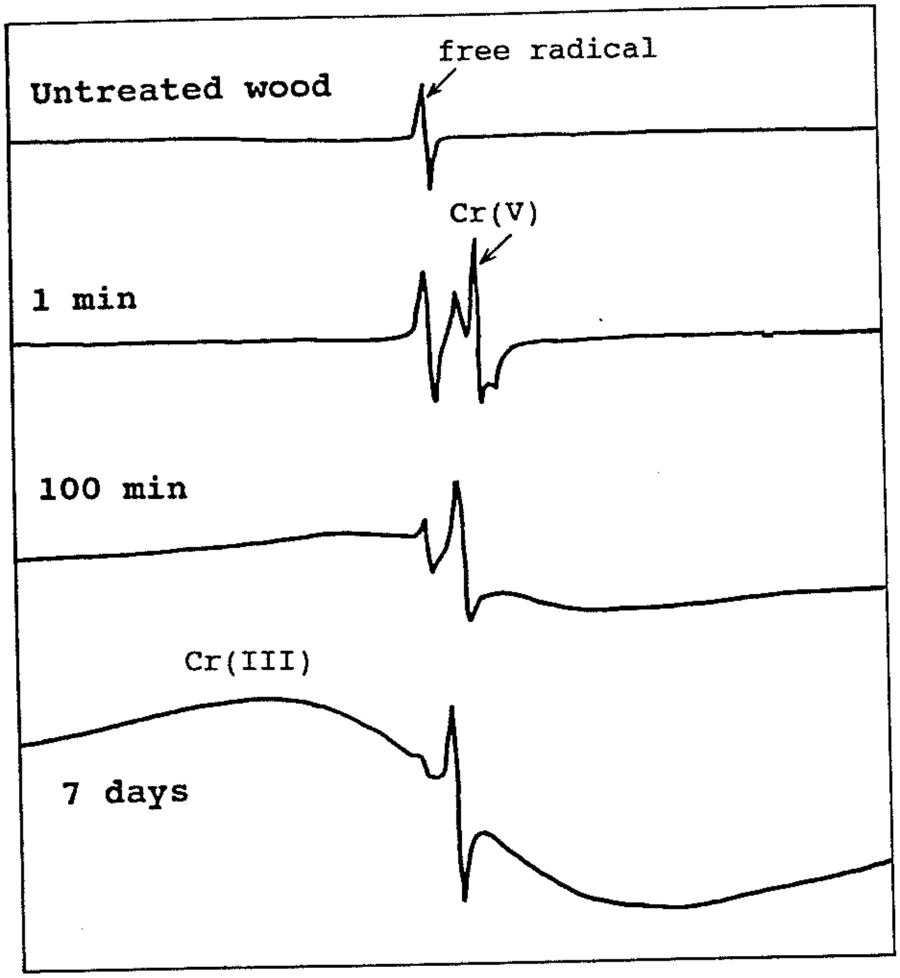

Figure 2. XPS Cr(2p) spectra of Japanese cedar soaked in chromic acid; a) untreated wood, b) 1 minute after CrO_3 treatment, c) 100 minutes after CrO_3 treatment, d) one week after CrO_3 treatment.

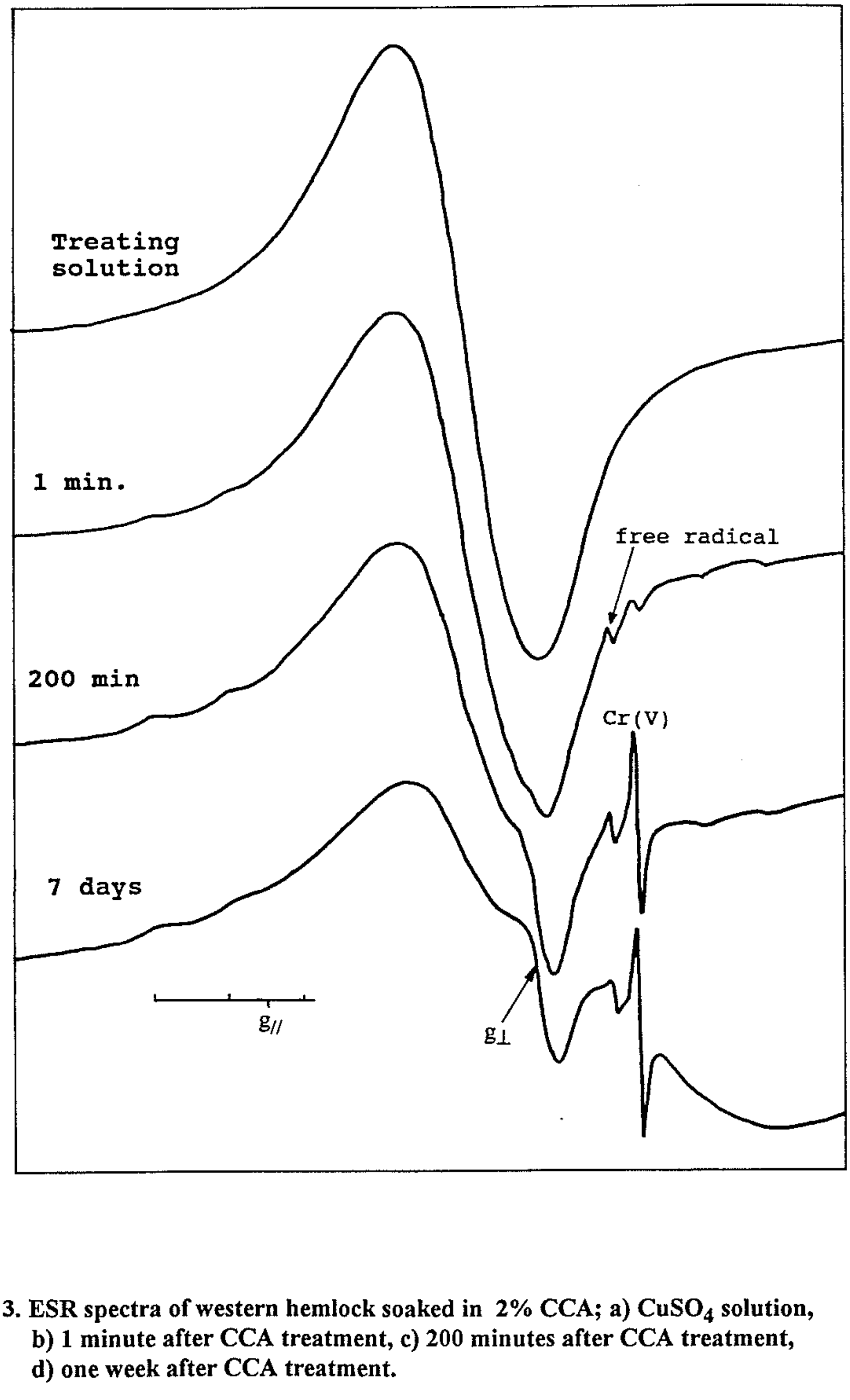

Figure 3. ESR spectra of western hemlock soaked in 2% CCA; a) $CuSO_4$ solution, b) 1 minute after CCA treatment, c) 200 minutes after CCA treatment, d) one week after CCA treatment.

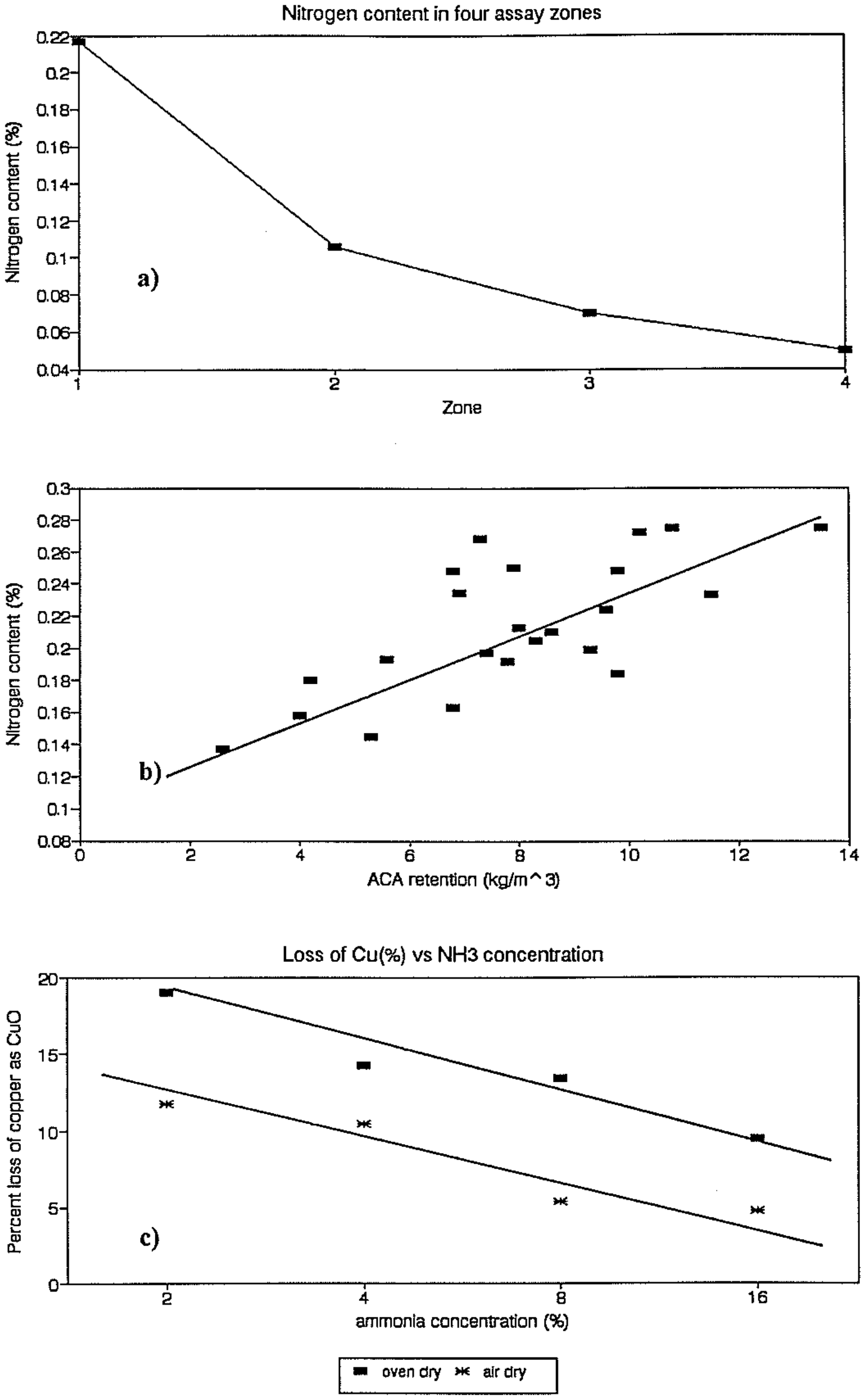

Figure 4. a) Analysis of nitrogen in ACA treated poles; b) nitrogen content as a function of ACA retention; c) copper leaching as a function of ammonia content in the ammoniacal copper carbonate treating solution.

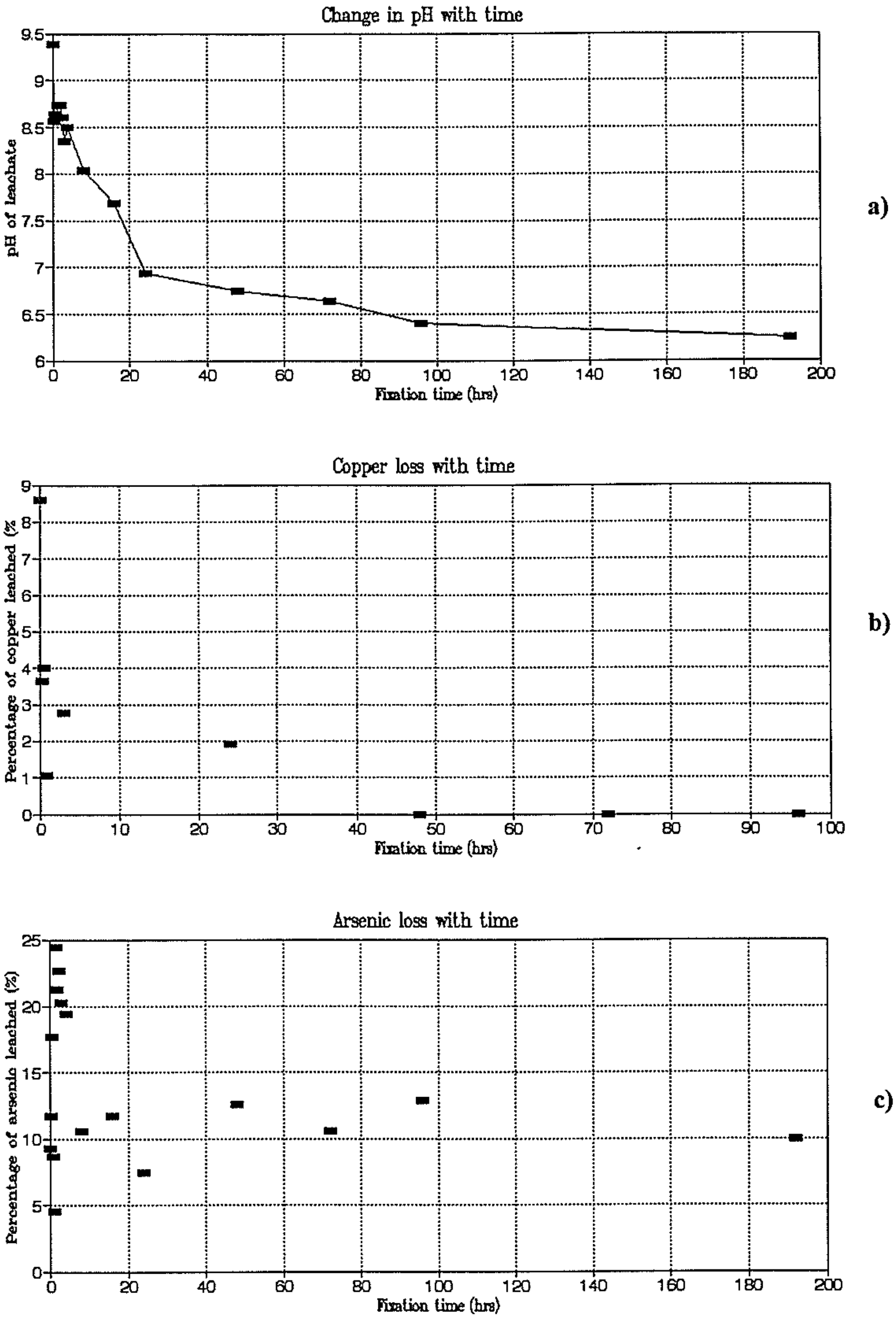

Figure 5. a) Change of pH of leachate with time; b) loss of copper with increasing fixation time; c) loss of arsenic with increasing fixation time.

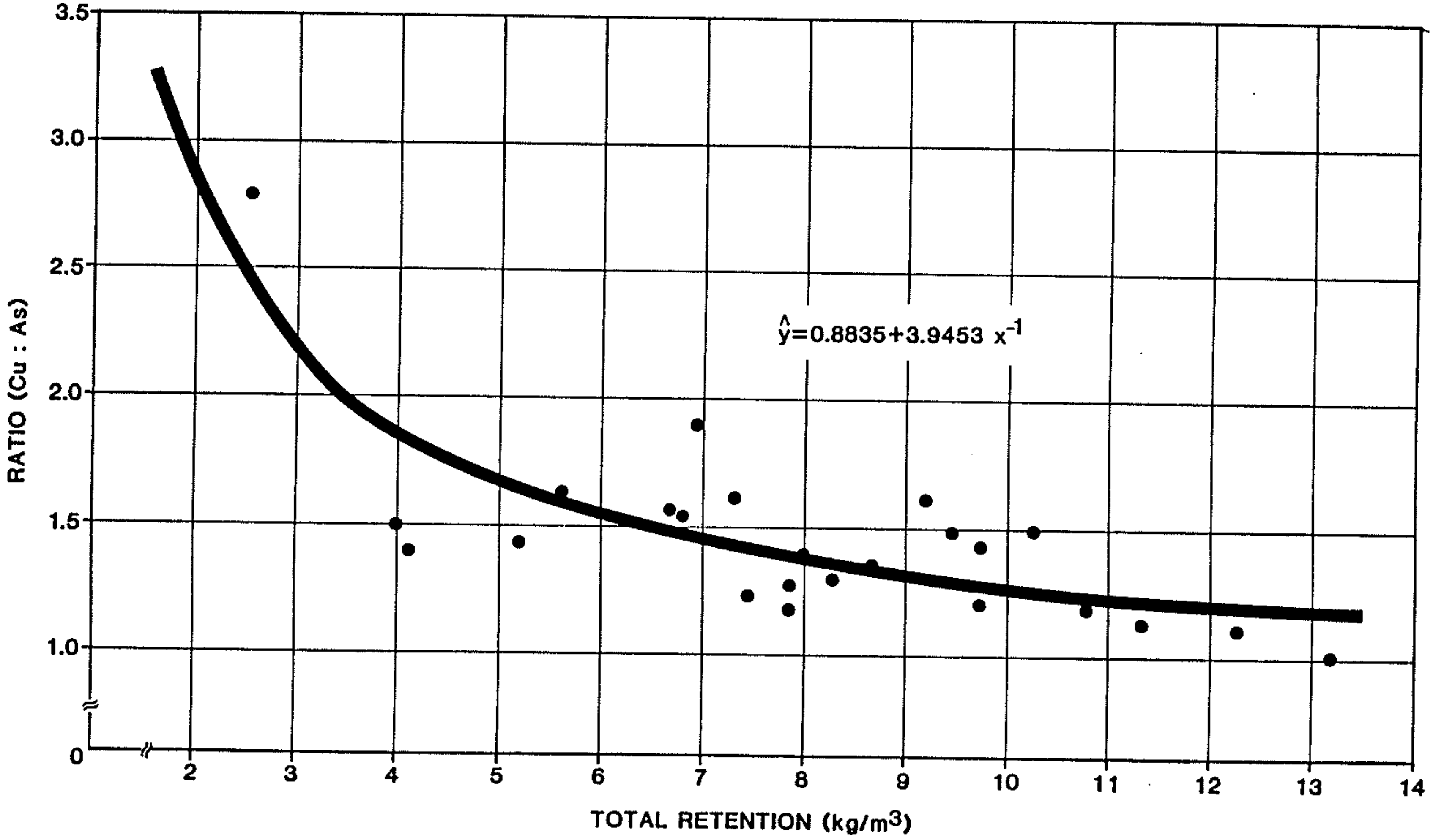

Figure 6. Ratio of CuO to As_2O_5 as a function of ACA retention.

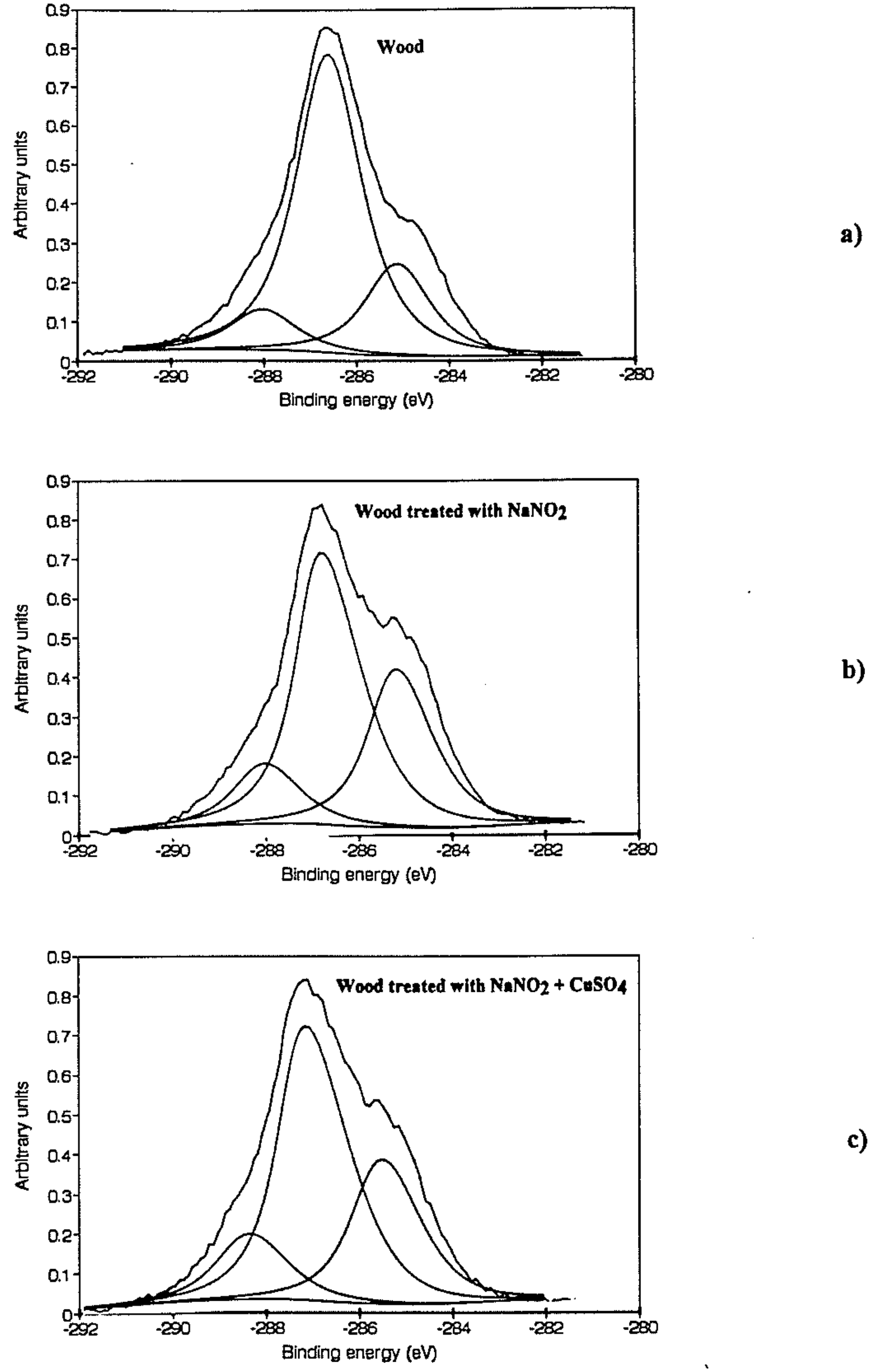

Figure 7. XPS C(1s) spectra of ponderosa pine a) untreated; b) treated with sodium nitrite; c) treated with sodium nitrite and copper sulphate

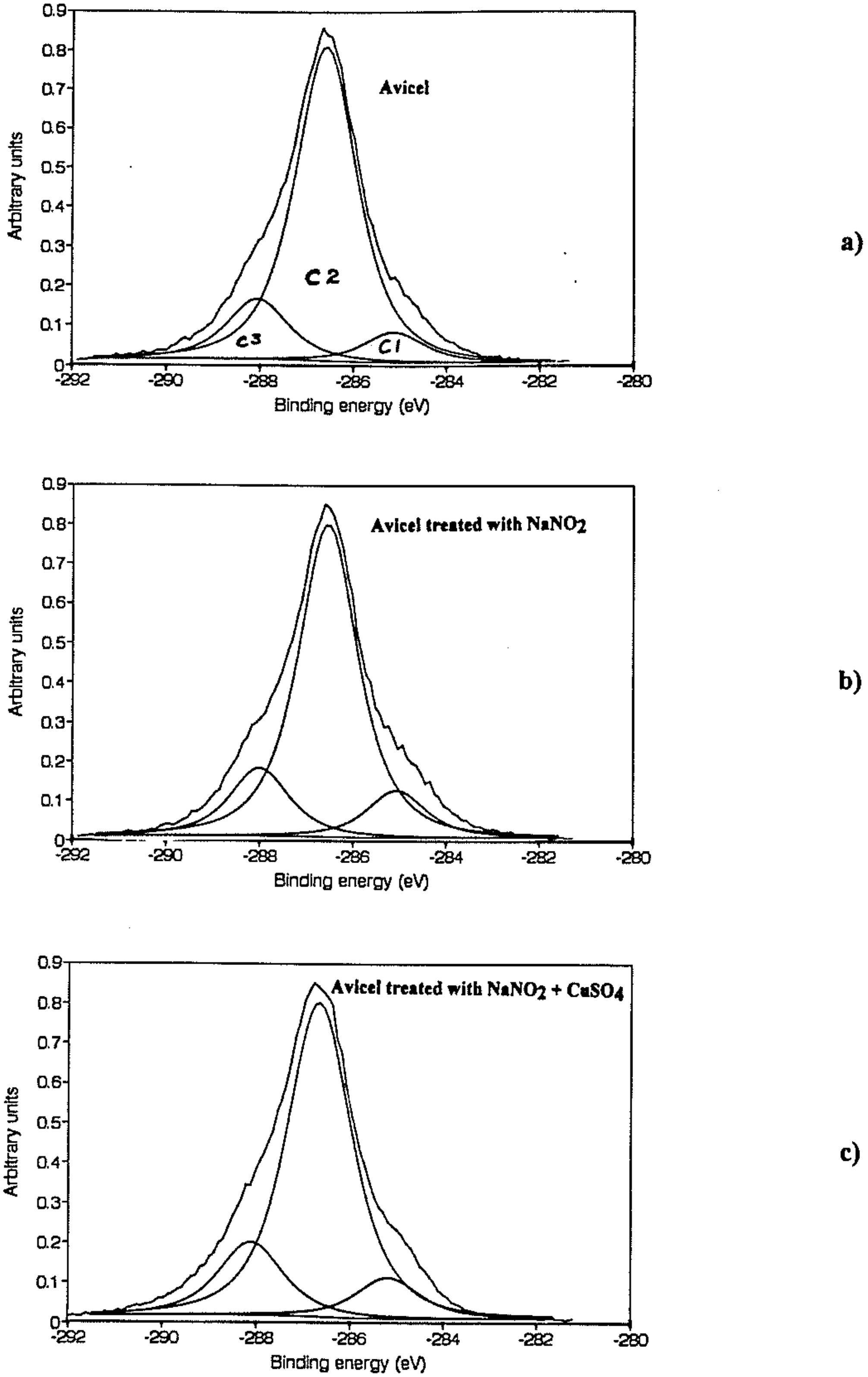

Figure 8. XPS C(1s) spectra of Avicel a) untreated; b) treated with sodium nitrite; c) treated with sodium nitrite and copper sulphate.