

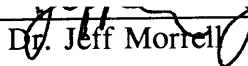
AN ABSTRACT OF THE THESIS OF

Stan T. Lebow for the degree of Doctor of Philosophy in Forest Products presented on November 6, 1992.

Title: Interactions of Ammoniacal Copper Zinc Arsenate (ACZA) Wood Preservative with Douglas-fir

Signature redacted for privacy.

Abstract approved: _____


Dr. Jeff Morrell

The use of the waterborne wood preservative, ammoniacal copper zinc arsenate (ACZA), is likely to increase in the near future because of environmental concerns associated with oilborne preservatives. Developing an understanding of the permanence of this preservative in wood will become important from both environmental and performance standpoints. Conventional thinking suggests that ACZA components are stabilized in the wood by the precipitation of metal/arsenate complexes as the ammonia evaporates, but little work has been done to confirm this theory. Experiments were conducted to clarify the mechanisms which stabilize, or "fix" copper, arsenic and zinc within ACZA treated wood.

Studies were undertaken to determine the effect of ACZA composition on fixation, the role of wood components in fixation, the role of precipitation in fixation, the order of precipitation of ACZA components, the sites of copper and zinc adsorption within the treated wood, the bonding environment of adsorbed

copper, and the microdistribution of copper, zinc and arsenic within treated wood. The results of these experiments generally support the finding that arsenic fixation occurs by precipitation of metal/arsenate, complexes as ammonia evaporates from the treated wood. Arsenic leaching was minimized when the metal oxide:arsenic pentoxide ratio in the treating solution exceeded 2.0, and when a portion of the copper was replaced with zinc. Subsequent tests revealed that zinc precipitated the majority of arsenic when the ammonia was allowed to evaporate from the treating solution. In contrast, the metal cations are not dependent on arsenic for fixation because they have low water solubility and undergo adsorption reactions with the wood. Copper, in particular was readily adsorbed by the lignin and heartwood components of wood, suggesting that phenolic groups were primary reaction sites. Further tests with lignin model compounds also suggested that copper reacted preferentially with the hydroxyl groups of phenolic compounds. Adsorption of the metals to the wood can interfere with arsenic fixation by reducing the availability of metal cations in the preservative solution. The severity of arsenic leaching due to metal adsorption could be affected by many treatment variables, and more work is needed to determine how these variables could be manipulated to minimize arsenic fixation.

INTERACTIONS OF AMMONIACAL COPPER ZINC ARSENATE (ACZA)
WOOD PRESERVATIVE WITH DOUGLAS-FIR

by

Stan T. Lebow

A Thesis

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

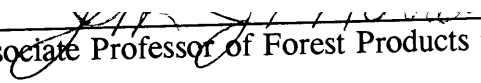
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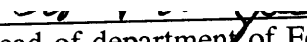
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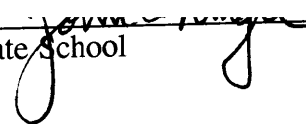
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TABLE OF CONTENTS

| | |
|---|----|
| 1.0. INTRODUCTION | 1 |
| 2.0. LITERATURE REVIEW | 3 |
| 2.1. Review of Wood Anatomy and Chemistry as it Relates to ACZA Fixation | 3 |
| 2.2. Wood Structure in Relation to ACZA Treatment | 8 |
| 2.3. ACZA Composition | 11 |
| 2.3.1. Historical Perspective | 11 |
| 2.3.2. Solution Characteristics | 13 |
| 2.4. Application of ACZA | 15 |
| 2.5. ACZA Fixation | 16 |
| 2.6. Summary | 22 |
| 3.0. OBJECTIVE | 24 |
| 4.0. EXPERIMENTAL | 25 |
| 4.1. Effect of ACZA Composition on Fixation | 25 |
| 4.1.1. Introduction | 25 |
| 4.1.2. Materials and Methods | 25 |
| 4.1.3. Results and Discussion | 27 |
| 4.2. Role of Wood Components in Fixation | 37 |
| 4.2.1. Introduction | 37 |
| 4.2.2. Materials and Methods | 37 |
| 4.2.3. Results and Discussion | 40 |
| 4.3. Role of Precipitation in Fixation | 46 |
| 4.3.1. Introduction | 46 |
| 4.3.2. Materials and Methods | 46 |
| 4.3.3. Results and Discussion | 47 |
| 4.4. Order of Precipitation of ACZA Components | 51 |
| 4.4.1. Introduction | 51 |
| 4.4.2. Materials and Methods | 51 |
| 4.4.3. Results and Discussion | 51 |
| 4.5. Site(s) of Metal Adsorption | 53 |
| 4.5.1. Introduction | 53 |
| 4.5.2. Role of Extractives | 53 |
| 4.5.2.1. Introduction | 53 |
| 4.5.2.2. Materials and Methods | 53 |
| 4.5.2.3. Results and Discussion | 54 |
| 4.5.3. Adsorption Tests of Lignin Functional Groups | 56 |
| 4.5.3.1. Introduction | 56 |
| 4.5.3.2. Materials and Methods | 56 |
| 4.5.3.3. Results and Discussion | 57 |

| | |
|--|-----|
| 4.5.4. Adsorption by Vanillin and Eugenol | 58 |
| 4.5.4.1. Introduction | 58 |
| 4.5.4.2. Materials and Methods | 58 |
| 4.5.4.3. Results and Discussion | 59 |
| 4.5.5. NMR Analysis | 61 |
| 4.5.5.1. Introduction | 61 |
| 4.5.5.2. Materials and Methods | 61 |
| 4.5.5.3. Results and Discussion | 62 |
| 4.5.6. FTIR Analysis | 65 |
| 4.5.6.1. Introduction | 65 |
| 4.5.6.2. Materials and Methods | 65 |
| 4.5.6.3. Results and Discussion | 65 |
| 4.5.7. FAB Mass Spectroscopy | 75 |
| 4.5.7.1. Introduction | 75 |
| 4.5.7.2. Materials and Methods | 76 |
| 4.5.7.3. Results and Discussion | 76 |
| 4.6. Analysis Of Preservative Distribution | 81 |
| 4.6.1. Introduction | 81 |
| 4.6.2. Materials and Methods | 81 |
| 4.6.3. Results and Discussion | 82 |
| 4.7. Bonding Environment of Copper | 95 |
| 4.7.1. Introduction | 95 |
| 4.7.2. Materials and Methods | 96 |
| 4.7.3. Results and Discussion | 97 |
| 5.0. SUMMARY | 101 |
| 6.0. LITERATURE CITED | 107 |
| 7.0. APPENDIX | 113 |

LIST OF FIGURES

| <u>Figure</u> | <u>Page</u> |
|---|-------------|
| Figure 4.1.1. Proportion of CuO in original treating solutions and treated Douglas-fir heartwood and sapwood for A.) ACZA or B.) ACA treatments. | 29 |
| Figure 4.1.2. Percentage of copper leached from Douglas-fir heartwood and sapwood following treatment with A.) ACZA or B.) ACA. | 30 |
| Figure 4.1.3. Percentage of zinc leached from Douglas-fir heartwood and sapwood treated with ACZA solutions of varying component ratios. . . | 33 |
| Figure 4.1.4. Percentage of arsenic leached from Douglas-fir heartwood and sapwood treated with A.) ACZA or B.) ACA. | 35 |
| Figure 4.2.1. Adsorption of A.) Copper, B.) Zinc or C.) Arsenic by heartwood, sapwood, lignin, cellulose and xylan. | 41 |
| Figure 4.3.1. Adsorption (ADS) and precipitation (PPT) of copper, zinc, and arsenic from an ACZA solution in the presence of A.) heartwood, B.) sapwood, or C.) lignin over a 74 hour period at 23 - 25 C. | 48 |
| Figure 4.4.1. Precipitation of copper, zinc, and arsenic from ACZA solution as the ammonia evaporates. | 52 |
| Figure 4.5.1. Precipitation of copper from ACZA solutions after addition of vanillin or eugenol. | 60 |
| Figure 4.5.2. Solid state NMR spectra of A.) untreated wood, B.) ammonia treated wood, or C.) ACZA treated wood. | 63 |
| Figure 4.5.3. FTIR spectra of Douglas-fir heartwood after A.) no treatment B.) ammonia treatment, or C.) ACZA treatment. | 66 |
| Figure 4.5.4. FTIR spectra of cellulose after A.) no treatment, B.) ammonia treatment, or C.) ACZA treatment. | 68 |
| Figure 4.5.5. FTIR spectra of xylan after A.) no treatment, B.) ammonia treatment, or C.) ACZA treatment. | 69 |

| | |
|--|-----|
| Figure 4.5.6. FTIR spectra of lignin after A.) no treatment, B.) ammonia treatment, or C.) ACZA treatment. | 71 |
| Figure 4.5.7. FTIR spectra of untreated vanillin and vanillin after ammonia or ACZA treatment for A.) 4000 - 2000 cm^{-1} or B. 2500 - 400 cm^{-1} . . . | 74 |
| Figure 4.5.9. FAB mass spectroscopy spectra of A.) vanillin in water, B.) vanillin in NH_4OH , C.) ACZA solution, or D.) vanillin in ACZA. . . . | 78 |
| Figure 4.6.1. Examples of copper, zinc and arsenic levels in an ACZA treated, unleached Douglas-fir sample at points shown in the photomicrographs. | 83 |
| Figure 4.6.2. Examples of copper, zinc, and arsenic levels in an ACZA treated, leached Douglas-fir sample at points shown in the photomicrographs. | 87 |
| Figure 4.6.3. Range of elemental levels of A.) copper, B.) zinc, or C.) arsenic in unleached and leached samples. | 93 |
| Figure 4.7.1. EPR spectra of spruce organosolve lignin after A.) ammonia treatment, B.) CuO treatment, or C.) ACZA treatment. | 98 |
| Figure 7.1. Correlation between acid/base titration method and A.) Kjeldahl analysis or B.) Alpkem RFA-300 colorimetric analysis for determining ammonia content in ACZA. | 113 |

LIST OF TABLES

| <u>Table</u> | <u>Page</u> |
|--|-------------|
| Table 4.1.1. Ratio of CuO:ZnO:As ₂ O ₅ in ACZA or ACA treating solutions and Douglas-fir heartwood or sapwood treated with these solutions. | 27 |
| Table 4.1.2. Effect of ACZA or ACA formulation on leaching of copper from Douglas-fir heartwood or sapwood. | 32 |
| Table 4.1.3. Effect of ACZA formulation on leaching of zinc. | 33 |
| Table 4.1.4. Effect of ACZA or ACA formulation on leaching of arsenic from Douglas-fir heartwood or sapwood. | 36 |
| Table 4.2.1. Effect of wood component and exposure time on adsorption of copper from ACZA solution. | 40 |
| Table 4.2.2. Effect of wood component and exposure time on adsorption of zinc from ACZA solution. | 42 |
| Table 4.2.3. Effect of wood component and exposure time on adsorption of arsenic from ACZA solution. | 45 |
| Table 4.3.1. Amounts of zinc and arsenic lost from ACZA solutions exposed to wood components in open or closed systems for 20 or 74 hours. | 49 |
| Table 4.5.1. ACZA component adsorption by solvent extracted and unextracted Douglas-fir heartwood powder. | 56 |
| Table 4.5.2. Adsorption of ACZA components in solutions containing selected lignin model compounds. | 58 |

INTERACTIONS OF AMMONIACAL COPPER ZINC ARSENATE (ACZA) WOOD PRESERVATIVE WITH DOUGLAS-FIR

1.0.

INTRODUCTION

Dwindling resources and increasing population place increased emphasis on the wise use of our raw materials. Although trees are a renewable resource, the forest ecosystem is not always easily regenerated, and we are becoming increasingly aware that the value of our forested lands does not lie solely in their ability to produce timber. Rising pressures on our wood supply have increased the cost of our timber products, and forced more efficient wood use.

One of the most practical ways to conserve wood is by extending its service life through preservative treatment. Preservative treatment also broadens the market for lumber and other wood products into areas that would otherwise be serviced by competitive materials and is likely to become increasingly important as the pressure on our timber supply grows. However, the growing demand for preservative-treated wood must be balanced with pressures to use wood preservatives that are safe as well as effective. The wood preservation industry must look ahead to ensure that preservative treatments will be environmentally acceptable for future wood users.

Two general types of wood preservatives are used in the pressure treating industry, oil-borne and water-borne. The commonly used oil-borne preservatives are creosote, pentachlorophenol, and most recently, copper naphthenate. Creosote is a complex mixture of oils produced as a by-product of the coking process in steel

manufacture, while the naphthenic acids used in preparing copper naphthenate are by-products of refining crude oils. Pentachlorophenol is a relatively pure compound, prepared specifically for use as a wood preservative. Water-borne preservatives include a variety of formulations based on inorganic arsenicals. The two most commonly used waterborne preservatives are ammoniacal copper zinc arsenate (ACZA) or chromated copper arsenate (CCA).

The use of water-borne preservatives in poles, piling, and lumber has increased steadily in recent years, principally because of the environmental concerns associated with oil-borne preservatives. In addition, waterborne preservatives are preferred for uses which require a clean, paintable surface. Although CCA remains the most commonly used water-borne preservative for many applications because of its low cost and ease of handling, ACZA is also replacing oil-borne preservatives, especially in western species. ACZA tends to penetrate Douglas-fir to greater depths than CCA, and is often used where more complete preservative protection is important. Such uses include lumber, poles, and piling in structural or high decay hazard applications.

As ACZA use increases, the resistance of ACZA to leaching will become important from both environmental and performance standpoints. Although ACZA has shown excellent performance and resistance to leaching, relatively little research has been done to clarify the mechanism of copper, zinc and arsenic stabilization in the wood. A more thorough understanding of the ACZA "fixation" mechanism will be essential for continued use of this chemical for wood treatment.

2.0

LITERATURE REVIEW2.1. **Review of Wood Anatomy and Chemistry as it Relates to ACZA Fixation**

The structure and composition of the wood govern the potential interactions between the wood and ACZA. Both the types of reactive sites and their accessibility must be considered.

As a tree develops, new cells grow around the outer circumference of the stem, forming the conductive tissues which comprise the sapwood. The older, inner sapwood cells eventually stop functioning, and form a darker core of nonconductive tissues called the heartwood. The thickness of the outer sapwood band of functioning cells varies from species to species and tree to tree, but in Douglas-fir is usually less than five centimeters (Lassen and Okkonen, 1969). Tree growth is fastest in the spring, producing relatively thin-walled cells (earlywood), while thick-walled cells are formed late in the season (latewood). These alternating bands of thick and thin walled cells form growth rings, or annual rings.

All softwoods are composed of two basic cell types; those oriented parallel to the grain (longitudinal) and those oriented perpendicular to the grain (transverse). The longitudinal cells, called longitudinal tracheids, constitute over 90% of the volume of Douglas-fir (Panshin and de Zeeuw, 1980) and average 3 to 6 millimeters in length and 25 - 40 micrometers in diameter (Krahmer, 1961). Also oriented parallel to the grain are the longitudinal resin canals, which compose about 0.35% of

Douglas-fir wood volume, and are primarily located in the latewood zone of the growth ring (Krahmer, 1961; Panshin and de Zeeuw, 1980).

The transverse cells, ray parenchyma and ray tracheids, are contained in the wood rays, which constitute about 7% of the wood volume (Panshin and de Zeeuw, 1980). In addition, a small number of rays possess transverse resin canals, which are surrounded by thin-walled epithelial cells.

Wood cell walls are composed of an interlocking network of polysaccharides (cellulose and hemicelluloses) and lignin. Cellulose consists of anhydroglucose units which are joined by B-(1-4) glycosidic linkages to form a molecular chain. The majority of cellulose chains in wood are bound to other cellulose chains by a regular, orderly system of hydrogen bonds. This type of cellulose is often referred to as crystalline cellulose (Fengel and Wegener, 1984). However, in some areas, the arrangement of the cellulose chains is more random, creating regions termed amorphous cellulose. Hemicelluloses, or polyoses, contain different sugar units, shorter molecular chains, and more molecular branching than cellulose. Sugars in hemicellulose include glucose, mannose, galactose, xylose, and arabinose. Softwoods tend to have a higher proportion of mannose and galactose units than hardwoods, while hardwoods are characterized by a higher percentage of xylose units and the presence of acetyl groups (Fengel and Wegener, 1984). In both types of wood, the hemicellulose side chains often contain hexuronic acid groups.

Lignin is an amorphous polymer of phenylpropane units which are often substituted with one methoxyl group, forming guaiacyl lignin, or two methoxyl

groups, forming syringyl lignin. Softwoods commonly contain guaiacyl units, while hardwoods have both lignin types (Panshin and de Zeeuw, 1980). The polysaccharide portions are gathered into long strands called microfibrils, which are laid down as aggregate sheets in the cell wall and bound together by lignin. The cell walls of tracheids are divided into several parts - the middle lamella, primary wall and secondary wall. The outside of the cell wall is marked by the primary wall, which is joined to the primary wall of an adjoining cell by the middle lamella. Because it is difficult to distinguish the primary wall from the middle lamella, the term compound middle lamella is often used to describe the area composed of the middle lamella and the two adjacent primary walls (Panshin and de Zeeuw, 1980). The compound middle lamella is typically composed of about 25% polysaccharides and 75% lignin (Panshin and de Zeeuw, 1980). The secondary wall is further divided into 3 layers, designated as S1, S2 and S3, with S3 being the farthest from the primary wall and next to the opening inside the cell, which is called the cell lumen. The S1 layer is thin, with the microfibrils oriented nearly perpendicular to the length of the cell, and contains 40 -70% polysaccharides, a sharp rise from the adjoining compound middle lamella. The S2 layer is much thicker, with microfibrils oriented almost parallel to the long axis of the cell, and with polysaccharides composing 70 - 85% of the material. The inner S3 layer is thinner, with microfibrils once again oriented nearly perpendicular to the long axis of the cell. It is characterized by the highest polysaccharide content, containing about 85% cellulose and hemicelluloses and only 15% lignin, as well as the presence of residual cell

contents left on the inner surface after the cell died. Although as a whole it has a much lower percentage of lignin than the primary wall, the secondary layer, because of its greater volume, actually contains most of the lignin within the cell wall (Panshin and de Zeeuw, 1980).

The ray parenchyma cells have primary walls similar to those of tracheids, but the three-layered secondary wall is replaced by a thickening which is much like an extension of the primary wall. Parenchyma cells also possess protective layers formed inside the cell wall surface, next to the protoplasm. Each protective layer is composed of three zones, with the outer and inner zone being much like the S1 and S3 layers in tracheids and the middle zone composed of an amorphous pectin-like material (Panshin and de Zeeuw, 1980). Ray tracheids have a cell wall structure similar to that of longitudinal tracheids.

To allow flow of nutrients, openings called pit pairs are formed between adjoining cells during development of the cell wall. Pit pairs between longitudinal tracheids are most numerous and have the largest diameter on the radial walls of earlywood cells, forming either one or two vertical rows. Pits on the tangential cell walls are smaller and usually confined to cells near the boundary of the growth ring (Panshin and de Zeeuw, 1980). Each longitudinal tracheid is also connected by pits to at least one ray cell.

Several researchers have noted that the limiting factor in flow through most coniferous species is the size of the openings in the pit pairs (Comstock and Côté, 1968; Bailey and Preston, 1970; Krahmer, 1961; Krahmer and Côté, 1963). The

smallest openings encountered in the unspirated pits of Douglas-fir are those in the margo of the pit membrane, which vary from less than 0.1 to 1.0 micrometers (Krahmer and Côté, 1963). These small openings allow adequate fluid flow and nutrient transfer through the sapwood of green Douglas-fir, but the pits become aspirated during heartwood formation, greatly reducing the paths for fluid flow.

Flow through aspirated pits is further reduced by two other changes which take place during heartwood formation; occlusion with extractives and incrustation with lignin-like substances (Krahmer and Côté, 1963; Siau, 1971). "Extractives" is a general term for extraneous wood components which are produced by physiological processes within the tree, but can be removed with solvents without altering the wood structure (Squire, et al., 1967). They may compose from less than 1% to more than 20% of the wood weight, depending on species, but commonly represent about 3 - 5% of the wood constituents (Squire, et al., 1967). Extractives include a wide range of compounds and vary between species and within areas of the tree. Nutrients such as sugars, starch and fats are commonly found in the sapwood portion, while phenolic materials are present in the heartwood.

Douglas-fir heartwood extractives, which are produced by dying ray parenchyma cells, can be divided into two general groups, oleoresin and parenchyma resin (Browning, 1975; Wenzyl, 1970; Foster, et al., 1980, Graham and Kurth, 1949). Total resin content has been reported as 6% in the inner heartwood, 5% in mature heartwood, and 2% in sapwood (Wenzyl, 1970). Oleoresin, found in the resin ducts, is a mixture of terpenes and complex phenolic constituents, while

parenchyma resin is a mixture of fatty acids, waxes, sterols and fatty alcohols (Wenzyl, 1970, Browning, 1975). Complex phenolic constituents include flavanoids and tannins, which help to give Douglas-fir heartwood its characteristic pinkish color (Squire, et. al., 1967; Graham and Kurth, 1949). Flavanoids are characterized by a $C_6C_3'C_6$ carbon skeleton, and in Douglas-fir are further divided into flavanols, which possess double-bond conjugation with the carbonyl group, and flavanonols which do not (Squire, et al. 1967). Douglas-fir tannins include catechins and catechols, which may form polymers as condensed tannins (Graham and Kurth, 1949; Kennedy, 1956).

Little is known about the lignin-like incrustations which form on the cell walls of Douglas-fir heartwood. However, unlike the extractives, they cannot be removed without the use of harsh chemical reactions which also break down the lignin within the cell walls (Krahmer, and Côté, 1963). Because of their position lining the cell lumen, these incrustations are readily available to react with preservative components.

2.2. Wood Structure in Relation to ACZA Treatment

When considering preservative movement, wood can be viewed as a series of long, narrow tubes (tracheids) connected by very small openings (pit pairs). Longitudinal flow encounters less resistance than transverse flow because the liquid must pass through fewer pit pairs to move a given distance. Although longitudinal flow greatly exceeds transverse flow, most treated wood pieces (poles, lumber, etc.)

are many times longer than they are wide, and longitudinal flow from the ends of the pieces cannot penetrate sufficiently within an economical treating time. Because of this, transverse movement of preservative is almost always necessary to obtain adequate preservative penetration.

Ammoniacal preservatives are reputed to penetrate some species better than preservatives dissolved in water alone, although findings in this area sometimes conflict. One study, which compared ammoniacal copper arsenate (ACA) and chromated copper arsenate (CCA) penetration in Douglas-fir and southern pine heartwood, reported that ACA generally penetrated as well as or better than CCA (Gjovik, 1983), while another study of these same species reported that CCA penetration was generally better than ACA penetration (Weaver and Levi, 1979). ACA has been reported to penetrate western hemlock more deeply than CCA, although retentions of CCA were higher (Blew, et al., 1967). Similarly, a permeability study with thin sections of spruce sapwood concluded that an aqueous ammonia solution of copper arsenate was able to penetrate radially 3 - 5 times as quickly as waterborne CCA (Rak, 1977).

Aqueous ammonia might be expected to penetrate wood more efficiently than water alone because of ammonia's volatility and its ability to dissolve incrusting material around the pit passages (Hulme, 1979). In addition, ammonia is capable of penetrating and swelling the crystalline cellulose within the cell walls (Bariska, et al., 1969) and thus may open new avenues of preservative flow.

ACZA solutions may also be able to penetrate wet wood better than other preservatives because of ammonia's affinity for water. ACZA penetration in spruce pole sections has been positively correlated with moisture contents from below the fiber saturation point to above 75% (Rak, 1977). Retention, however, appeared to decrease slightly in samples with higher initial moisture contents. Although solution viscosity plays a major role in preservative penetration, this same study found no significant increase in penetration when the solution was heated from 49 C to 77 C (Rak, 1977).

When considering the reactions which may occur between ACZA components and the wood, it is also important to consider the availability of the various wood functional groups to the preservative components. The path of least resistance of preservative flow through wood is along the cell lumens. Thus, wood components lining the cell walls would be most available for reaction with the preservative. However, during or after the initial penetration, preservative components may begin to diffuse into the cell wall. It has been suggested that in ammoniacal formulations hydroxyl ions, accompanied by cuprammonium ions, form hydrogen bonds with the cellulose, permitting deep diffusion of copper into the cell wall (Immergut, 1963).

Cooper (1988), studied diffusion of waterborne preservative components into wood cell walls by treating small red pine and quaking aspen blocks and then pressing out excess solution at set intervals after treatment. He reported that the amount of copper in the solution expressed from treated pine dropped almost instantly to about one-half of its original level and then stabilized, suggesting that

diffusion of copper solute into the cell wall was almost immediate and greatly exceeded that of the solvent. In quaking aspen however, the drop of copper concentration in the expressed solution was much more gradual, and the copper concentration actually increased initially, suggesting that for a short time the solvent penetrated the cell wall faster than the copper. Diffusion of arsenic was much slower than copper for both species, as would be expected if cation exchange reactions within the cell wall were the driving force for the diffusion process (Cooper, 1988). In related work, scanning electron microscope energy dispersive x-ray analysis (SEM - EDXA) of thick sections cut from ACZA treated red pine blocks showed no concentration gradient of copper, zinc, or arsenic across the cell wall immediately after treatment, suggesting rapid equalization of all three elements.

2.3. ACZA Composition

2.3.1. Historical Perspective

Ammoniacal formulations have drawn interest as wood preservatives since early in the 20th century. One of the first formulations, azcol, was developed in Belgium in 1907 and patented in the US in 1910. Azcol employed a solution of phenols in an ammoniacal copper and zinc solution. Although initially expected to afford long-term protection by forming an insoluble metal precipitate, by the 1920's it had become apparent that azcol quickly lost its preservative activity (Van Groenou, et al., 1951). A solution of copper, arsenic and ammonium acetate dissolved in aqueous ammonia (Chemonite) was subsequently developed and tested at the

University of California during the mid 1920's. Copper was selected for its known fungicidal properties and arsenic as an insecticide, while ammonia provided a volatile solvent that could quickly evaporate, precipitating the toxic copper - arsenic salts in the wood. In 1925, the Chemonite was injected into living white fir trees prior to felling, and in 1934 inspectors for the Diamond Match Company noticed that these stumps and the wood chips surrounding the stumps were in unusually sound condition (Gordon, 1947). This discovery prompted construction of the first commercial Chemonite treating plant in 1935 (Gordon, 1947) and similar ACA formulations are still used commercially.

In the late 1960's and early 1970's, however, safety and environmental concerns were raised about the high levels and leachability of arsenic contained in the ACA treated wood. This concern led to research with formulations in which some of the arsenic and/or copper was replaced with zinc (Rak and Clark, 1974). Zinc has a relatively low mammalian toxicity, while still maintaining some fungitoxic properties; it is also more economical than copper or arsenic. The advantages of using zinc led to widespread use of a formulation in which one-half of the arsenic was replaced with zinc. This formulation, called ACZA, has since replaced ACA as the predominant ammoniacal formulation.

Other cation/anion mixtures dissolved in ammonium salts have been suggested, but have never gained widespread acceptance. For example, researchers have employed cadmium as a cation in ammoniacal formulations (Hulme, 1979). Although arsenic has been the favored anion, it has been completely replaced in

ammoniacal copper borate (Johnson and Gutzmer, 1978) and ammonium copper pentachlorophenate formulations (Takamoto, 1961).

2.3.2. Solution Characteristics

Two ammoniacal formulations are currently approved by the American Wood Preservers' Association for treatment of wood, ACA and ACZA (AWPA Standards, 1991). ACA is composed of 49.8% copper oxide and 50.2% arsenic pentoxide dissolved in a solution of ammonia and water. AWPA standards stipulate that the weight of the ammonia must be at least 1.5 times the weight of the copper (oxide basis) and that a maximum of 1.7% acetic acid may be added to help solubilize the copper. In the ACZA formulation, 50% CuO, 25% ZnO and 25% as As₂O₅ are dissolved in ammonia and water, with the weight of ammonia required to exceed 1.38 times the weight of CuO. In addition, ammonium bicarbonate in an amount 0.94 times the weight of the CuO must be added to maintain a solution balance between ammonium ions and ammonia, thus ensuring solubility of the toxic cations (Hulme, 1979).

Within the treating solution, copper and zinc are thought to occur primarily as tetrammine ions, although the number of water molecules replaced by ammonia groups may vary from 1 - 4, depending on the amount of ammonia in solution and the ratio of ammonia to ammonium ions (Hulme, 1979). As ammonia is lost from the solution due to evaporation, as in the treated wood, this coordination substitution gradually decreases and the metal cations become less soluble, precipitating into the wood. The pH of ACZA treating solutions, without ammonia loss, usually varies

between 10 and 12. Arsenic probably exists as H_2AsO_4^- or HAsO_4^{2-} within this pH range (Bodek, et al., 1988).

The AWPAs Standards do not instruct treaters on how to prepare these formulations, and a variety of techniques have been used in the past. Initially, copper sulphate was precipitated with sodium hydroxide, washed with water, and then stirred in with arsenic trioxide and ammonia (Anonymous, 1975). However, this formulation left residual ammonium sulfate in the wood; a compound considered undesirable because of its electrical conductivity, corrosive effects and potential leachability (Anonymous, 1975). Hydrated cupric oxide was subsequently utilized as a source of copper until the late 1960's, when its cost became prohibitive. More recently, ACA has been prepared by adding finely divided metallic copper to a solution of arsenic acid and aqueous ammonia, followed by vigorous stirring and aeration and then addition of acetic acid (Anonymous, 1975). Concentrated ACA or ACZA may be prepared by dissolving copper or zinc compounds in a mixture of concentrated aqueous ammonia and ammonium salts and then slowly adding the arsenic acid (Hulme, 1979). Ammoniacal solutions are relatively stable until the ammonia evaporates, and unlike chromated copper arsenic (CCA) formulations, the salts are not easily precipitated by reactions with wood extractives or sawdust (Hulme, 1979). These formulations also may be heated without catalyzing precipitation reactions, provided care is taken not to volatilize the ammonia (Hulme, 1979).

2.4. Application of ACZA

ACZA preservative solution is typically applied to dry, incised wood using a full cell pressure treating process. The wood is air or kiln dried before treatment to remove moisture and make room for adequate preservative penetration and retention. Pre-treatment incising has become an accepted technique to improve preservative penetration in refractory species (Nicholas, 1973). Incising is accomplished by running the wood between rollers with closely spaced teeth, thus increasing the amount of end grain exposed to preservative solution.

After drying and incising, the wood is ready for preservative treatment. ACZA treaters typically steam the wood in the treating cylinder for several hours to soften the surface and improve penetration. A full cell treating process is then used, consisting of a short vacuum period (560 mm Hg for 15 - 60 minutes) followed by a longer pressure period (2 - 24 hours at 690 - 1034 kilopascals). After the pressure period a final vacuum may be pulled to remove excess preservative and clean the wood surface. Typically, the preservative is introduced while the wood is still under a vacuum, and then the pressure is applied. Alternatively, the preservative solution may be added at the start of the treating process, and the vacuum applied with the wood immersed in solution. For species more permeable than Douglas-fir, the vacuum period may be shortened or by-passed to prevent excessive preservative retention.

The length and intensity of the pressure period varies between treating plants and is usually based on the experience of the plant operator. Penetration and

retention increase if either the amount of pressure or length of pressure period is increased, but extremely high pressures may damage the wood, while long pressure periods may be uneconomical. AWPAs Standards limit pressure used in the treatment of Douglas-fir to a maximum of 1034 kilopascals and stipulate that a minimum of 345 kilopascals should be used (AWPA, Standard C2, 1991). However, the length of the pressure period is not stipulated; the wood-treater must simply obtain adequate treatment. Previous studies have shown that moderate pressures and relatively long pressure periods generally produce better treatments than short treatments at high pressure, although increases in absorption become minimal after prolonged pressure periods (Hunt and Garrett, 1967).

Combined retentions of copper oxide, zinc oxide, and arsenic pentoxide within the treated zone of the wood vary between 4 and 40 kg/m³, depending on the intended use of the end product. Required penetrations also vary, depending on the product and the species. Penetration in Douglas-fir lumber, for example, must exceed only 1 cm, while penetration in Douglas-fir piling must exceed 1.9 cm or 85% of the sapwood depth (AWPA Standards, 1991).

2.5. ACZA Fixation

The term "fixation" as used in the field of wood preservation refers to the mechanism by which preservative components become stabilized in the wood to resist leaching by rain or ground water. The basic premise of fixation in ammoniacal formulations is that the toxic compounds are water-soluble only when

the solution contains sufficient ammonia. Once the ammonia evaporates, the salts are precipitated onto the surface of the wood. In ACZA, the copper and zinc cations and arsenic anion are thought to precipitate as metal arsenates (Nicholas, 1973). Thus, although they are not actually bonded to the wood, they are no longer soluble in rain or ground water at ordinary pHs.

The theory of ACZA fixation described above implies that no interactions take place between the ACZA and the wood substrate. However, previous studies of ACZA and other preservatives containing copper suggest that copper undergoes some type of adsorption reaction with the wood substrate (Cooper, 1991; Dahlgren, 1972; Pizzi, 1982). In a recent study of copper adsorption from ACA, ACZA, and other copper salts, it was found that up to 10 mg of copper was adsorbed per gram of pine or aspen sapwood sawdust (Cooper, 1991). Zinc and arsenic were also adsorbed, but to a lesser degree than copper, and their presence reduced the amount of copper adsorption. Copper adsorption was reported to be highly pH dependent, possibly due to an increased capacity for the wood to undergo cation exchange reactions at higher pHs. In these types of reactions, weak acid groups in the wood are dissociated, exposing anions which could react with the positively charged copper or zinc amine ions. This type of reaction does not explain the adsorption of the anionic arsenic, which was attributed to complexation with positively charged copper ions already fixed to the wood (Cooper, 1991). Cuprammonium ions have also been reported to absorb to wood or cellulose in other studies, although these tests did not specifically measure copper adsorption from ACZA solutions (Hulme, 1979).

More evidence for copper adsorption exists in research examining the fixation of chromated copper arsenate (CCA) in wood. Although the pH of CCA preservatives is much lower than that of ACZA, this work may still be pertinent since adsorption appears to increase with increasing pH (Cooper, 1991; Rennie, et al., 1987). Several researchers have noted the rapid adsorption of copper from CCA treating solutions (Dahlgren and Hartford, 1972; Pizzi, 1982; Wilson, 1971). One study reported that 40 - 50% of the copper in CCA was fixed directly to the wood substance (Eadie and Wallace, 1962), while others have reported that 5-20% of the copper was adsorbed to wood (Kubel and Pizzi, 1982) and that 32% of a copper sulphate solution resisted leaching from treated sawdust within one hour of treatment (Gray and Dickinson, 1988). As in ACZA, copper adsorption from CCA has been attributed to an acid form ion-change mechanism in which an H^+ from an acid site is displaced by a Cu^{2+} cation (Rennie, et al., 1987).

Further evidence of copper adsorption is provided by evidence of unequal preservative composition within the treated wood. As the preservatives move through the wood, some components may penetrate more quickly or completely than others, resulting in a phenomenon sometimes called "screening". Screening may be caused by reactions of preservative components with the wood as the preservative moves through minute flow paths. If screening occurs, the distribution and fixation of toxic constituents within the wood can be significantly altered. Although copper screening has been reported for CCA formulations (Levy and Greaves, 1978; Cech, et al., 1974), it is not well established in ACZA treatments. It has been suggested

that the large number of ammonium ions in ACZA compete for copper with ion-exchange reactions sites within the wood, thus reducing screening (Hulme, 1979). However, researchers conducting ACA treatments of Douglas-fir heartwood noted that the copper appeared to be deposited near the surface while the arsenic penetrated much more deeply (Weaver and Levi, 1979). In addition, other work employing X-ray analysis at successive depths into ACA treated spruce poles found that the ratio of copper to arsenic declined rapidly as the distance from the wood surface increased (Ruddick, 1979). Factors that might influence the amount and type of screening in ACZA treatments remain largely unexplored.

Some researchers have also proposed possible bonding sites for copper during ACZA or CCA treatment. In some of the earlier studies cellulose was postulated as the likely site for copper adsorption from CCA (Belford, et al., 1957; Eadie and Wallace, 1962), although concurrent research suggested that the carboxylic acid groups of the hemicelluloses were a more likely reaction site (Bayley and Rose, 1960; Knight, et al., 1961). More recently, however, studies have demonstrated that lignin adsorbs copper from CCA (Pizzi, 1982; Gray and Dickinson, 1988; Rennie, et al., 1987).

As noted by Cooper (1991) and others (Rennie, et al., 1987; Pizzi, 1982), the sites of ion exchange may vary with pH. Thus at low pHs the uronic acids in hemicelluloses may be the primary sites of ion exchange, but other cell wall constituents such as carbonyl groups, methoxy groups, and hydroxyl groups may dissociate and become potential ion exchange sites as the pH increases. Once the pH

exceeds 7, copper may complex with the ortho-dihydroxy phenols and ortho-hydroxymethyl phenols in wood extractives and lignin (Pizzi, 1982). Most of the functional groups in lignin would become dissociated and possible ion exchange sites at the pH's typical of ACZA treatment (Cooper, 1991). However, the actual site(s) of copper adsorption in ACZA treated wood have yet to be investigated.

Further insight into the form in which copper is deposited in treated wood has been provided by recent studies using electron paramagnetic resonance (EPR) analysis. EPR spectroscopy is a technique which can be used to study the bonding environment of materials, such as copper, which have an unpaired electron. The manner in which this unpaired electron absorbs energy from an applied magnetic field is influenced by the presence and type of bonds to the copper atom. Although this type of study is relatively new in wood preservation, and has been concentrated on CCA formulations, one study did include an ammoniacal copper complex. In this work it was noted only that copper in the treated wood did not appear to be bonded to nitrogen (Hughes, et al., 1992). This study did not address the effects of zinc or arsenic in the formulation, or the possibility of copper adsorption to the wood. Further work in this area may provide much needed information about the nature of copper adsorption in ACZA treated wood.

Although copper has been shown to adsorb from CCA and ACZA onto the wood substrate, much less is known about such reactions involving zinc or arsenic. Only Cooper (1991) has employed this type of analysis for ACZA, and researchers working with CCA have not noted arsenic adsorption that is independent of reactions

with chrome or copper. Because zinc is not present in CCA, the study of this metal's adsorption reactions with wood have been limited.

Further information about the fixation of ACZA has also been gained by analysis of leachate from wood treated with various ACZA formulations. In work that helped establish the use of zinc in ACZA, Canadian researchers treated white spruce with ammoniacal solutions containing varying ratios of copper, zinc, and arsenic, leached the treated wood, and then analyzed the leachate for preservative components (Rak and Clark, 1974; Rak, 1976). This study reported that copper and zinc were highly leach resistant regardless of formulation, but that arsenic fixation was dependent on the presence and amount of metal cations. Even when metal oxide and arsenic oxide were added in stoichiometric amounts the arsenic still leached significantly; a metal oxide:arsenic oxide ratio exceeding 2.0 was needed to minimize arsenic leaching. In addition, it was reported that replacing a portion of the copper with zinc reduced arsenic leachability. Very similar results were reported in a later leachability study of various ACZA formulations (Best and Coleman, 1981). Both of these studies support the premise of arsenic fixation through the formation of a water insoluble copper or zinc arsenate precipitate.

In addition, however, the results of these studies complement those from the adsorption studies discussed above. It appears that a much larger proportion of the copper and zinc are adsorbed to the wood than arsenic, and are no longer available to precipitate the arsenic in the wood. Thus, additional metal cation is needed in the formulation to prevent leaching of arsenic. This problem decreases as preservative

concentration increases, possibly because smaller proportions of the toxic cations are tied up on adsorption sites in the wood (Johnson and Gutzmer, 1978; Hulme, 1979).

2.6. Summary

The use of water-borne preservatives to protect wood from decay and insect attack is likely to increase as environmental concerns further restrict the use of oil-borne preservatives. ACZA will probably be the preservative of choice for difficult to treat species such as Douglas-fir, because the ammonia allows better penetration than can be achieved with CCA. However, little work has been done to determine the mechanism which stabilizes or "fixes" the toxic components of ACZA in the wood to prevent leaching into rain or ground water. Although ACZA formulations have provided excellent service to this point, a better understanding of the fixation mechanisms is needed as the use of ACZA increases.

One reason that ACZA fixation mechanisms are so poorly understood is that wood is an extremely complex reaction substrate. Wood contains cellulose, hemicellulose, and lignin in varying concentrations across the cell wall, as well as phenolic incrustations lining the heartwood cells. In addition, there are resinous and phenolic extractives whose concentration and composition vary between and within the sapwood and heartwood. Preservatives flowing and diffusing through the wood structure may contact all or none of these components.

Past concerns over leaching of ammoniacal preservatives led to development of the current ACZA formulation. Leaching studies have shown that while copper

and zinc are fairly leach resistant regardless of the ACZA formulation, arsenic requires more than a stoichiometrically equivalent amount of metal cations in the wood for fixation. These results lend credence to the basic premise of ACZA fixation; that water insoluble copper arsenate and zinc arsenate precipitates form as ammonia evaporates. However, this premise implies that no interaction with the wood substrate occurs, a position which is contradicted by studies reporting that wood adsorbs copper from ACZA solutions. The reaction sites for this copper adsorption have not been studied for ACZA, but at the pHs prevalent during ACZA treatment many constituent groups in the wood could become active ion exchangers.

It is apparent that some reactions between the preservative and the wood do occur. More research is needed to determine the nature of these reactions, and the reactive sites within the wood. In addition, further studies are needed to determine if precipitation reactions are the sole mechanism of zinc and arsenic fixation. The results of such studies will improve our knowledge of fixation mechanisms for ammoniacal based inorganic arsenicals, and will answer essential questions concerning the resistance of these compounds to leaching during service.

3.0.

OBJECTIVE

Clarify the mechanisms which stabilize copper, zinc, and arsenic within ACZA treated Douglas-fir.

4.0. EXPERIMENTAL

4.1. Effect of ACZA Composition on Fixation

4.1.1. Introduction

One step in understanding ACZA fixation mechanisms is to determine how copper, zinc and arsenic interact to resist leaching. This facet was studied by treating Douglas-fir heartwood and sapwood sawdust with varying ratios of copper, zinc, and arsenic, leaching the wood and comparing the levels of these elements in leachate to those in the original treating solution.

4.1.2. Materials and Methods

One hundred sixty cubes (1.5 cm) were cut from adjacent heartwood and sapwood zones on each of four Douglas-fir (Psuedotsuga menziesii (Mirb.) Franco) boards and conditioned to 10% moisture content. ACZA solutions (Table 4.1.1.) were prepared by adding solutions of cupric carbonate, zinc oxide, or arsenic acid to a commercial ACZA solution which contained 50% CuO, 25% ZnO and 25% As₂O₅. ACA solutions were also prepared from cupric carbonate and arsenic acid solutions. The arsenic acid was purchased as a 62% solution, while concentrated zinc oxide or cupric carbonate solutions were prepared by stirring the metal powder and ammonium bicarbonate powder into a solution of ammonium hydroxide and water. Air was bubbled through the mixing flask to aid in solubilizing the metal powders. For both ACA and ACZA solutions, ammonium hydroxide was added so that the weight of ammonia was equal to 1.38 the weight of the metal oxide, while

ammonium bicarbonate was added at rate of 0.92 times the weight of the metal oxide. Concentrations of the active ingredients in the solutions were determined using an ASOMA 8620 X-ray Fluorescence Analyzer (XRF). Overall solution concentrations were adjusted to 2.65% (oxide basis).

Eight heartwood or sapwood cubes were treated with each preservative formulation; two cubes from each of the original four boards were combined in each treatment group. The treatments were replicated four times. The cubes were pressure treated using a full cell process in which an initial vacuum (635 mm Hg) was applied to the dry cubes for 1/2 hour and then 100 grams of solution was drawn, under vacuum, into the treatment flask. Stainless steel weights were used to ensure that the blocks remained submerged in treating solution. Immediately following addition of the preservative solution, the vacuum was released and the treatment flasks were placed into the treating cylinder and subjected to 862 kilopascals of pressure for 30 minutes.

The treated cubes were air dried for 10 days, and then split along the grain into six 0.25 cm thick wafers to increase the exposure of tangential surfaces and promote leaching of preservative components. One-third of the wafers in each group were randomly selected, combined, ground to pass through a 30 mesh screen, and analyzed using x-ray fluorescence spectroscopy to determine the preservative content in the wood. The remaining wafers were placed in 250 ml glass bottles and submerged in 70 mls of distilled water with stainless steel weights. The bottles were then subjected to 1/2 hour of vacuum (635 mm Hg) to saturate the

wood, and placed on a wrist shaker for 72 hours of mild agitation. Following agitation, the leachate was drained from the wafers, filtered to remove particulate matter, and analyzed for copper, zinc, and arsenic using atomic absorption spectroscopy.

Table 4.1.1. Ratio of CuO:ZnO:As₂O₅ in ACZA or ACA treating solutions and Douglas-fir heartwood or sapwood treated with these solutions.

| TREAT SOLUTION | | | HEARTWOOD | | | SAPWOOD | | |
|----------------|------|--------------------------------|-----------|------|--------------------------------|---------|------|--------------------------------|
| Ratio | | | Ratio | | | Ratio | | |
| CuO | ZnO | As ₂ O ₅ | CuO | ZnO | As ₂ O ₅ | CuO | ZnO | As ₂ O ₅ |
| ACZA | | | | | | | | |
| 0.25 | 0.25 | 1.00 | 0.35 | 0.25 | 1.00 | 0.31 | 0.25 | 1.00 |
| 0.50 | 0.50 | 1.00 | 0.88 | 0.56 | 1.00 | 0.81 | 0.57 | 1.00 |
| 0.75 | 0.75 | 1.00 | 1.28 | 0.84 | 1.00 | 1.25 | 0.88 | 1.00 |
| 1.00 | 1.00 | 1.00 | 1.58 | 1.27 | 1.00 | 1.44 | 1.26 | 1.00 |
| 2.00 | 2.00 | 1.00 | 3.21 | 2.93 | 1.00 | 2.87 | 2.80 | 1.00 |
| ACA | | | | | | | | |
| 0.50 | 0 | 1.00 | 0.62 | 0 | 1.00 | 0.56 | 0 | 1.00 |
| 1.00 | 0 | 1.00 | 1.38 | 0 | 1.00 | 1.27 | 0 | 1.00 |
| 1.50 | 0 | 1.00 | 2.13 | 0 | 1.00 | 2.03 | 0 | 1.00 |
| 2.00 | 0 | 1.00 | 2.70 | 0 | 1.00 | 2.57 | 0 | 1.00 |
| 4.00 | 0 | 1.00 | 6.14 | 0 | 1.00 | 5.67 | 0 | 1.00 |

4.1.3. Results and Discussion

X-ray fluorescence analysis suggested that the ratios of preservative components in the treated wood differed from those in the treating solution (Table 4.1.1.). Statistical analysis of these differences (t-tests, 99% confidence) confirmed

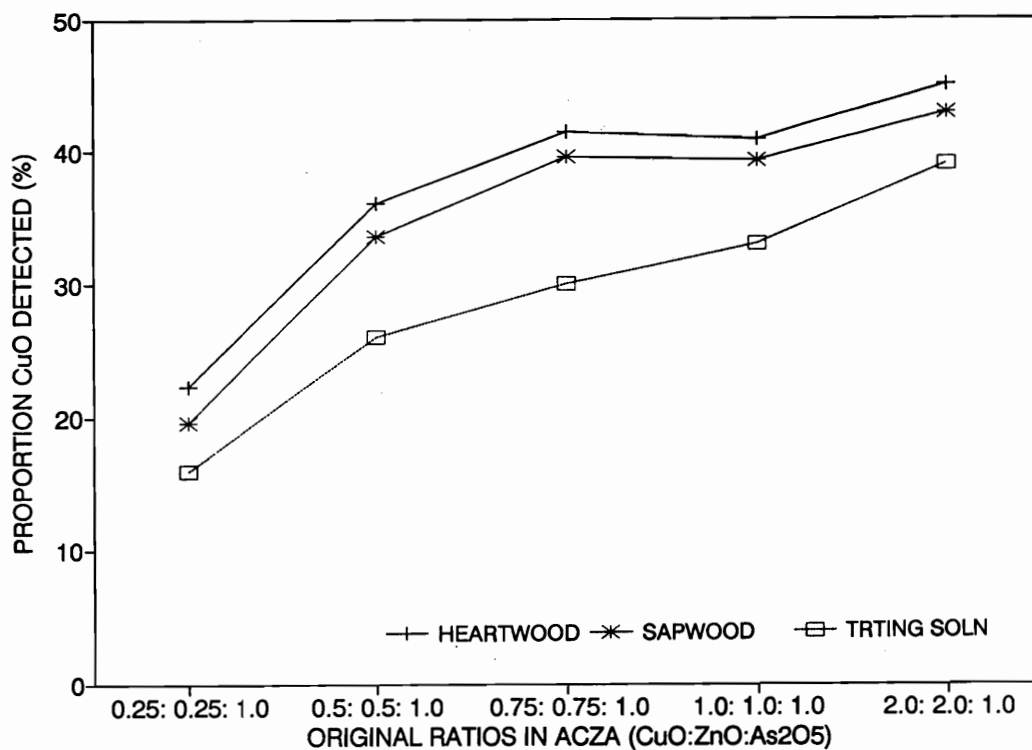
that both heartwood and sapwood contained a significantly higher proportion of CuO than the original treatment solutions, with a corresponding significant decrease in the proportion of As₂O₅. The increased CuO levels in the wood probably reflect copper adsorption by the wood substrate. Previous studies have demonstrated that wood adsorbs copper from ammoniacal wood preservatives (Cooper, 1991).

Although adsorption trends were similar for both heartwood and sapwood, CuO loading appeared to be higher in the heartwood (Figure 4.1.1.). The increased CuO adsorption in the heartwood suggests that complexes with extractives or the phenolic incrustations on the cell walls may represent a fixation mechanism. This possibility will be addressed more thoroughly in later sections.

Both copper and zinc were highly resistant to leaching, regardless of preservative formulation (Figures 4.1.2., 4.1.3.), while the leach resistance of arsenic was strongly influenced by preservative formulation. These results concur with previous studies of ACZA leaching from spruce (Rak, 1976) or ponderosa pine (Best and Coleman, 1981). Both of these studies reported that zinc and copper were leach resistant regardless of formulation, while arsenic fixation was highly dependent on the amount and type of cation. The leach resistance of copper and zinc may result from reactions with wood components, but probably also reflects the low water solubility of these metals at moderate pHs.

Maximum copper leaching, on a percentage basis, occurred when the formulations included zinc and contained the least copper (Table 4.1.2.). These trends were especially evident in the Douglas-fir heartwood, where copper leaching

A.



B.

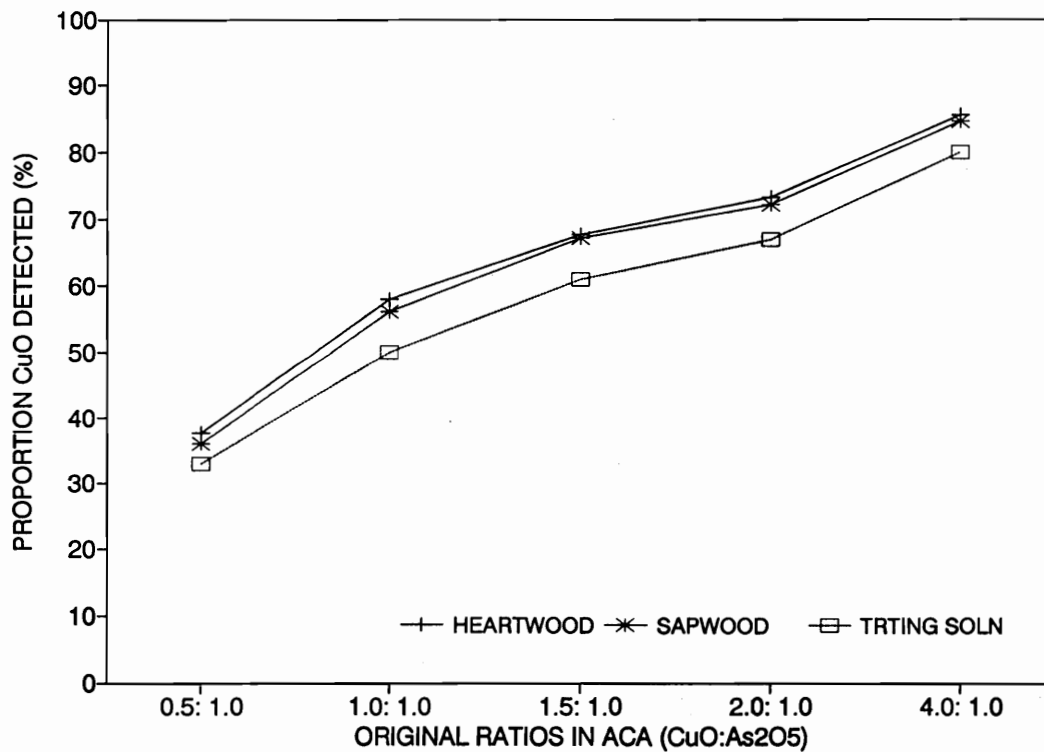


Figure 4.1.1. Proportion of CuO in original treating solutions and treated Douglas-fir heartwood and sapwood for A.) ACZA or B.) ACA treatments.

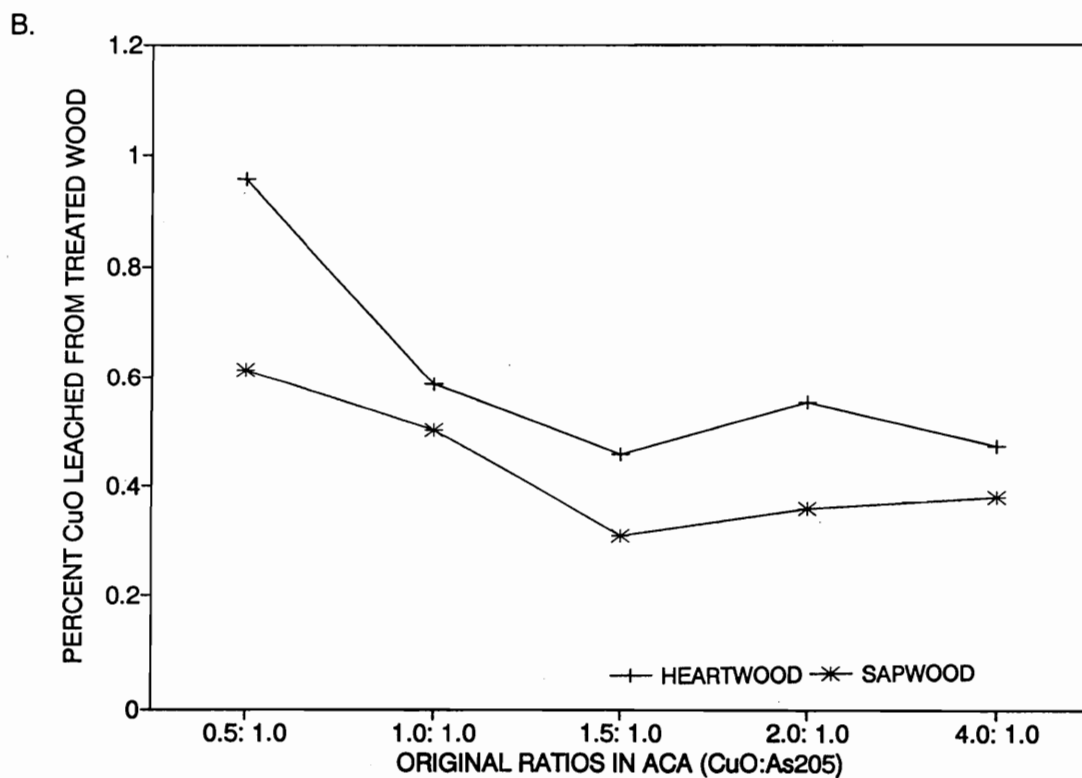
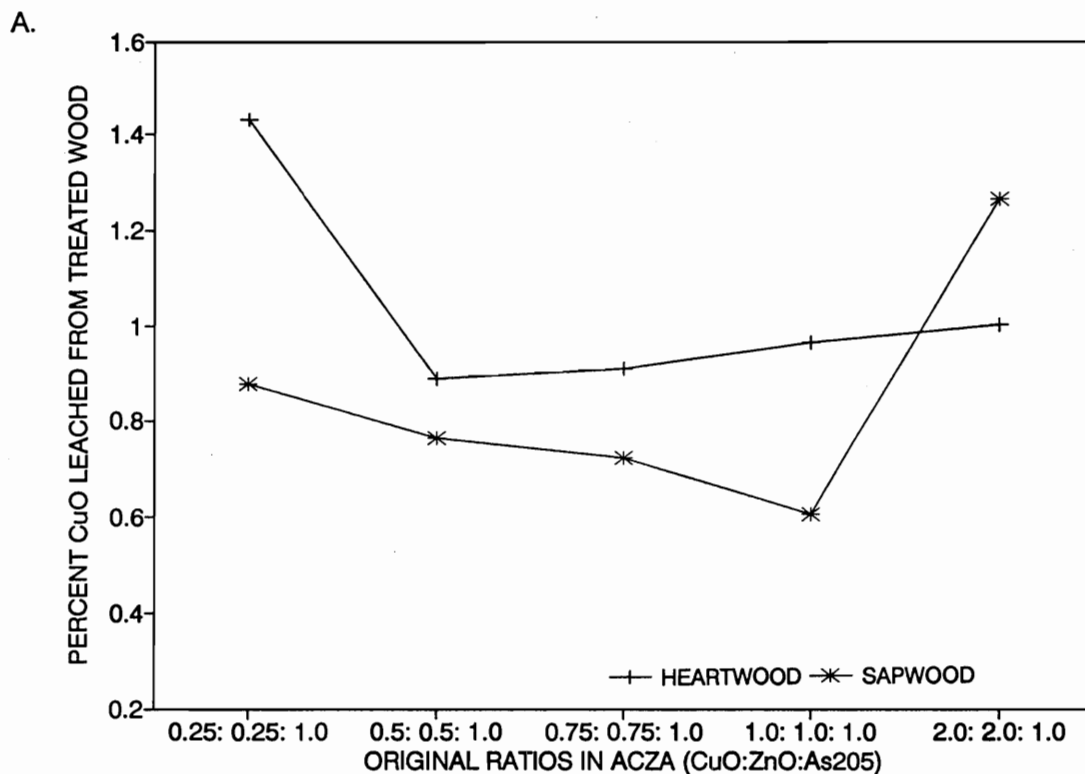


Figure 4.1.2. Percentage of copper leached from Douglas-fir heartwood and sapwood following treatment with A.) ACZA or B.) ACA.

was highest in the ACZA formulation with the least copper ($\text{CuO}:\text{ZnO}:\text{As}_2\text{O}_5$ ratio = 0.25:0.25:1). The increased leaching at lower concentrations suggests that copper leaching is more strongly influenced by water solubility than by interactions with the wood. However, with the exception of the ACA formulation containing the least copper, copper leaching was significantly higher from ACZA solutions than ACA solutions. This result suggests that zinc interfered with copper fixation, perhaps by competing for bonding sites within the wood. Copper leaching from sapwood was also greater from ACZA than ACA treated wood, except in the case of the ACA solution containing the lowest copper concentration. However, copper concentration appeared to have less of an effect on leaching in sapwood. The percentage copper leached was consistently higher from the heartwood than sapwood, although this difference was only statistically significant for six of the formulations tested. This trend may be due to loss of copper bonded to water-soluble heartwood extractives.

Zinc was highly leach-resistant, never exceeding 0.5% of that deposited in the wood (Figure 4.1.3.). Zinc fixation was not significantly influenced by formulation in the heartwood tests, but in the sapwood trials the two formulations containing the least zinc leached at a significantly higher rate (Table 4.1.3.). This trend may have been caused by the increased proportion of water soluble zinc at lower solution concentrations. The absence of such a trend in the heartwood treatments suggests that other factors, such as leaching of zinc complexed with water soluble extractives, also contributed to the leaching of zinc.

Table 4.1.2. Effect of ACZA of ACA formulation on leaching of copper from Douglas-fir heartwood or sapwood.

| HEARTWOOD | | SAPWOOD | |
|--|--------------------------------|--|--------------------------------|
| SOLUTION RATIOS | AVERAGE % LEACHED ^a | SOLUTION RATIOS | AVERAGE % LEACHED ^a |
| CuO:ZnO:As ₂ O ₅ | | CuO:ZnO:As ₂ O ₅ | |
| 1.50: 0 :1.00 | 0.46 a | 1.50: 0 :1.00 | 0.31 a |
| 4.00: 0 :1.00 | 0.47 a | 2.00: 0 :1.00 | 0.36 a |
| 2.00: 0 :1.00 | 0.55 a | 4.00: 0 :1.00 | 0.38 a |
| 1.00: 0 :1.00 | 0.59 a | 1.00 : 0 :1.00 | 0.50 ab |
| 0.50:0.50:1.00 | 0.89 b | 1.00:1.00:1.00 | 0.61 bc |
| 0.75:0.75:1.00 | 0.91 b | 0.50: 0 :1.00 | 0.73 bc |
| 0.50 : 0 :1.00 | 0.96 b | 0.75:0.75:1.00 | 0.77 cd |
| 1.00:1.00:1.00 | 0.96 b | 0.50:0.50:1.00 | 0.83 cd |
| 2.00:2.00:1.00 | 1.00 b | 0.25:0.25:1.00 | 0.88 d |
| 0.25:0.25:1.00 | 1.44 c | 2.00:2.00:1.00 | 1.26 e |

a. Values followed by the same letter are not significantly different using Duncan's Multiple Range test at $\alpha = 0.05$.

Table 4.1.3. Effect of ACZA formulation on leaching of zinc.

| HEARTWOOD | | SAPWOOD | |
|--|--------------------------------|--|--------------------------------|
| SOLUTION RATIOS | AVERAGE % LEACHED ^a | SOLUTION RATIOS | AVERAGE % LEACHED ^a |
| CuO:ZnO:As ₂ O ₅ | | CuO:ZnO:As ₂ O ₅ | |
| 2.00:2.00:1.00 | 0.28 a | 1.00:1.00:1.00 | 0.14 a |
| 1.00:1.00:1.00 | 0.29 a | 2.00:2.00:1.00 | 0.15 a |
| 0.50:0.50:1.00 | 0.30 a | 0.75:0.75:1.00 | 0.18 a |
| 0.25:0.25:1.00 | 0.31 a | 0.25:0.25:1.00 | 0.34 b |
| 0.75:0.75:1.00 | 0.31 a | 0.50:0.50:1.00 | 0.50 c |

a. Values followed by the same letter are not significantly different using Duncan's Multiple Range Test at $\alpha = 0.05$.

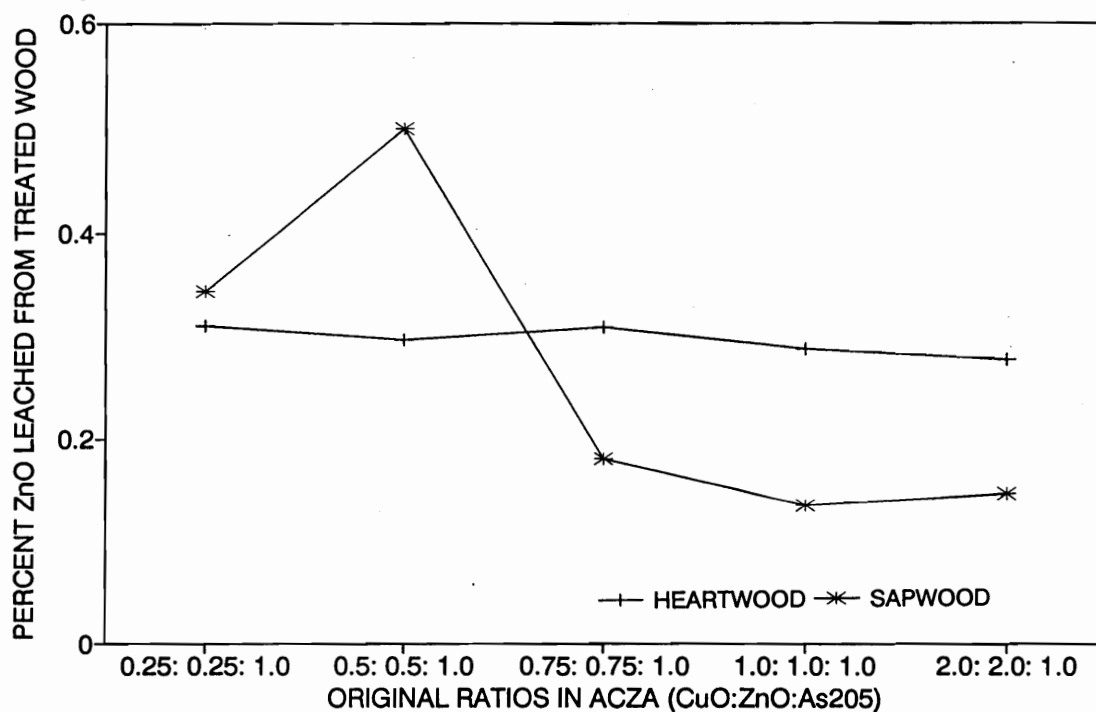


Figure 4.1.3. Percentage of zinc leached from Douglas-fir heartwood and sapwood treated with ACZA solutions of varying component ratios.

The degree of arsenic leaching was highly dependent on the presence of metal cations which appeared to stabilize this component in the wood. The

percentage of arsenic (as As_2O_5) leached ranged from over 60% down to almost zero, depending on the cation:anion ratio, the type of cation, and whether sapwood or heartwood was treated (Figure 4.1.4.). Arsenic leaching from sapwood samples treated with solutions containing zinc was virtually eliminated when the metal oxide:arsenic pentoxide ratio exceeded 1.5:1. However, arsenic losses from heartwood samples were not minimized until the cation:anion ratio exceeded 2:1. These findings are in general agreement with previous studies of leaching of ACZA from spruce, where arsenic leaching was minimized when the metal oxide:arsenic oxide ratio in the treating solution exceeded 2:1 (Rak, 1976).

Solutions containing copper as the sole cation were less effective in fixing the arsenic, especially in the heartwood treatments, where 15% of the arsenic continued to leach at a 2:1 copper oxide:arsenic pentoxide ratio. In several cases, formulations without zinc leached as much arsenic as ACZA formulations containing only one-half the total metal oxide (Table 4.1.4.). For example, the ACZA formulation with a 1:1:1 $\text{CuO}:\text{ZnO}:\text{As}_2\text{O}_5$ ratio provided as much arsenic leach resistance as an ACA formulation with a 4:1 $\text{CuO}:\text{As}_2\text{O}_5$ ratio. Arsenic leaching from the sapwood was also minimized at higher copper levels with ACA, but fixation was considerably better in the presence of zinc. Other researchers have suggested that the availability of copper to complex with and precipitate arsenic may be reduced by competitive adsorption reactions which tie-up the copper within the wood (Hulme, 1979). Arsenic leaching appeared to be higher from heartwood than sapwood for all the formulations tested, although these differences were only

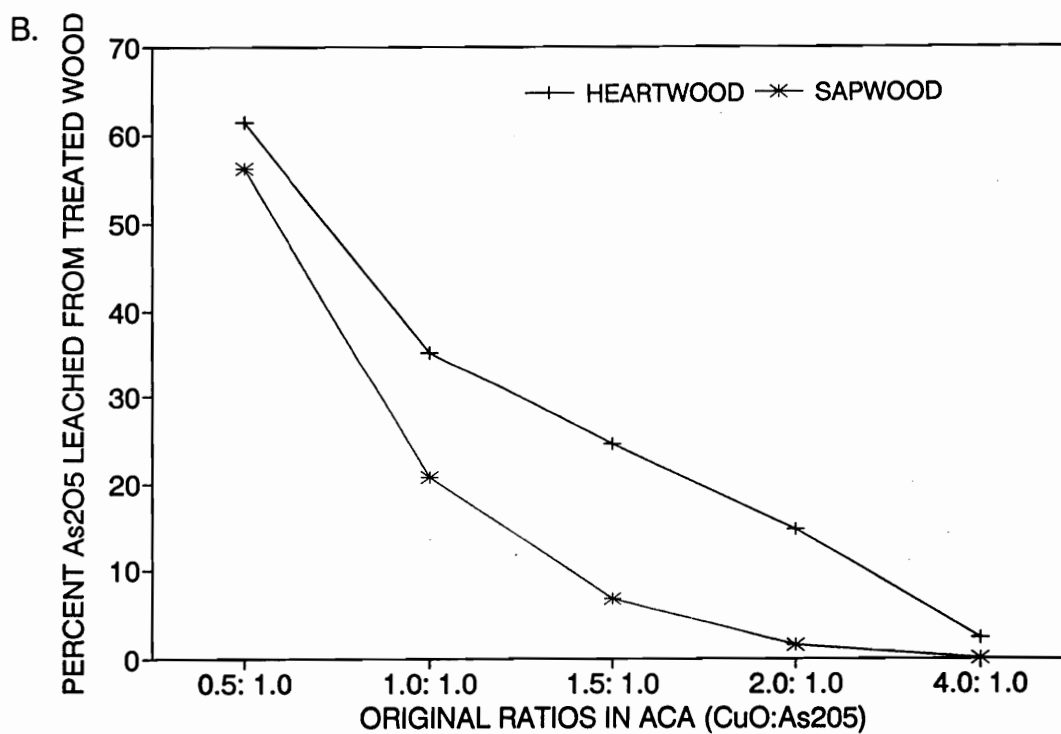
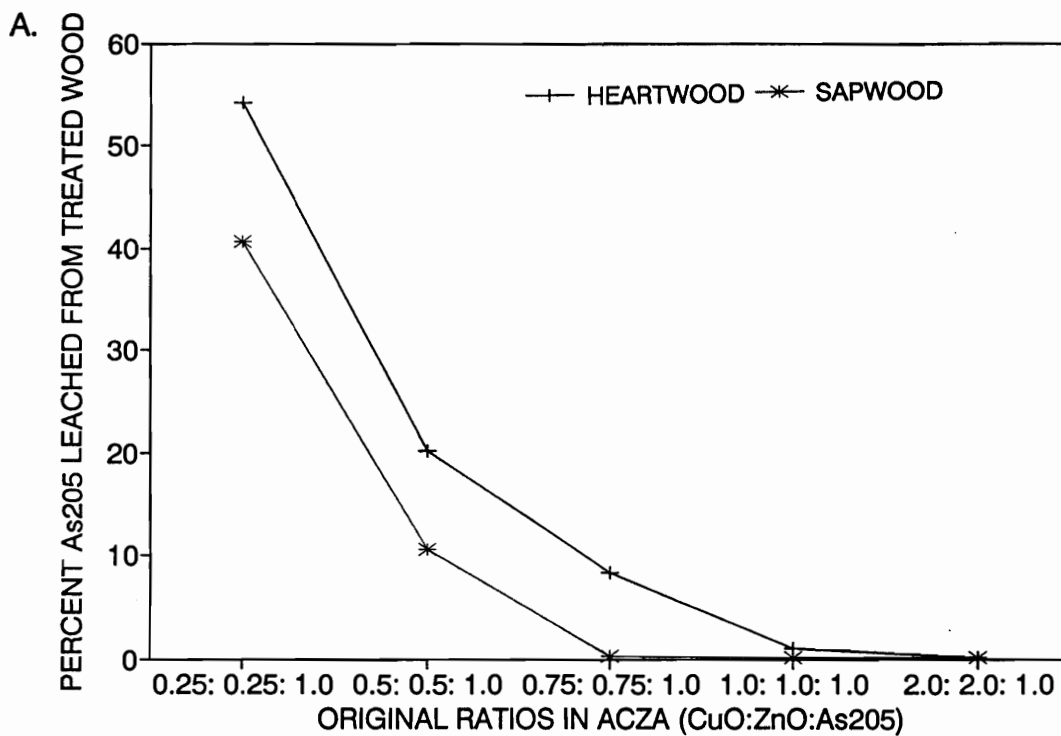


Figure 4.1.4. Percentage of arsenic leached from Douglas-fir heartwood and sapwood treated with A.) ACZA or B.) ACA.

significant in eight treatments (Table 4.1.4.). This increased rate of arsenic leaching from the heartwood might also be attributed to competitive adsorption reactions which reduced the availability of copper, since the heartwood adsorbed more copper from the treating solution than did the sapwood. Alternatively, the increased arsenic leaching from heartwood could reflect the bonding of arsenic to copper which has complexed with water soluble heartwood extractives.

Table 4.1.4. Effect of ACZA or ACA formulation on leaching of arsenic from Douglas-fir heartwood or sapwood.

| SOLUTION RATIOS | AVERAGE % LEACHED ^a | |
|--|--------------------------------|----------------------|
| | HEARTWOOD | SAPWOOD ^b |
| CuO:ZnO:As ₂ O ₅ | | |
| 2.00:2.00:1.00 | 0.16 a | 0.13 a |
| 1.00:1.00:1.00 | 1.09 ab | 0.12 a * |
| 4.00: 0 :1.00 | 2.26 ab | 0.12 a * |
| 0.75:0.75:1.00 | 8.36 bc | 0.31 a * |
| 2.00: 0 :1.00 | 14.84 cd | 1.51 a * |
| 0.50:0.50:1.00 | 20.20 de | 10.56 a * |
| 1.50: 0 :1.00 | 24.63 e | 6.66 a * |
| 1.00: 0 :1.00 | 35.22 f | 20.76 b * |
| 0.25:0.25:1.00 | 54.13 g | 40.58 c * |
| 0.50: 0 :1.00 | 61.51 h | 56.21 d |

a. Values followed by the same letter are not significantly different using Duncan's Multiple Range Test at $\alpha = 0.05$.

b. Values followed by an asterisk are significantly different from those in heartwood using Duncan's Multiple Range Test at $\alpha = 0.05$.

4.2. Role of Wood Components in Fixation

4.2.1. Introduction

Although ACZA fixation is believed to be primarily a precipitation process (Nicholas, 1973), the initial results of this study suggest that copper adsorbs to the wood substrate. The purpose of this test was to determine whether selected wood components were involved in adsorption of copper, zinc, or arsenic.

4.2.2 Materials and Methods

Wood is composed of three major constituents: cellulose, hemicellulose (or polyoses), and lignin (Panshin and de Zeeuw, 1980). Douglas-fir also exhibits distinct differences between the heartwood and sapwood, partially due to the presence of phenolic incrustations on the cell walls (Krahmer and Côté, 1963). In this test cellulose, lignin, Douglas-fir heartwood and sapwood, and a polyose model compound, xylan, were exposed to the ACZA solution. The Douglas-fir heartwood and sapwood were cut from the same boards used in Section 4.1. The cellulose, lignin, and xylan were obtained from outside sources due to difficulty in extracting sufficient quantities of these constituents from wood in an unaltered form.

Organosolve lignin was used because the aqueous ethanol extraction process minimizes alterations in lignin structure relative to conventional industrial pulping techniques (Lora, et al., 1988). Although the molecular weight of this organosolve lignin averages less than 1000, many of the constituent groups present in native lignin (as represented by milled wood lignin) are preserved (Lora, et al., 1988).

Only spruce organosolve lignin was available, but this was considered acceptable as

differences between softwood lignins are minor (Sarkanen, et al., 1976b). The xylan, derived from oat spelt, was composed of xylose, arabinose, and glucuronic acid units. The lignin, cellulose, xylan, heartwood and sapwood were all ground to pass through a 60 mesh screen prior to use.

An ACZA solution containing 0.752% copper oxide, 0.385% zinc oxide, and 0.372% arsenic pentoxide was used in this test. Approximately 5 grams of each wood substrate was weighed (0.01g) and added to a 125 ml flask. Approximately 50 grams of preservative solution was weighed (0.01g) into the flasks, which were tightly stoppered and agitated on a wrist-shaker for 10 minutes, 40 minutes, 90 minutes, 20 hours, or 74 hours. Following agitation, the wood substrate in the flasks was allowed to settle for 5 minutes and then approximately 20 grams of the preservative solution was decanted and filtered twice through glass fiber filters. The preservative was then analyzed by XRF to determine the level of copper, zinc, and arsenic remaining in solution. Differences in copper, zinc and arsenic concentration in the original and used solutions were presumed to reflect adsorption to the test substrate. Each substrate/time combination was evaluated on three replicates.

Because xylan does not represent all of the principle constituents of Douglas-fir polyoses, such as the mannans, a subsequent adsorption test was conducted using polyoses extracted from Douglas-fir sapwood. To extract the polyoses, 20 grams of wood flour (ground to pass a 40 mesh screen) and 300 mls of distilled water were combined in a 500 ml erlenmeyer flask and heated to 90 C.

Five mls of a 10% acetic acid solution were added, followed by 4.5 grams of sodium chlorite. A 125 ml erlenmeyer flask was inverted over the mouth of the 500 ml flask to trap escaping vapors. The flask was continually stirred and at 15 minute intervals additional dosages of acetic acid and sodium chlorite were added. After 90 minutes, the mixture was filtered and the resulting holocellulose solids washed with distilled water and then methanol. The holocellulose was air dried, and then stirred for one hour with 300 mls of 17.5% aqueous NaOH to solubilize the polyose components. The mixture was filtered, and the filtrate neutralized to pH = 6 with 50% acetic acid and then stirred into a 2000 ml erlenmeyer flask containing 1200 mls of methanol. The polyose components were allowed to precipitate for 2 hours and then filtered out of the methanol solution and oven dried (50 C) for 16 hours. The approximately five grams of dried polyose solids obtained from this procedure were then ground to pass through a 60 mesh screen.

The adsorption test procedure was modified from that described above to compensate for the limited quantity of polyoses available. Approximately 1 gram of the polyoses was weighed (.001 g) into each of three 20 ml scintillation vials, and 12 grams of an ACZA solution (0.346% CuO, 0.175% ZnO, 0.171% As₂O₅) was weighed (0.01 g) into each vial. The vials were then sealed and agitated on a wrist-shaker for 74 hours to allow adsorption reactions to proceed. Following agitation, the solids in the vials were allowed to settle for 24 hours and then approximately 8 mls of the preservative solution was decanted, filtered, and analyzed as described above.

4.2.3. Results and Discussion

Substantial copper and lesser amounts of zinc were adsorbed onto some wood substrates (Figure 4.2.1). Lignin was a particularly effective reaction substrate, adsorbing significantly more copper and zinc than the other wood constituents (Tables 4.2.1., 4.2.2.). Heartwood also adsorbed significantly more copper than did sapwood, xylan, the polyoses or cellulose, but was not especially effective in adsorbing zinc. In contrast, xylan adsorbed significantly more zinc than heartwood after 40 minutes and 74 hours, and zinc adsorption by sapwood exceeded that by heartwood after 20 hours. Adsorption of zinc by the polyoses was much lower than that by xylan, and very similar to that of the sapwood. These results suggest that copper and zinc do not always compete for the same reaction sites within the wood, and that xylan possesses more reactive sites than the polyoses as a whole.

Table 4.2.1. Effect of wood component and exposure time on adsorption of copper from ACZA solution.

| | AVERAGE COPPER ADSORPTION ^a (mg/g substrate) | | | | |
|-----------|---|--------|--------|--------|---------|
| SUBSTRATE | 10 MIN | 40 MIN | 90 MIN | 20 HRS | 74 HRS |
| CELLULOSE | 1.1 a | 2.6 a | 1.1 a | 1.9 a | 2.5 a |
| POLYPOSES | - | - | - | - | 4.4 b |
| SAPWOOD | 5.6 b | 7.6 b | 7.0 b | 8.6 b | 8.2 b |
| XYLAN | 8.4 c | 9.2 c | 8.9 b | 9.2 b | 11.0 bc |
| HEARTWOOD | 12.8 d | 14.4 d | 13.0 c | 13.9 c | 14.5 c |
| LIGNIN | 14.5 d | 18.2 d | 19.1 d | 25.1 d | 27.7 d |

a. Values followed by the same letter are not significantly different using Duncan's Multiple Range Test at $\alpha = 0.05$.

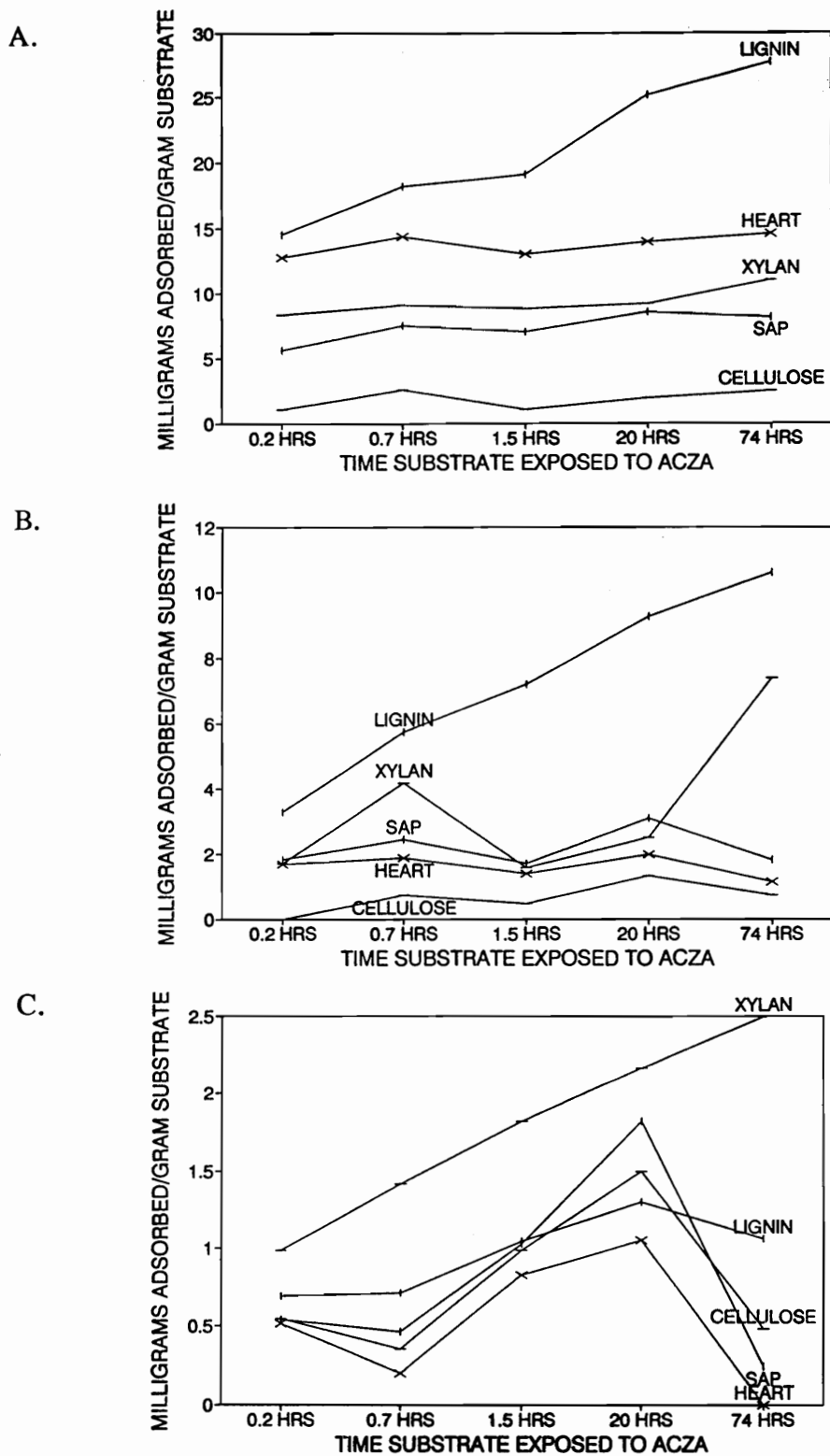


Figure 4.2.1. Adsorption of A.) Copper, B.) Zinc or C.) Arsenic by heartwood, sapwood, lignin, cellulose and xylan.

Table 4.2.2. Effect of wood component and exposure time on adsorption of zinc from ACZA solution.

| SUBSTRATE | AVERAGE ZINC ADSORPTION ^a (mg/g substrate) | | | | |
|-----------|---|--------|--------|--------|--------|
| | 10 MIN | 40 MIN | 90 MIN | 20 HRS | 74 HRS |
| CELLULOSE | 0.0 a | 0.7 a | 0.5 a | 1.3 a | 0.7 a |
| HEARTWOOD | 1.7 b | 1.9 b | 1.4 b | 2.0 ab | 1.1 a |
| SAPWOOD | 1.9 b | 2.5 b | 1.7 b | 3.1 b | 1.8 a |
| POLYPOSES | - | - | - | - | 2.0 a |
| XYLAN | 1.7 b | 4.2 c | 1.6 c | 2.5 bc | 7.5 b |
| LIGNIN | 3.3 c | 5.8 d | 7.3 c | 9.4 c | 10.7 c |

a. Values followed by the same letter are not significantly different using Duncan's Multiple Range Test at $\alpha = 0.05$.

The high affinity of copper for lignin suggests that phenolic groups may be primary reaction sites in both heartwood and sapwood. This possibility is also suggested by the increased reactivity of heartwood as compared to sapwood. As mentioned earlier, heartwood cells contain phenolic extractives and the cell walls are often coated with lignin-like phenolic incrustations in addition to the normal lignin content of the wood cell walls. Previous studies of copper adsorption from CCA have also noted the high reactivity of lignin (Pizzi, 1982; Rennie, et al., 1987); however, reaction sites in the low pH CCA system cannot be assumed to be the same as those involved in copper adsorption from more basic ACZA.

Although cellulose has been suggested as a site for copper adsorption (Belford, et al., 1957; Eadie and Wallace, 1962), this component was fairly unreactive in this study, especially in comparison to xylan and the polyoses. The

lower cellulose reactivity may have been due to the high degree of intramolecular hydrogen bonding, which decreases the availability of OH groups relative to the more branched polyose and xylan structures. However, xylan and the polyoses may have also adsorbed more copper because both of these components possess uronic acid groups. Previous studies have reported that copper is adsorbed by carboxylic acid groups in wood and other plant materials (Bayley and Rose, 1960; Knight, et al., 1961). Copper adsorption by uronic acid groups is further indicated by the higher reactivity of xylan relative to the polyoses, since xylan has a higher proportion of uronic acid groups than softwood polyoses (Fengel and Wegener, 1984).

When copper adsorption occurred, it appeared to do so quite rapidly, as in most cases the majority of the metal was withdrawn from solution within the first 10 minutes of exposure. There was no significant increase in copper adsorption over time except in the case of lignin. Rapid copper adsorption by wood has been noted for both ACZA and CCA, and was attributed to cation exchange reactions (Cooper, 1991; Dahlgren, 1972; Pizzi, 1982). Although zinc also participates in ion exchange reactions, it has a lower charge density and ionization potential than copper, and so may be adsorbed less readily by the wood (Cooper, 1991).

In contrast to copper, little arsenic was removed from solution by the wood substrates, although arsenic adsorption by xylan was significantly higher than for all other wood substrates except for the 74 hour exposure period (Table 4.2.3.). Arsenic does not appear to bond strongly to the wood on its own or as part of a

metal arsenate complex. This finding disagrees with earlier work, in which arsenic adsorption from ACZA exceeded zinc adsorption on pine and aspen sawdust (Cooper, 1991), but agrees with work in that same study which reported little arsenic adsorption from ACA. In that work, ACZA adsorption was measured by uptake of preservative components in the treated wood, and it is possible that some of the arsenic detected was physically entrapped, not adsorbed. In addition, Cooper (1991) attributed arsenic adsorption to the reaction of arsenic with copper atoms which were previously bonded to the wood by ion exchange reactions. If this were the case, increased copper adsorption should be associated with increased arsenic adsorption. In the current study, however, increased adsorption of copper, as was noted with lignin as a substrate, was not associated with increased arsenic adsorption. Similar reasoning could be used to correlate arsenic adsorption by xylan to the relatively high affinity of zinc for that substrate, although there was no corresponding increase in arsenic adsorption by lignin. However, it is possible that zinc forms a different type of bond when it reacts with xylan, one that allows it to also complex with arsenic. It is also possible that some of the differences in arsenic adsorption reported between this study and Cooper's work may be a function of the different wood species used.

Table 4.2.3. Effect of wood component and exposure time on adsorption of arsenic from ACZA solution.

| | AVERAGE ARSENIC ADSORPTION ^a (mg/g substrate) | | | | |
|-----------|--|--------|--------|--------|--------|
| SUBSTRATE | 10 MIN | 40 MIN | 90 MIN | 20 HRS | 74 HRS |
| HEARTWOOD | 0.5 a | 0.2 a | 0.8 a | 1.1 a | 0.0 a |
| SAPWOOD | 0.5 a | 0.5 a | 1.0 a | 1.8 ab | 0.2 a |
| CELLULOSE | 0.5 b | 0.4 a | 1.0 a | 1.5 ab | 0.5 a |
| LIGNIN | 0.7 a | 0.7 a | 1.1 a | 1.3 a | 1.1 ab |
| POLYPOSES | - | - | - | - | 1.4 ab |
| XYLAN | 1.0 a | 1.4 b | 1.8 b | 2.2 b | 2.5 b |

a. Values followed by the same letter are not significantly different using Duncan's Multiple Range Test at $\alpha = 0.05$.

4.3. Role of Precipitation in Fixation

4.3.1. Introduction

Although copper and zinc in ACA and ACZA appear to react with the wood substrate, the evaporation of ammonia from the preservative treated wood after removal from the treating cylinder is also a major factor in fixation. The role of ammonia evaporation in fixation was evaluated in a manner similar to the methods described in Section 4.2.

4.3.2. Materials and Methods

The procedures used in this test were similar to those described in Section 4.2., except that the ammonia was allowed to evaporate from the reaction flasks. Five grams of either heartwood powder, sapwood powder, or lignin powder was weighed (0.01g) into to a 125 ml erlenmeyer flask. Fifty grams of the ACZA solution prepared as described in Section 4.2. was added and the flasks were then placed unstoppered on a wrist shaker for agitation. Agitation times of 90 minutes, 20 hours and 74 hours were used since little evaporation occurred at shorter exposure times. After agitation, the flasks were allowed to settle for 5 minutes before 20 grams of ACZA solution was decanted, filtered twice through glass fiber filters, and analyzed for copper, zinc and arsenic content by XRF spectroscopy using the ASOMA 8620 Analyzer (ASOMA Instruments, Austin, Texas). The difference in preservative component concentration in the original and used solutions was used to estimate the combined effects of adsorption and precipitation. Ammonia content in the used solution was also determined using an acid-base

titration in which methyl red is first added to the ACZA to produce a green color, and then 0.1 N HCL is added until the solution turns red. Although less precise than the Kjeldahl method, this technique was rapid and correlated well with ammonia contents as determined by an Alpkem RFA-300 Colorometric Analyzer and Kjeldahl analysis (Appendix A).

4.3.3. Results and Discussion

The open flask results of this test are best understood in comparison to those of the closed flask study (Section 4.2), in which the ammonia was not allowed to evaporate (Figure 4.3.1). In general, copper was less sensitive to solution ammonia content than zinc. In addition, zinc precipitation appeared to be closely associated with arsenic precipitation (Figure 4.3.1.). Since relatively little ammonia was lost after 90 minutes and precipitation was insignificant, the amount of copper, zinc and arsenic lost from solution was primarily attributed to adsorption. Accordingly, the results at 90 minutes compare closely to those in the previous closed-system study (Figure 4.3.1.). After 20 hours in the test, the loss of zinc and arsenic from the open solutions appeared to be greater than that from the closed solutions for each of the three substrates, although the differences were not statistically significant (Table 4.3.1.). After 74 hours, however, zinc and arsenic losses from the open solutions were significantly higher than those from the closed systems for all three substrates. These results suggest that ammonia loss caused precipitation of the zinc. Arsenic, which is not dependent on ammonia for solubility, was lost from the treating solution in direct proportion to the loss of

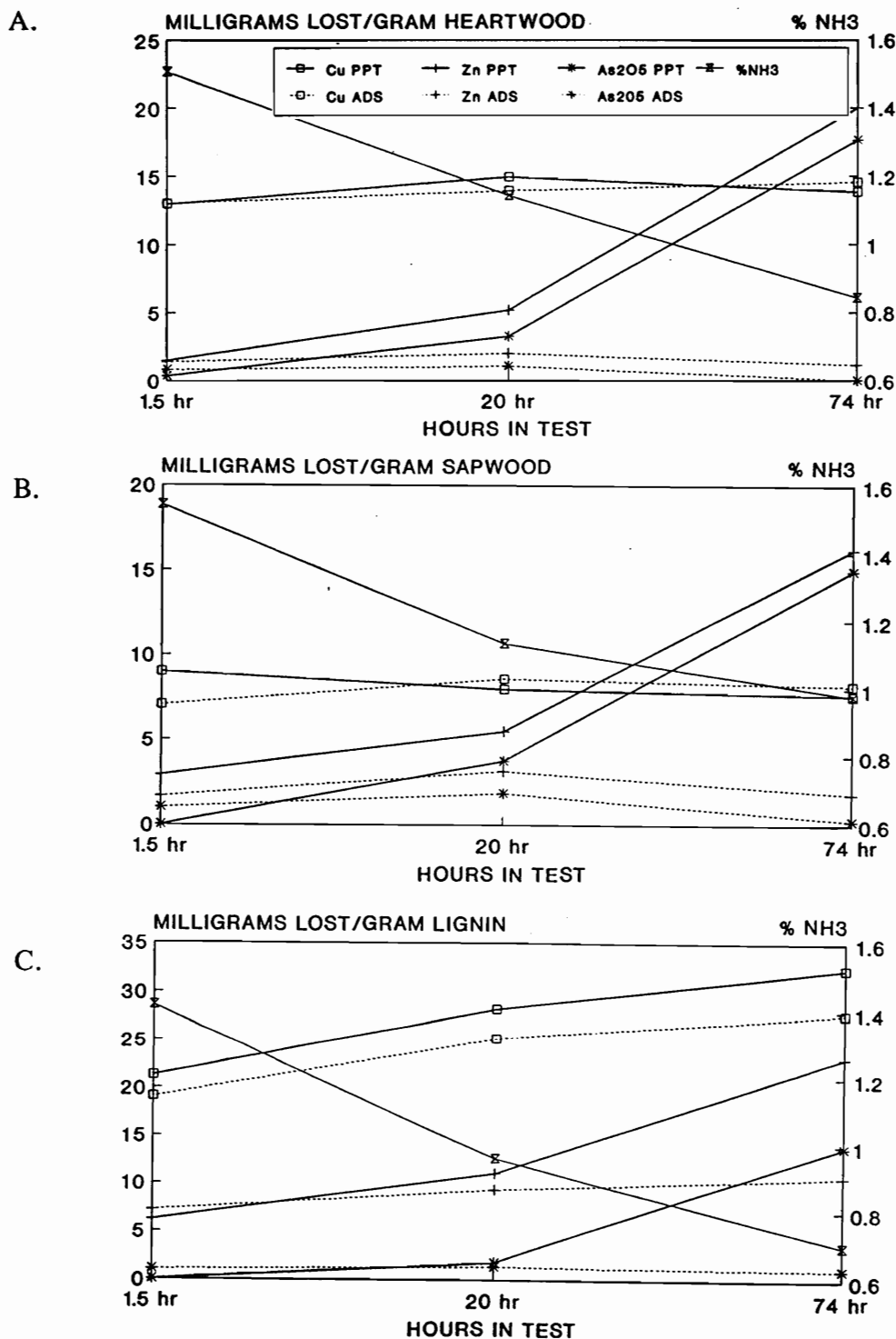


Figure 4.3.1. Adsorption (ADS) and precipitation (PPT) of copper, zinc, and arsenic from an ACZA solution in the presence of A.) heartwood, B.) sapwood, or C.) lignin over a 74 hour period at 23 - 25 C.

zinc, suggesting that zinc precipitation occurs as a zinc arsenate complex.

Although there were consistent differences between the amounts of zinc and arsenic lost from solution at all three times points, this probably reflects the adsorption of zinc by the wood substrates, especially lignin. The previous closed flask test (Section 4.2) indicated that zinc adsorption by heartwood, sapwood or lignin exceeded arsenic adsorption, and the results of this test after 90 minutes of exposure (when little precipitation had occurred) also reflect this trend.

Table 4.3.1. Amounts of zinc and arsenic lost from ACZA solutions exposed to wood components in open or closed systems for 20 or 74 hours^a.

| | LOSS OF ACZA COMPONENT (mg/g substrate) | | | |
|-----------|---|--------|----------|--------|
| | ZINC | | | |
| | 20 HOURS | | 74 HOURS | |
| | OPEN | CLOSED | OPEN | CLOSED |
| HEARTWOOD | 5.2 | 2.0 | 20.2 | 1.1 * |
| SAPWOOD | 5.5 | 3.1 | 16.4 | 1.8 * |
| LIGNIN | 11.0 | 9.3 | 23.5 | 10.7 * |
| | ARSENIC | | | |
| | 20 HOURS | | 74 HOURS | |
| | OPEN | CLOSED | OPEN | CLOSED |
| | OPEN | CLOSED | OPEN | CLOSED |
| HEARTWOOD | 3.3 | 1.1 | 12.6 | 0.0 * |
| SAPWOOD | 3.7 | 1.8 | 15.0 | 0.24 * |
| LIGNIN | 1.8 | 1.3 | 13.8 | 1.06 * |

a. Values represent the means of 3 samples. Closed system values followed by an asterisk are significantly different from corresponding open system values by Duncan's Multiple Range Test at $\alpha = 0.05$.

The amounts of copper lost from solution in this test agree closely with those in previous tests where the loss was due only to adsorption, suggesting that copper precipitation due to ammonia loss was minimal, even after 74 hours (Figure 4.3.1.). This finding implies that zinc is primarily responsible for "fixation" of arsenic in systems where both zinc and copper are present, and supports earlier results (Section 4.1.) in which replacement of a portion of the copper with zinc reduced arsenic leaching.

4.4. Order of Precipitation of ACZA Components

4.4.1. Introduction

The role of precipitation in ACZA fixation in the absence of the wood substrate was evaluated using a simple evaporation study.

4.4.2. Materials and Methods

Thirty milliliters of the ACZA solution described in Section 4.3. was added to unstoppered 125 ml flasks and placed on a wrist agitator for time periods ranging from 90 minutes to 98 hours. Three flasks were removed at the end of each time period, tightly stoppered, and then stored for 24 hours to allow precipitation to occur. A sample of solution was decanted from the flask, filtered through a glass fiber filter, and analyzed for copper, zinc, arsenic, and ammonia content as described in Section 4.1. Chemical levels were compared to the original ACZA solution and decreases in preservative concentration in the used solution were attributed to precipitation of that component.

4.4.3 Results and Discussion

Preservative composition remained stable in the solutions until the ammonia content dropped below about 1.1 percent (Figure 4.4.1.). At this time zinc and arsenic began rapidly dropping out of solution while the copper remained stable. Eventually, however, copper began to precipitate as the ammonia content of the solutions continued to decline. These results concur with those of a previous experiment using wood substrates (Section 4.3.) in which zinc and arsenic precipitated while copper did not.

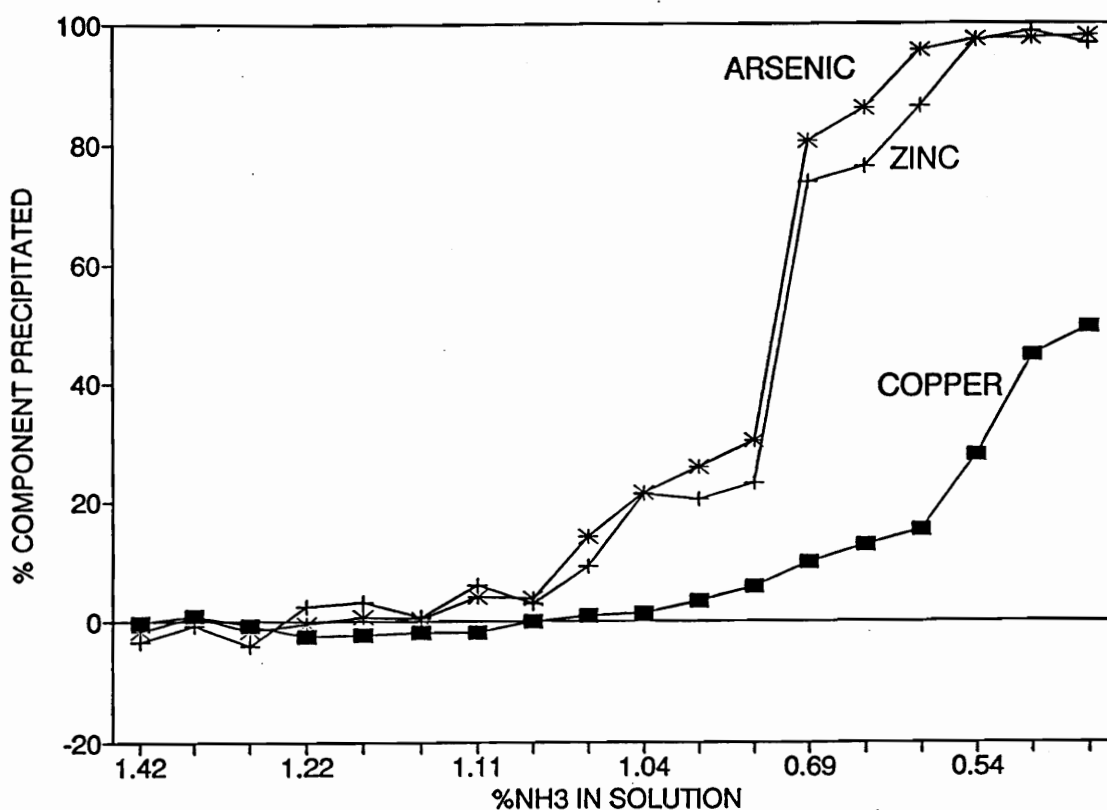


Figure 4.4.1. Precipitation of copper, zinc, and arsenic from ACZA solution as the ammonia evaporates.

Arsenic once again precipitated in direct proportion to zinc. A regression of percent elemental arsenic remaining in solution against percent elemental zinc remaining in solution for ammonia contents below 1.1% yields an $R^2 = 0.99$ and these components appear to be precipitating in an approximately 1:1 ratio, suggesting the formation of a zinc arsenate complex such as $\text{Zn}_2\text{As}_2\text{O}_7$.

4.5. Site(s) of Metal Adsorption

4.5.1. Introduction

Copper, and to some extent zinc, appear to be adsorbed to wood components; however, there is little data on the reactive sites for these metals within the wood. The purpose of this part of the study was to identify reactive sites within the wood using further adsorption tests, solid state NMR spectroscopy, FTIR spectroscopy and Fast Atom Bombardment (FAB) mass spectrophotometry.

4.5.2. Role of Extractives

4.5.2.1. Introduction

The high copper adsorption in heartwood relative to sapwood noted in section 4.2. suggests that constituents produced during heartwood formation may have provided reactive sites for copper. These heartwood constituents include the complex phenolic compounds termed "extractives". Extractives, by definition, can be removed with solvents without altering the wood structure. In this test, the ACZA adsorption capabilities of unextracted Douglas-fir heartwood was compared to that of heartwood which had been treated with solvents to remove the extractives.

4.5.2.2. Materials and Methods

Douglas-fir heartwood flour (60 mesh screen) was obtained from the same boards as in Sections 4.1. - 4.3. Twenty grams of wood flour was measured into an extraction thimble and placed into a 500 ml soxhlet extractor. Three hundred mls of a solution containing 2 parts toluene and 1 part ethanol was refluxed through

the extraction thimble 2 - 3 times per hour for six hours. The extracted wood flour, as well as a sample of unextracted heartwood flour, was then spread in a glass tray and dried in a 60 C oven for 36 hours. Approximately 3.6 grams of the extracted or unextracted heartwood powder and 36 grams of a 2.2% ACZA solution were weighed (0.01g) into 125 ml erlenmeyer flasks. Three replicates of each type of substrate were prepared, and agitated on a wrist shaker for one hour. Following agitation, the flasks were allowed to settle for 30 minutes before 15 grams of ACZA solution was decanted, filtered twice through glass fiber filters, and analyzed for copper, zinc and arsenic content using XRF spectroscopy. The differences in preservative component concentration between the original and used solutions was attributed to adsorption by the wood substrate. The remaining substrate was washed 5 times with 50 mls of a pH 9.8 ammonium hydroxide solution to remove as much unadsorbed preservative as possible. The samples were agitated for 15 minutes during each wash and allowed to settle for 5 minutes before the wash water was decanted. The final wash water was analyzed by XRF and no preservative components were detected. The washed substrates were filtered and air dried before being analyzed by XRF spectroscopy for the presence of copper, zinc, and arsenic.

4.5.2.3. Results and Discussion

The extraction of toluene and ethanol components appeared to cause a slight decrease in the copper adsorption capacity of Douglas-fir heartwood (Table 4.5.1.). This difference was statistically significant at the 90th percentile for the used

treating solution and at the 99th percentile for the treated wood. This finding agrees with past research, in which copper has been shown to strongly complex with tannins during CCA treatments of pine and extractives have been found to play a major role in CCA fixation (Pizzi, et al., 1986). Copper has been reported to form bonds with adjacent phenolic hydroxyl groups, coordinating with one to three polyflavanoid tannins (Pizzi, et al., 1986). However, decreased copper adsorption associated with extraction in the current study was not as dramatic as the difference in copper adsorption between heartwood and sapwood noted in Section 4.2. The role of extractives in copper adsorption may have been underestimated by this test, as it is likely that a portion of the wood extractives were soluble in the ACZA solution and were inadvertently removed from the control samples during the treatment process. ACZA soluble copper/extractive complexes would not have been detected in either the used treating solution or the treated wood. However, it is likely that the build-up of insoluble phenolic incrustations on the cell walls during heartwood formation also contributed to the increased copper adsorption capacity of heartwood.

The effect of extractive removal on zinc and arsenic adsorption was less clear (Table 4.5.1.). Although the amount of zinc adsorbed from the treating solution appeared to decrease significantly (90th percentile) due to extraction, no significant differences were noted in the treated wood. Arsenic adsorption from the solutions appeared to be negative; suggesting that solvent was absorbed by the wood more readily than the arsenic. However, the arsenic present in the treated

wood probably reflects the physically entrapped preservative that was not removed by washing.

Table 4.5.1. ACZA component adsorption by solvent extracted and unextracted Douglas-fir heartwood powder.

| Treatment | mg Adsorbed/gram Wood | | | Percent In Treated Wood | | |
|-------------|-----------------------|-----|------|-------------------------|------|------|
| | Cu | Zn | As | Cu | Zn | As |
| Unextracted | 18.6 | 1.8 | -0.8 | 2.07 | 0.38 | 0.21 |
| Extracted | 15.1 | 0.5 | -0.8 | 1.96 | 0.42 | 0.24 |

4.5.3. Adsorption Tests of Lignin Functional Groups

4.5.3.1. Introduction

Adsorption tests were conducted using lignin model compounds which contained reaction sites similar to those found in softwood lignin.

4.5.3.2. Materials and Methods

Approximately 2 grams of vanillin, tannic acid, pyrogallol, catechol, 3,5 dimethoxybenzyl alcohol, or quercetin were mixed with 20 - 50 grams of ACZA solution and agitated for 40 minutes. The solution used in this test was composed of 0.31% copper oxide, 0.30% zinc oxide, and 0.31% arsenic pentoxide (Table 4.5.2.). In a subsequent test 3.65 grams of eugenol was agitated in 32.12 grams of 1.5% ACZA (0.75% copper oxide, 0.38% zinc oxide, 0.38% arsenic pentoxide) for 3 hours. Following agitation, the mixtures were allowed to precipitate for 24 hours so that the used ACZA solution could be collected and filtered for analysis. The difference in concentration of copper, zinc and arsenic in the used solution was

compared to that in the original solution to estimate the degree of ACZA adsorption and precipitation.

4.5.3.3. Results and Discussion

The results were strongly influenced by the solubility of the substrate in the preservative solution as adsorbed preservative components which remained soluble were not detected. After 24 hours of storage only tannic acid, eugenol and 3,5 dimethoxybenzyl alcohol appeared to have completely precipitated from the preservative solution, although quercetin and vanillin appeared to have precipitated to a large extent. The remaining compounds precipitated very little and were discarded since it was not possible to separate the ACZA in solution from that adsorbed to the substrate. ACZA solutions exposed to tannic acid, eugenol, 3,5 dimethoxybenzyl alcohol, vanillin, and quercetin were analyzed using x-ray fluorescence spectroscopy. Although incomplete precipitation may have led to underestimates of the amount of adsorption that occurred, the lignin model compounds, with the exception of 3,5 dimethoxybenzyl alcohol, adsorbed over 60% of the copper and some zinc from the ACZA solutions (Table 4.5.2.). In contrast, almost no adsorption of copper by 3,5 dimethoxybenzyl alcohol occurred, suggesting that the phenolic hydroxyl groups are a major reactive site for the metal cations, while methoxyl groups are much less reactive. However, the reactivity of 3,5 dimethoxybenzyl alcohol may have been lower because unlike the other compounds tested, none of the reactive sites are positioned on adjacent carbon atoms of the aromatic ring.

Table 4.5.2. Adsorption of ACZA components in solutions containing selected lignin model compounds.

| Compound | Chemicals Levels in Original Solution (%) | | | Chemical Levels in Reacted Solution (%) | | |
|------------------------------|---|-------|--------------------------------|---|-------|--------------------------------|
| | CuO | ZnO | As ₂ O ₅ | CuO | ZnO | As ₂ O ₅ |
| Tannic Acid | 0.305 | 0.303 | 0.310 | 0.026 | 0.020 | 0.303 |
| Vanillin | 0.305 | 0.303 | 0.310 | 0.094 | 0.170 | 0.185 |
| Quercetin | 0.305 | 0.303 | 0.310 | 0.029 | 0.097 | 0.319 |
| 3,5 dimethoxy-benzyl alcohol | 0.305 | 0.303 | 0.310 | 0.302 | 0.304 | 0.308 |
| Eugenol | 0.759 | 0.378 | 0.356 | 0.325 | 0.235 | 0.347 |

4.5.4. Adsorption by Vanillin and Eugenol

4.5.4.1. Introduction

The copper adsorption properties of vanillin and eugenol were explored in more detail to determine the role of the aldehyde group in copper adsorption.

4.5.4.2. Materials and Methods

A series of ACZA/vanillin or ACZA/eugenol solutions were prepared to obtain ratios of 0.5:1, 1:1, 1.5:1, 2:1, 3:1 or 4:1 moles vanillin or eugenol per mole of copper. In each case, 50 grams of 2.08% ACZA solution containing 0.835% elemental copper was weighed (0.01g) into a 125 ml flask, and then the appropriate amount of vanillin or eugenol was added. The flasks were tightly stoppered, agitated for 2.5 hours, and then allowed to precipitate over a 40 hour period at 23 - 25 C. Twenty mls of the ACZA solution were then decanted from

the flask and analyzed for copper content by XRF spectroscopy. The difference in copper concentration between the original and reacted ACZA solution reflected copper adsorption and precipitation in the presence of the test compound.

4.5.4.3. Results and Discussion

The results of this test were also influenced by the solubility of the copper/vanillin or copper/eugenol complexes formed. Both vanillin and eugenol precipitated greater amounts of copper as the ratio of the test compound to copper increased (Figure 4.5.1.). This trend continued to the highest vanillin level; however, copper precipitation appeared to level-off at a eugenol:copper molar ratio of 2:1. While these results suggest that vanillin complexes more copper than eugenol, it more is likely that the high copper precipitation by vanillin is a function of the solution pH. The pH of the vanillin/ACZA solutions was lower than that of the eugenol/ACZA solutions, and at the two highest vanillin/copper ratios, dropped so low that the zinc and arsenic also precipitated. Solubility of the copper and vanillin/copper complexes was probably also reduced in these solutions.

Comparison of copper precipitation from the vanillin and eugenol solutions when the pH levels from each were still relatively high (molar ratios 0.5:1 and 1:1) suggests that eugenol adsorbed and precipitated at least as much copper as vanillin, and that the aldehyde group in vanillin was not a major adsorption site for copper.

The effect of pH on precipitation was evaluated with an additional vanillin/copper adsorption test. This test was prepared identically to that described above, except that each solution was adjusted to pH = 10.5 with ammonium

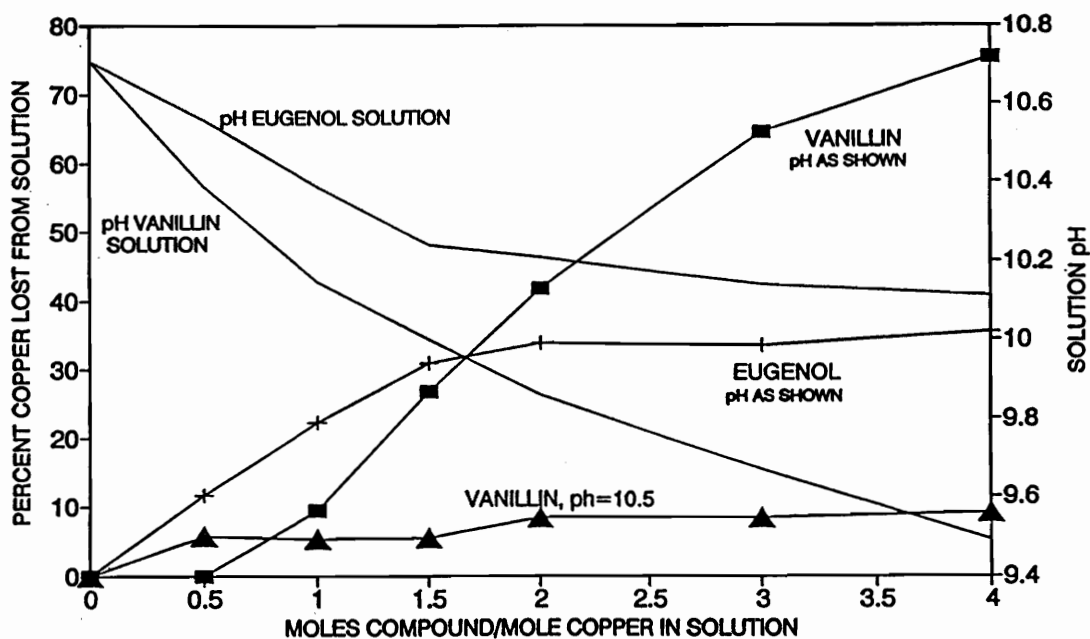


Figure 4.5.1. Precipitation of copper from ACZA solutions after addition of vanillin or eugenol.

hydroxide. Precipitation of copper in these solutions was minimal (Figure 4.5.1.), suggesting either that little adsorption of copper by vanillin occurred, or that the resulting vanillin/copper complexes remained soluble. This finding further suggests that the high levels of copper precipitation from the vanillin/ACZA solutions initially tested were a function of copper and or vanillin/copper complex insolubility.

4.5.5. NMR Analysis

4.5.5.1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy can be a valuable tool for detecting changes in substituent groups within complex organic molecules. This technique was used to identify the reaction sites involved in copper and zinc adsorption to the wood. Solid state NMR was selected because it avoided the unknown effects of dissolving the ACZA treated wood.

4.5.5.2. Materials and Methods

Five grams of Douglas-fir heartwood ground to pass through a 60 mesh screen was added to a flask containing 100 grams of 10% ACZA and agitated for one hour at room temperature. The high solution strength was used to provide an excess of chemical for the wood reaction sites. The wood was then vacuum filtered and washed 5 times with 50 mls of a pH 9.8 ammonium hydroxide solution to remove any preservative which had not adsorbed to the wood. During each wash, the sample was agitated for 15 minutes, and then allowed to settle for 5 minutes. The wash water was decanted, and clean wash water added. The washed, air dried wood powder contained 4.80% copper oxide, 2.00% zinc oxide, and 1.27% arsenic pentoxide as determined by X-ray fluorescence analysis. Samples of untreated heartwood as well as heartwood treated with 10% ammonia (from ammonium hydroxide) in water were prepared as controls. The ACZA treated, ammonia treated, and untreated samples were sent to Colorado State University for solid state NMR analysis. ^{13}C CP/MAS spectra of the wood samples were run at 1.4 T

(100MHzH, 25.27 MHz ^{13}C) using a 1 millisecond cross polarization contact time and a 1 second recycle delay time. The spinning speed was approximately 3.5 kHz.¹

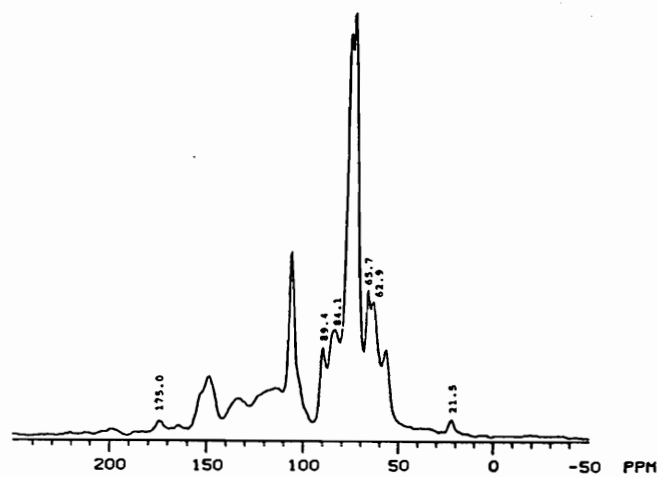
4.5.5.3. Results and Discussion

Comparison of the three samples revealed that while ammonia treatment changed the wood spectra, little additional change resulted from the addition of copper, zinc, and arsenic to the ammonia (Figure 4.5.2.). The ammonia treatment eliminated peaks at 22 ppm and 175 ppm which are assigned to the acetyl methyl and acetyl carbonyl groups, respectively, in hemicellulose (Taylor, et al., 1983). A portion of the intensity of the peak at 174 ppm has also been attributed to the carbonyl groups of uronic acids in hemicellulose (Haw, et al., 1984). In addition, there was an increase in the size of the peaks at 89 and 66 ppm (carbons 4,6 in amorphous carbohydrates) relative to the size of the peak at 84 and 63 ppm (carbons 4,6 crystalline cellulose), suggesting a decrease in the amorphous cellulose content (Haw, et al., 1984).

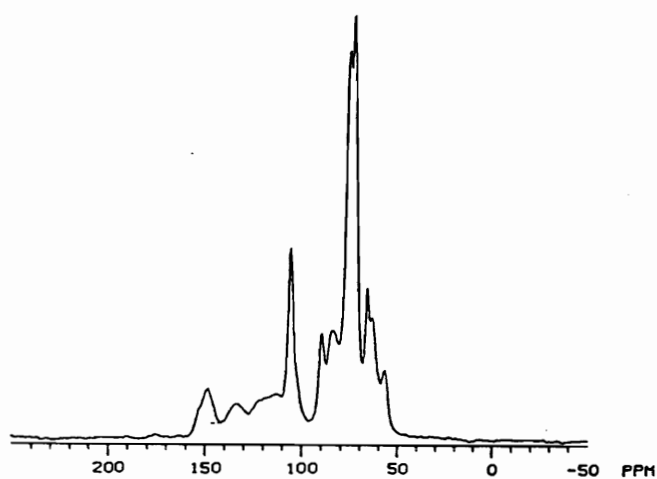
Addition of copper, zinc, and arsenic to the ammonia may have caused a slight decrease in the 130 - 110 ppm region, an area of the spectrum which has been attributed to aromatic carbons in lignin (Hatfield, et al., 1987). However, the change was quite small and in an area where the peaks were poorly defined. It appears that changes in the wood due to adsorption of copper and zinc were

¹The author is indebted to Mark Davis, Colorado State University, for his assistance in spectral interpretation.

A.



B.



C.

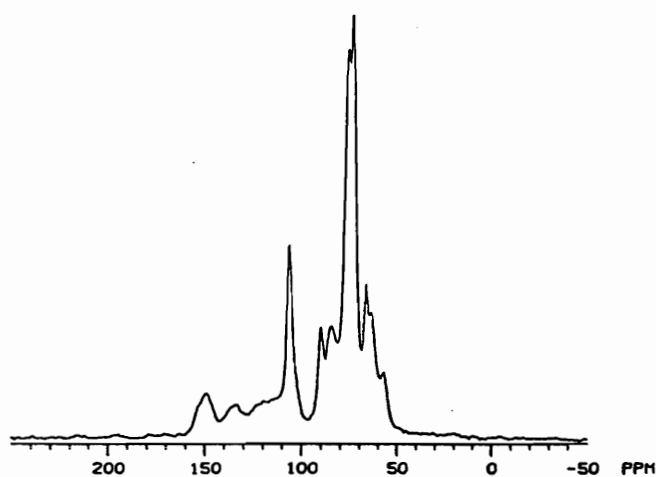


Figure 4.5.2. Solid state NMR spectra of A.) untreated wood, B.) ammonia treated wood, or C.) ACZA treated wood.

insufficient to significantly alter the broad peaks of the solid state NMR spectra.

Although experimentation with different treatment conditions or with treatment of model compounds might eventually provide better results, the cost of this analysis was prohibitive.

4.5.6. FTIR Analysis

4.5.6.1. Introduction

Fourier transform infra-red spectroscopy (FTIR) is a valuable tool for fingerprinting the structure of organic molecules (Socrates, 1980). In this study, FTIR was employed to determine if the absorption bands of any of the functional groups in the wood were altered by metal adsorption during ACZA treatment.

4.5.6.2. Materials and Methods

All spectra were determined on KBr discs for wavelengths of 4000 - 400 cm^{-1} using a Nicolet 5DXB FTIR spectrophotometer. The discs were prepared by thoroughly mixing 20 to 40 milligrams of powdered sample with 200 milligrams of powdered KBr and then pressing approximately 120 mg of the mixed powders to 103 MPa for one minute. ACZA and ammonia treated samples were obtained by agitating 2 grams of the powdered substrate (60 mesh screen) in 50 mls of solution for one hour and then allowing the treated substrate to precipitate. The treating solution was decanted and the precipitate washed with water which had been adjusted to pH 9.8 with ammonium hydroxide to remove as much unfixed preservative as possible. The precipitate was then stored in a 50 C oven for at least 48 hours prior to analysis.

4.5.6.3. Results and Discussion

Initial trials compared untreated Douglas-fir heartwood to heartwood treated with a solution of 10% ammonia (as ammonium hydroxide) or 9% ACZA (Figure 4.5.3.). The ammonia treatment caused the peak at 1735 cm^{-1} , an area of

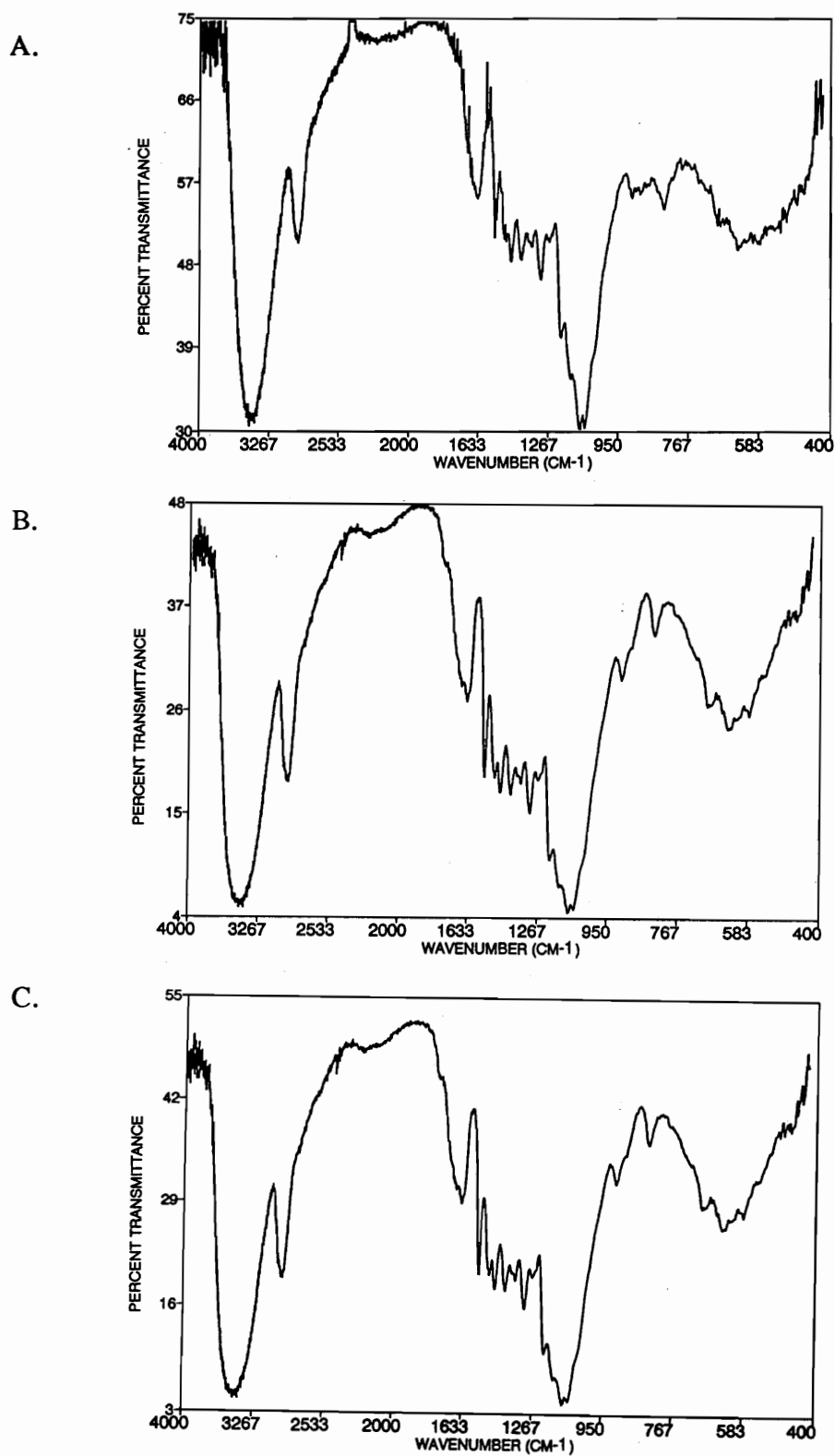


Figure 4.5.3. FTIR spectra of Douglas-fir heartwood after A.) no treatment B.) ammonia treatment, or C.) ACZA treatment.

absorption associated with the stretching vibration of carboxylic acid and acetyl groups in hemicellulose (Harrington, et al., 1964) or nonconjugated ester groups in lignin (Sarkanen et al., 1967), to disappear from the heartwood spectrum. These functional groups are reported to be sensitive to alkaline hydrolysis (Harrington, et al, 1964; Sarkanen et al, 1967). However, the addition of copper, zinc, and arsenic to the ammonia caused no significant additional change in the spectrum. As with the solid state NMR spectrum, copper and zinc adsorption apparently did not affect a high enough proportion of bonding sites in the wood to significantly alter the FTIR spectra.

Subsequently, the spectra of ammonia or ACZA treated cellulose, xylan, and lignin was compared to that of untreated controls. Lower ammonia (5%) and ACZA (3.8%) concentrations were used in these trials to more closely simulate concentrations used commercially and reduce the risk of creating falsely harsh reaction conditions. Comparison of the spectra of untreated, ammonia treated, and ACZA treated cellulose shows that little change was caused by the ACZA treatments (Figure 4.5.4.). This is probably once again due to the low proportion of reaction sites involved in metal adsorption, especially in the case of cellulose where earlier results indicated that little adsorption occurs.

Treatment of xylan with the solution of ammonium hydroxide in water caused the peak at 1560 cm^{-1} to disappear (Figure 4.5.5.). This peak has not been assigned in past work with xylan components (Harrington, et al., 1964; Liang, et al., 1960), and few functional groups absorb in this area of the spectrum. One

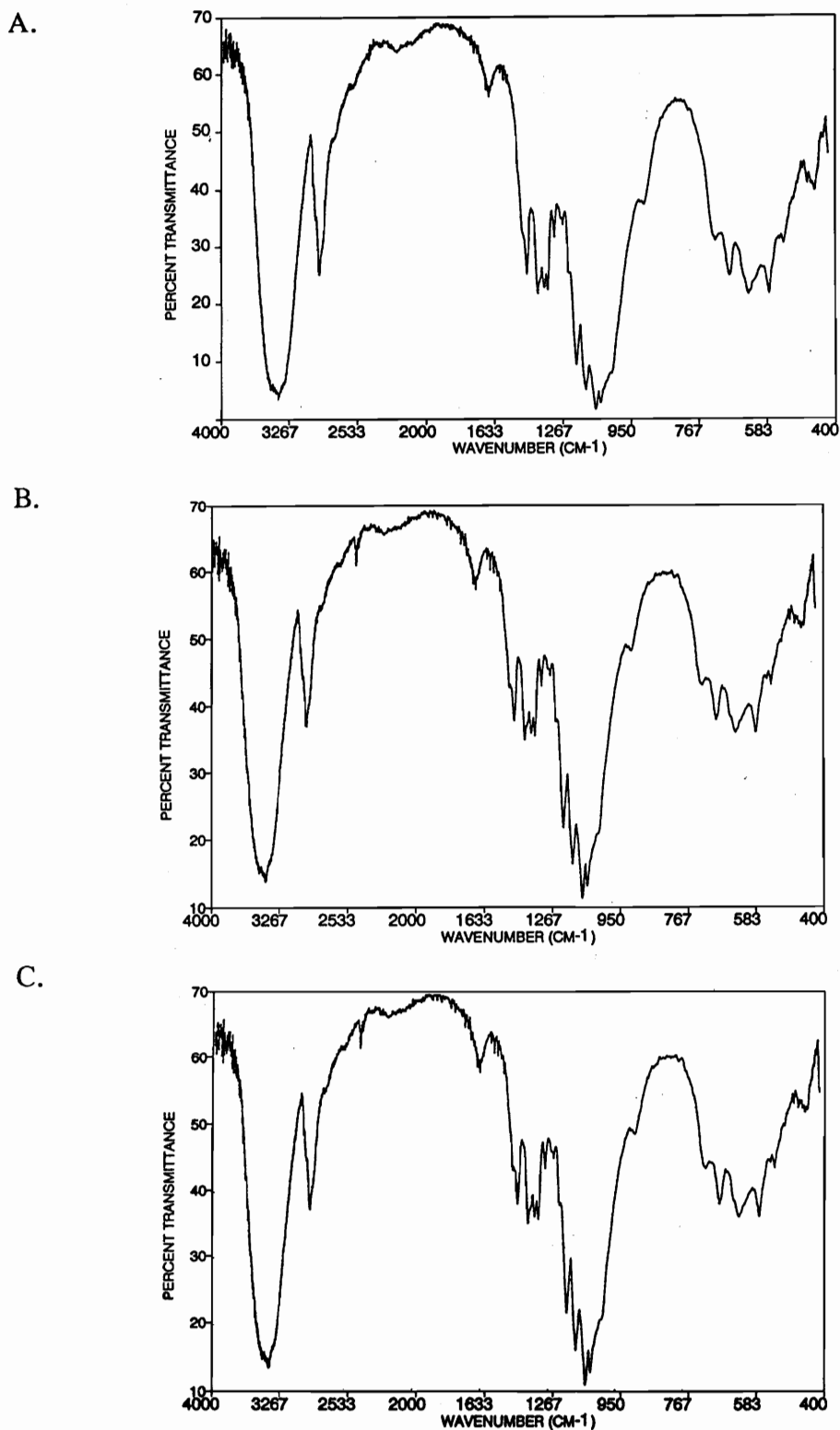
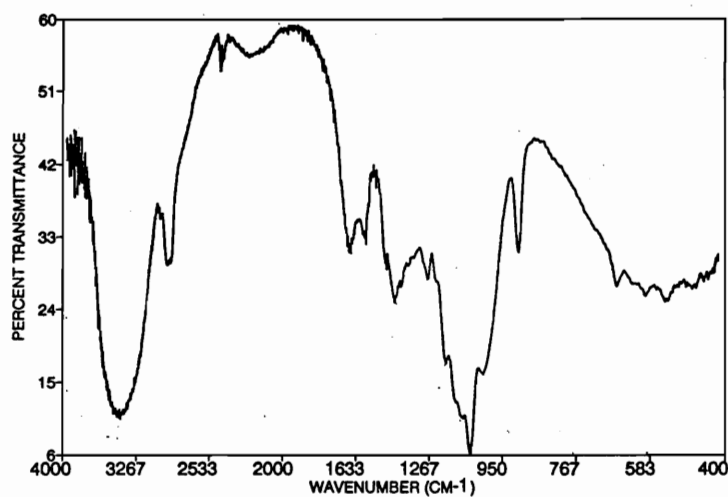
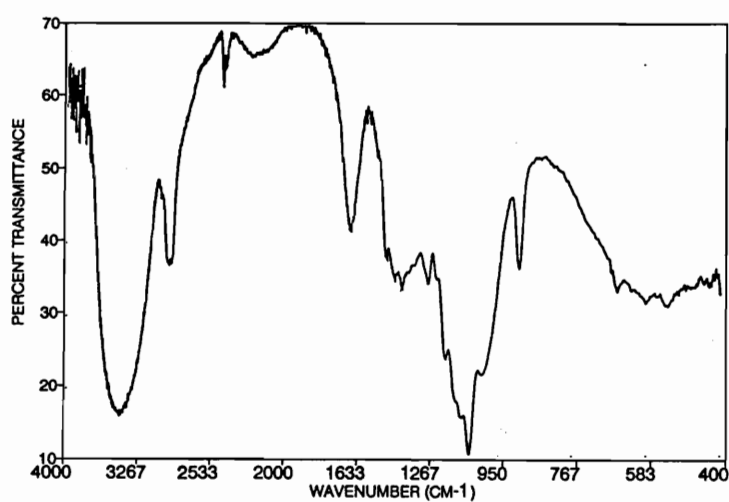


Figure 4.5.4. FTIR spectra of cellulose after A.) no treatment, B.) ammonia treatment, or C.) ACZA treatment.

A.



B.



C.

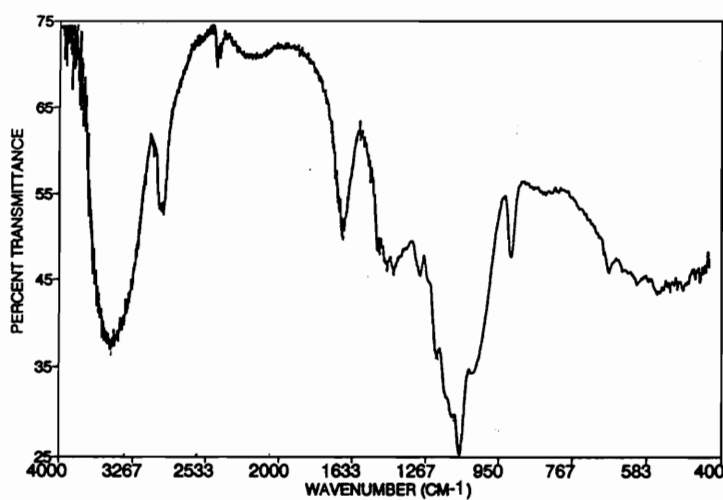


Figure 4.5.5. FTIR spectra of xylan after A.) no treatment, B.) ammonia treatment, or C.) ACZA treatment.

group that does adsorb in this region is the C-H stretching vibration of various substituted furans (Socrates, 1980). It is possible that the dry, powdered xylan contained some arabinose in the furanose form, which was converted to a pyranose sugar by the ammonia treatment. Little additional change in the spectra occurred, however, with the addition of copper, zinc, and arsenic.

Surprisingly, the FTIR spectra of lignin, a primary adsorption site in earlier tests, also showed little significant change after ACZA treatment (Figure 4.5.6.). Comparison of these spectra was made more difficult and less sensitive because of the opacity of the lignin/KBr wafers, especially with ACZA-treated lignin. There was some change in the peak at 2400 cm^{-1} , but this peak is not attributed to lignin in the literature and may be due to some unrelated absorbance such as that caused by carbon dioxide (Socrates, 1980). The shoulder at about $1715 - 1700\text{ cm}^{-1}$ also appears to be diminished by both the ammonia and ACZA treatments. This band has been attributed to conjugated esters which link various types of benzoic acids in lignin (Sarkanen, et al., 1967). These types of esters are somewhat susceptible to removal by alkaline hydrolysis (Sarkanen et al., 1967), and their loss may explain the decreased absorption in this region. Although other areas of the spectra may be slightly affected by the ACZA treatment, the relatively poor quality of the spectra and the difficulty in obtaining comparable spectra after ACZA treatment obscures these changes. In addition, even in the case of the highly metal adsorbing lignin, the number of reactive sites involved in bonding appears to be small compared to the total number of potential reactive sites present.

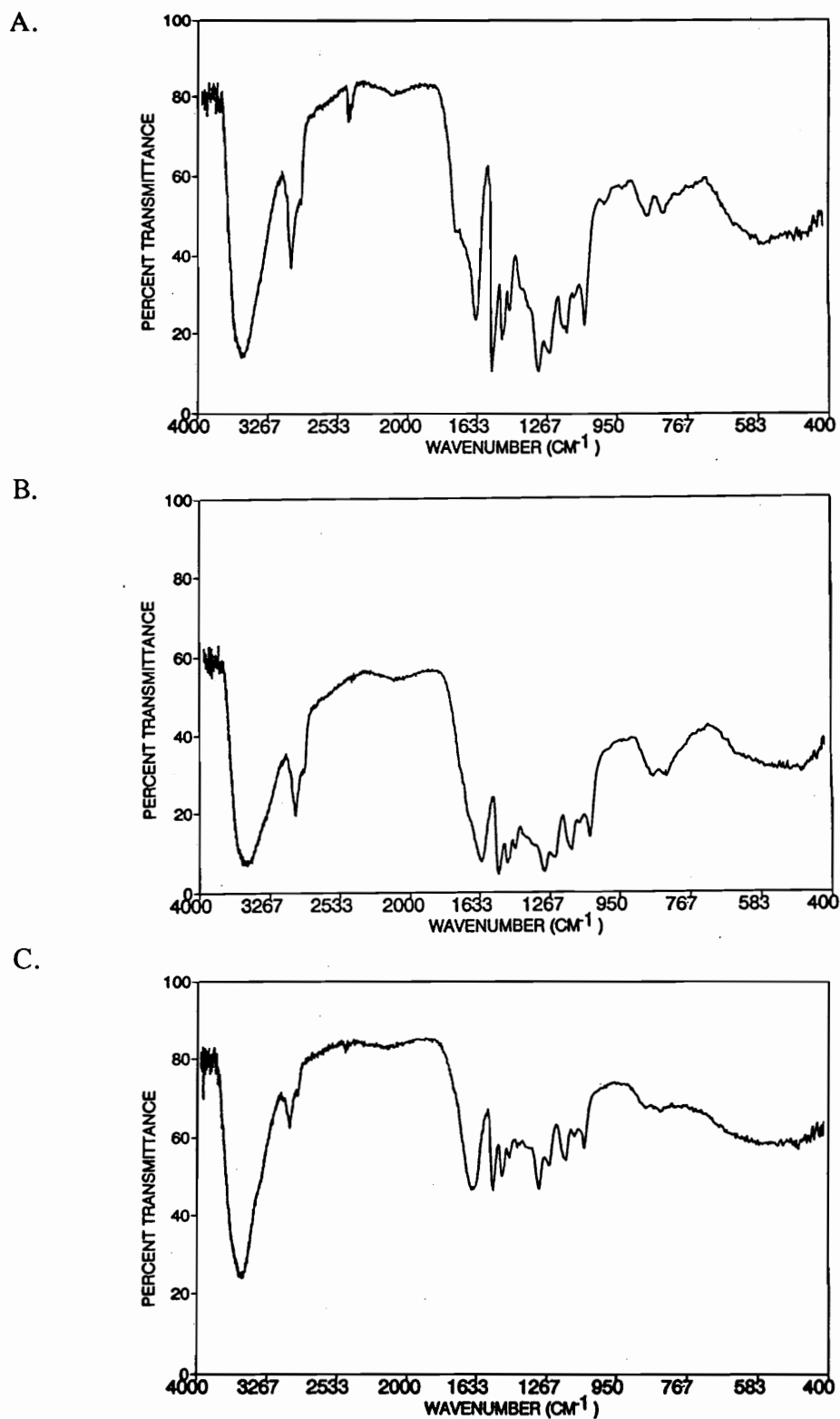


Figure 4.5.6. FTIR spectra of lignin after A.) no treatment, B.) ammonia treatment, or C.) ACZA treatment.

To overcome these problems, FTIR analysis was performed on ACZA treated vanillin, a readily available model compound which possesses some of the same reactive sites present in lignin. As mentioned in Section 4.5.3., much of the vanillin precipitated when mixed with ACZA solution, and this was assumed to be due to complexation with the preservative metals, and especially copper. In this test it was anticipated that only the reacted vanillin would precipitate, and the proportion of reactive sites affected by metal adsorption would be high enough to alter the FTIR spectra of the precipitated vanillin.

Two grams of vanillin were agitated for 1 hour in 50 mls of 3.8% ACZA, and then allowed to precipitate for 24 hours. As before, the precipitate was washed to remove as much unreacted preservative as possible. No precipitate formed when vanillin was dissolved in a solution of ammonium hydroxide in water, although the solution turned yellow and then eventually brown. As a result, the ammonia treated vanillin was obtained for FTIR analysis by evaporating the entire vanillin/ammonia solution and analyzing the remaining solids.

A comparison of the spectra of untreated and ammonia treated vanillin reveals that the treatment altered the relative heights of several peaks in the 1500 - 1000 cm^{-1} range (Figure 4.5.7.). The intensity of peaks at 1464 cm^{-1} , 1370 cm^{-1} , 1203 cm^{-1} , 1124 cm^{-1} and 1030 cm^{-1} appear to be slightly lowered by the treatment. In addition, a new peak was visible at 784 cm^{-1} , possibly due to the narrowing of the peak at 734 cm^{-1} .

Addition of copper, zinc, and arsenic to the solution caused additional changes in the spectra (Figure 4.5.7.). In general, the spectra were complex and difficult to interpret because of the interrelationships between many of the functional group absorbencies and the unknown affects of the wood preservative. Absorption at some bands, such as 1558, 1339, 1230, 652, and 449 cm^{-1} were intensified by the ACZA treatment. The assignment of these bands would be extremely complex and beyond the scope of this study. However, analysis of vanillin bands that were reduced or shifted from the original spectra was somewhat more straight-forward.

The broad peak in the 3500 - 2500 cm^{-1} region, commonly attributed to oxygen - hydrogen stretching (Harrington, et al., 1964; Sarkanen and Ludwig, 1971), was significantly altered, revealing peaks that were previously hidden or only small shoulders. These peaks are probably due to C-H stretching vibrations, although they may be due to water or ammonia bands if copper or zinc was adsorbed while still complexed to these components. The total disappearance of peaks at 1370 and 1173 cm^{-1} , assigned to phenolic hydroxyls (Sarkanen et al., 1967a), provides further evidence that the hydroxyl group is a major reactive site for metal adsorption. In addition, the peak at 1203 cm^{-1} , probably due to O-H bending frequency (Sarkanen et al., 1967a), is substantially reduced.

Conversely, there was less evidence that the methoxyl methyl group was displaced during metal adsorption. The band associated with aromatic C-O stretching, 1610 - 1590 cm^{-1} (Sarkanen and Ludwig, 1971), did appear to be shifted

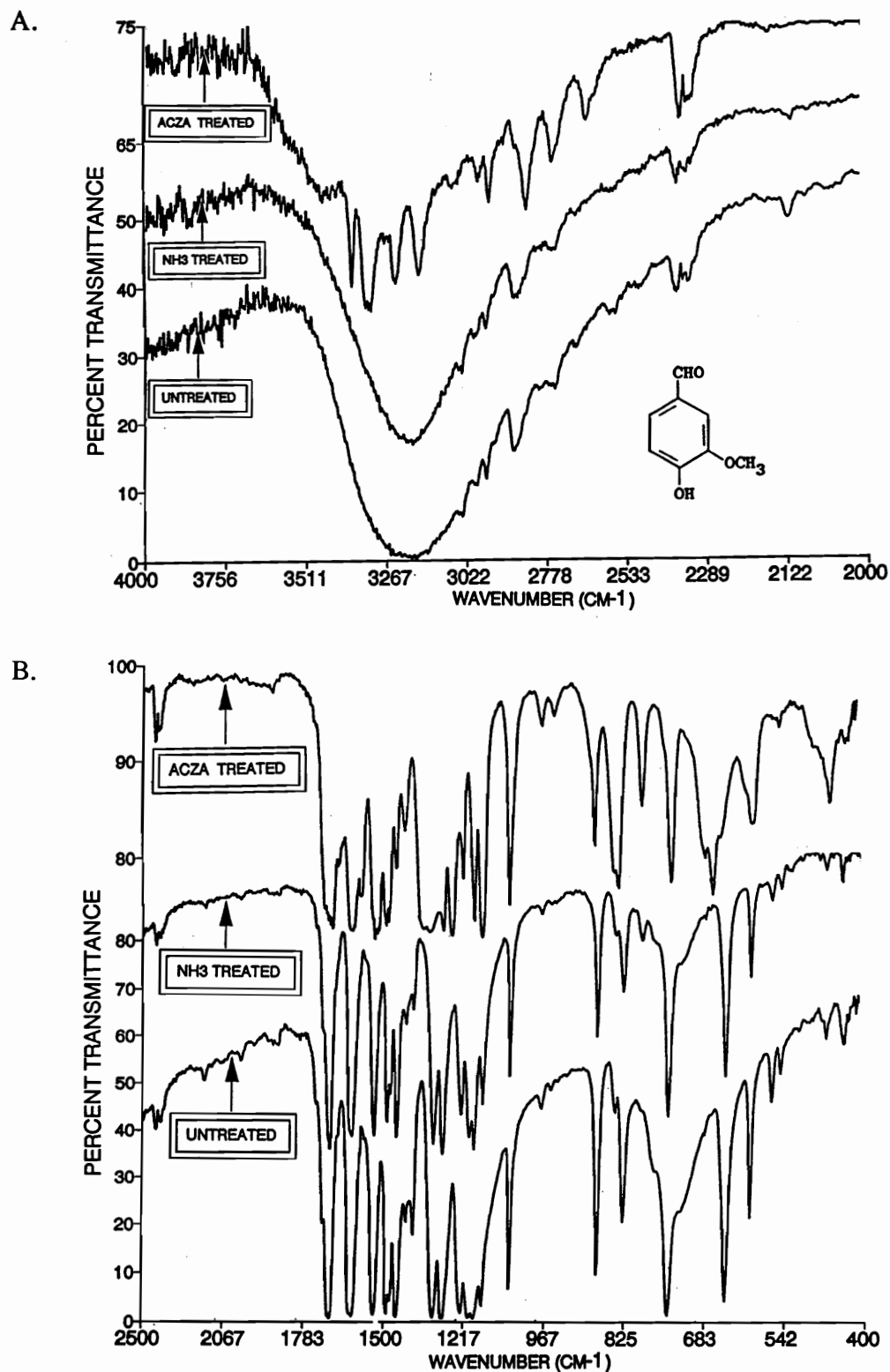


Figure 4.5.7. FTIR spectra of untreated vanillin and vanillin after ammonia or ACZA treatment for A.) 4000 - 2000 cm^{-1} or B. 2500 - 400 cm^{-1} .

to a slightly lower frequency, but the band at $1470 - 1460\text{ cm}^{-1}$, associated with C-H deformation in methyl groups (Sarkanen and Ludwig, 1971), was affected very little by metal adsorption.

Several peaks appear to have been shifted or broadened by the ACZA treatment, including the peaks at about 1666 cm^{-1} , a region associated with the carbonyl stretching of the aldehyde group (Sarkanen et al., 1967b), and those at 1594 cm^{-1} and 1514 cm^{-1} , assigned to aromatic skeletal vibrations (Sarkanen and Ludwig, 1971). Another band assigned to aromatic skeletal vibrations, at approximately 1427 cm^{-1} , was greatly reduced by the ACZA treatment. This band is highly sensitive to the nature of the ring substituents (Sarkanen et al., 1971) and the lessening of its intensity suggests that the substituents have been changed.

Although the spectra were complex and affected in multiple ways by the ACZA treatment, it appears that bands associated with the hydroxyl group were most significantly altered, especially in comparison to bands due to methoxyl group absorptions. This finding agrees with earlier tests in this study (Section 4.5.3.) which suggested that model compounds with hydroxyl groups adsorbed significant amounts of copper from ACZA solutions.

4.5.7. FAB Mass Spectroscopy

4.5.7.1. Introduction

Mass spectroscopy may also provide insights into reaction products formed when copper and zinc adsorb to the wood. However, once again it seemed

desirable to avoid dissolving and volatilizing the ACZA substrate because of the unknown effects this might have on the bond formed between the substrate and the adsorbed metal. To overcome this problem, Fast Atom Bombardment (FAB) mass spectroscopy was used.

4.5.7.2. Materials and Methods

The tests were once again carried out using the model compound vanillin, both to simplify the spectral interpretation and to insure that a significant proportion of reaction sites were involved in metal adsorption. As in the FTIR analysis, the sample was collected from the precipitate formed when vanillin was mixed with 3.8% ACZA. This sample, as well as samples of pure vanillin, vanillin dissolved in dilute ammonium hydroxide (5% ammonia), and the preservative solution, were analyzed by Fast Atom Bombardment (FAB) using a Kratos MS-50 mass spectrophotometer. The sample was suspended in glycerol and placed on the end of a probe which was inserted into the mass spectrometer and bombarded with a beam of high energy xenon atoms to produce ions for mass analysis.

4.5.7.3. Results and Discussion

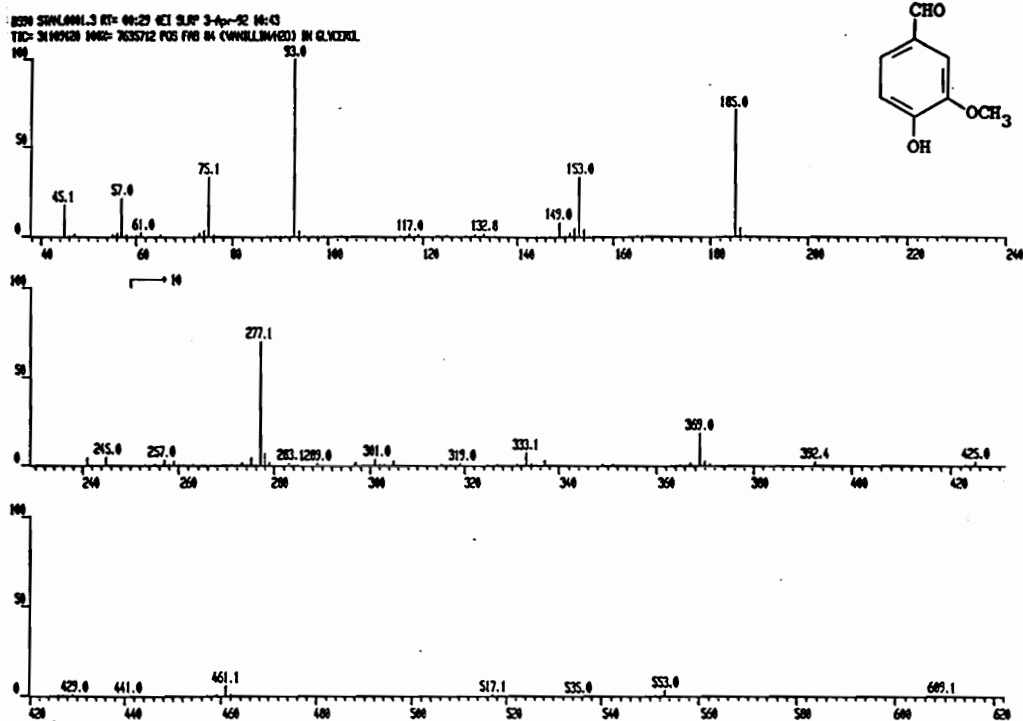
The mass spectrum of the ACZA treated vanillin revealed that a large number of fragments were formed but that the most common mass/charge ratio, once the preservative and glycerol lines were subtracted, was simply due to vanillin itself ($m/e = 152.9$) (Figure 4.5.9.). The lowest mass/charge ratio detected which may reflect a vanillin - metal complex was found to be $m/e = 200.9$. This mass could be formed if both the hydroxyl hydrogen and methoxyl methyl groups were

displaced and both oxygens then formed bonds to a copper atom. Similarly, the line at 215.9 could be attributed to vanillin losing a hydrogen and gaining a mass equivalent to a copper atom, and the line at 217.9 to the same phenomenon involving a zinc atom.

A question which might arise when trying to assign the mass/charge ratios is the form or environment that the copper or zinc atom was in when it complexed with the vanillin. One of the dominant forms of copper in the preservative is presumed to be $\text{Cu}(\text{NH}_3)_4 2(\text{H}_2\text{O})^{2+}$, but it does not necessarily follow that this was the form in which copper was complexed. In addition, it is difficult to tell which of the bonds might be broken during bombardment of the sample in the mass spectrophotometer. Because of these factors it is not surprising that a line corresponding to vanillin plus $\text{Cu}(\text{NH}_3)_4 2(\text{H}_2\text{O})^{2+}$ does not appear in the spectrum. However, other lines could be attributed to vanillin plus various copper or zinc species. The line at 232.8 could be attributed to vanillin plus CuO or vanillin minus H + CuOH^+ , and the line at 234.8 attributed to the same form of zinc complexing with vanillin. Similarly, the stronger line at 250.8 could be attributed to vanillin plus $\text{Cu}(\text{OH})_2$, and the line at 322.8 to vanillin plus $\text{Cu}(\text{NH}_3)_2 4(\text{H}_2\text{O})$ or vanillin minus H + $\text{Cu}(\text{NH})_5(\text{H}_2\text{O})$. Another possibility is the complexing of a copper atom with two vanillin molecules by dislodging the hydroxyl hydrogen from each vanillin ($m/e = 366.7$).

Many of the above mass/charge ratios suggest displacement of a hydrogen from a vanillin followed by formation of a bond to a copper or zinc species. It

A.



B.

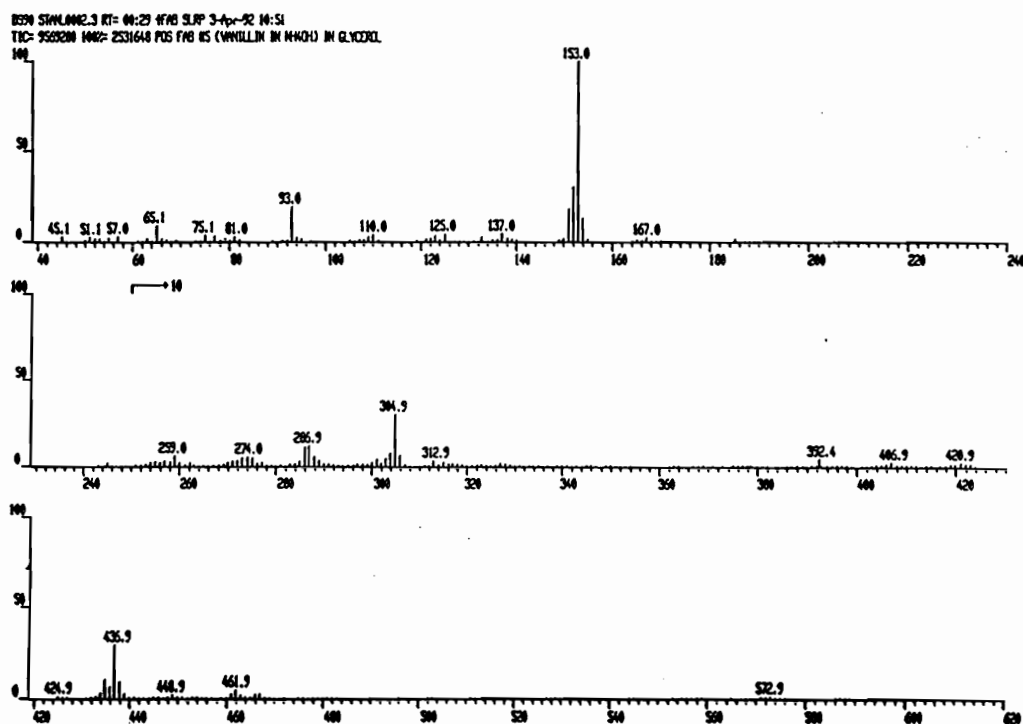
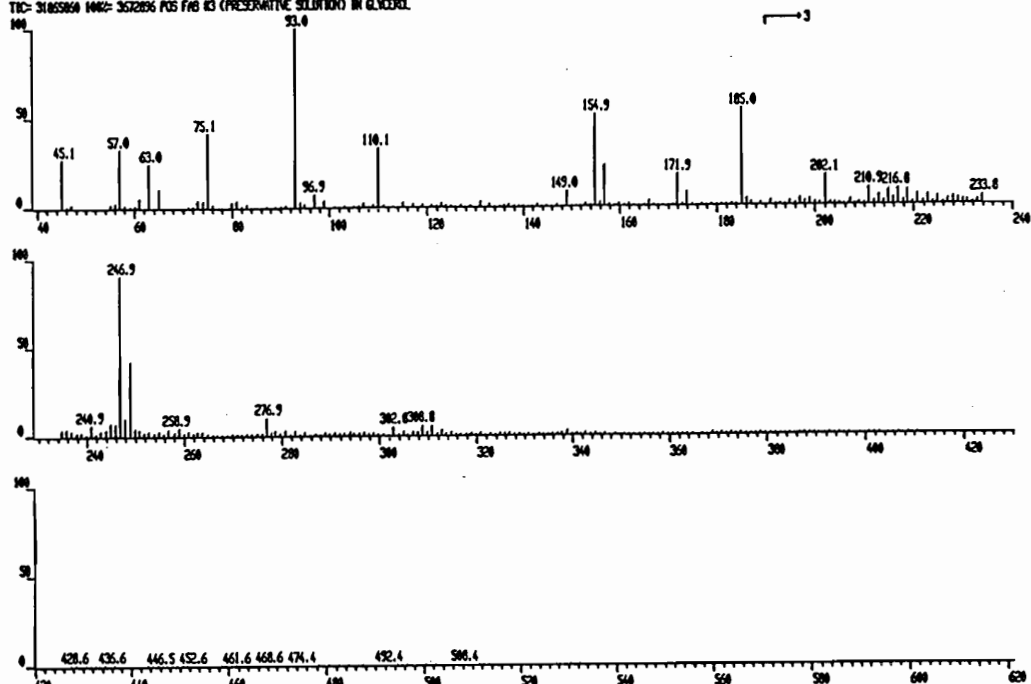


Figure 4.5.9. FAB mass spectroscopy spectra of A.) vanillin in water, B.) vanillin in NH_4OH , C.) ACZA solution, or D.) vanillin in ACZA.

Figure 4.5.9. (continued).

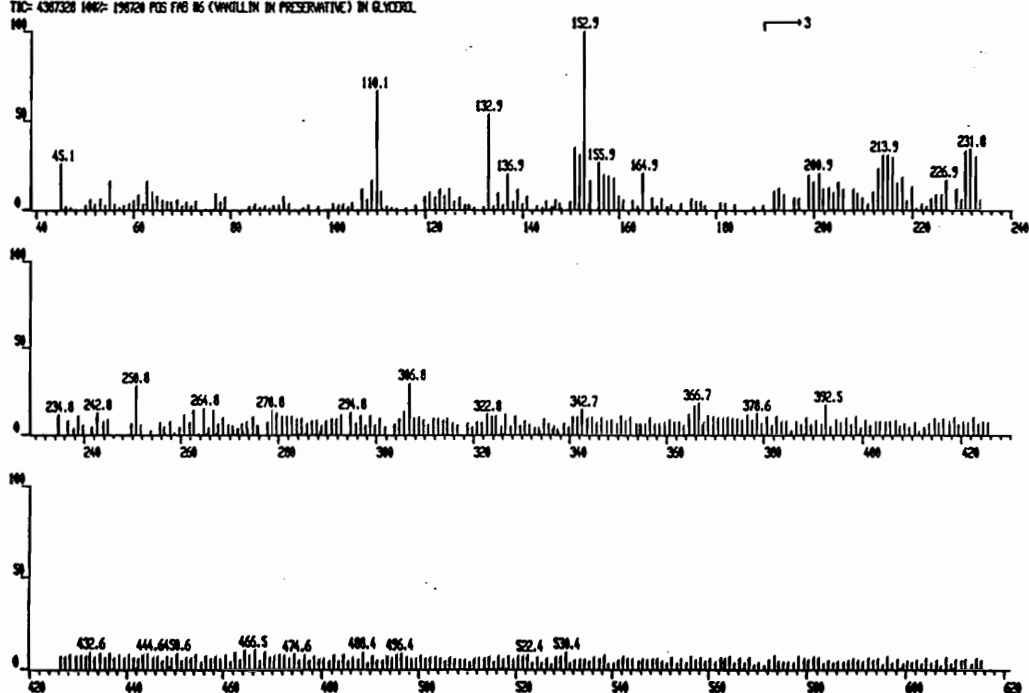
C.

8398 SWVL0004.S RT= 00:56 1F10 SUP 3-Apr-92 11:03
TIC= 3185389 1442= 357285 POS F10 10 (PRESERVATIVE SOLUTION) IN GLYCEROL



D.

8398 SL3181.S RT= 00:28 1F10 SUP 3-Apr-92 11:07 Sub
TIC= 4387328 1442= 156789 POS F10 10 (WHOLLIN IN PRESERVATIVE) IN GLYCEROL



appears likely, based on other parts of this study, that it was the hydroxyl hydrogen being removed, but many of the same mass/charge ratios could be achieved by bond formation with the aldehyde group oxygen.

4.6. Analysis Of Preservative Distribution

4.6.1. Introduction

Previous work in this paper has provided theories about the proportions in which copper, zinc, and arsenic were delivered to the wood. These theories can be supported by bulk analysis of treated samples, but it is also desirable to determine the proportions of these chemicals in the wood on a scale which is relevant to the wood structure. The electron microscope is a valuable tool which has been used in the past to detect preservative constituents in wood (Greaves, 1974). Energy dispersive x-ray analysis scanning electron microscopy is the most commonly employed technique, but this technique has poor arsenic sensitivity (Nielson, 1992). In this study an electron microprobe microanalyzer (EMMA) was used. The EMMA performs elemental assays based on wavelength dispersive properties of x-ray analysis, and is able to detect arsenic in wood at levels below 500 parts per million (Chou, et al., 1973; Nielson, 1992; Petty and Preston, 1968).

4.6.2. Materials and Methods

Small cubes (approximately 0.5 cm^3) were cut from the springwood of a single growth ring in a Douglas-fir board. These cubes were vacuum impregnated with 3.25% ACZA solution (1.63% CuO, 0.82% ZnO, 0.80% As_2O_3), then solution was removed and the wood was subjected to another vacuum to remove excess preservative. The treated cubes were then stored in a plastic bag for 24 hours to slow drying and ammonia loss, thus simulating the conditions inside a

larger board. The cubes were then removed from the bag, air dried for one week, and split parallel to the grain to reveal two fresh radial faces. One-half of the original cube was then leached by agitating for 48 hours in distilled water. In this way, the same radial face of leached and unleached samples could be compared. The leached and unleached samples were then analyzed in four selected locations for copper, zinc, and arsenic by traversing the microprobe across the cell wall between two longitudinal tracheids. Readings were taken every micrometer; the width of the zone of excitation was about 5 micrometers.

4.6.3. Results and Discussion

Analysis of the EMMA results show that there was a wide variation in copper, zinc and arsenic content both within different areas of the sample and within a single traverse for both the leached and unleached material (Figures 4.6.1., 4.6.2.). Some of this variation also may be due to the proximity of the edge of the sample or paths of least resistance to fluid flow. Much of the variation in spectra was probably simply due to the probe encountering areas where a larger than usual volume of preservative was trapped and subsequently precipitated. Variation also appeared to be tied to the wood structure, but not in any consistent manner. Wood structure is difficult to relate to chemical content in this work because most of the cells split down along the cell wall. Although it was evident from the photomicrographs when the traverse crosses from one longitudinal tracheid to another, it was not as easy to determine the "depth" of the traverse within the cell wall, which was dependent on where the split occurred. Position within the cell

Figure 4.6.1. A.

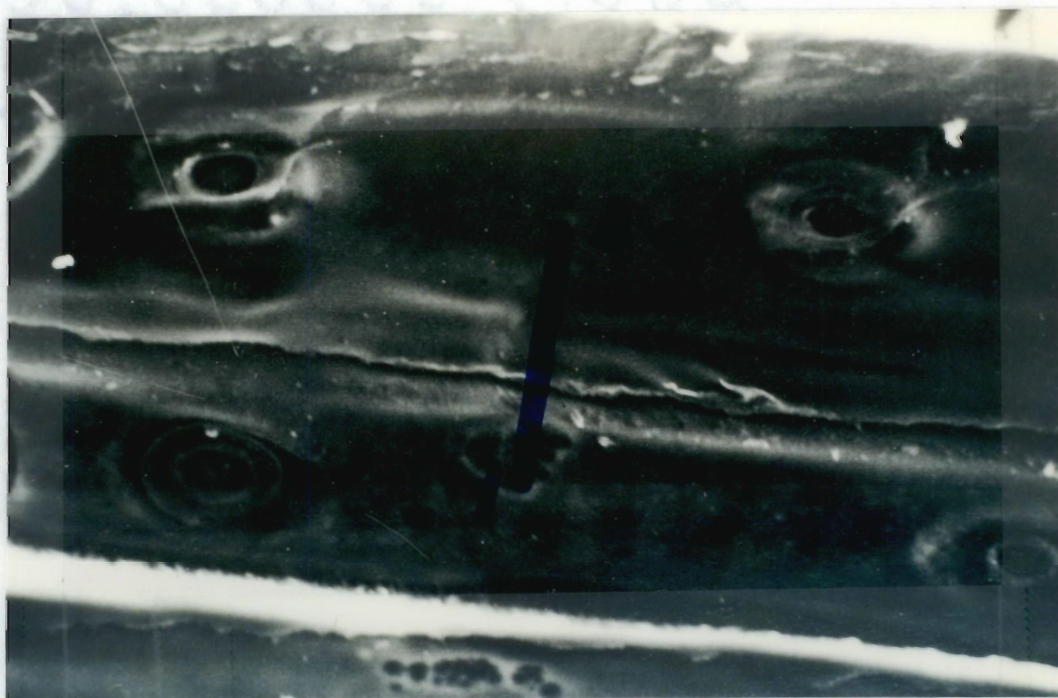
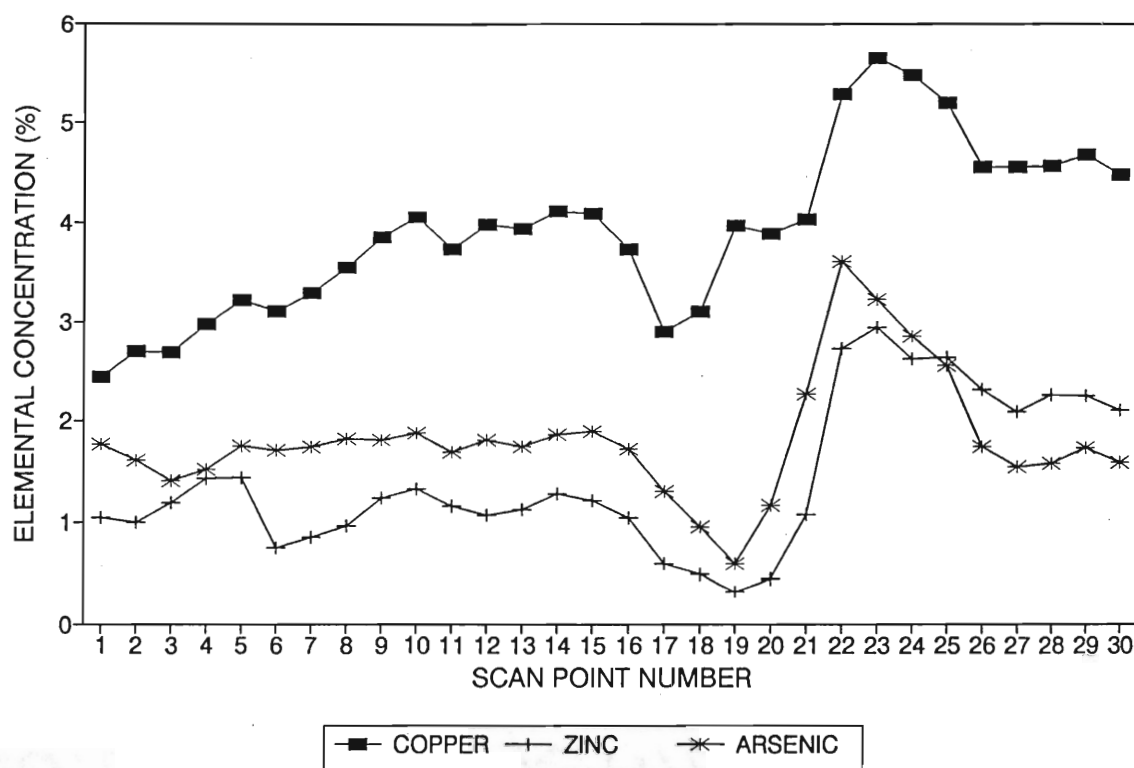


Figure 4.6.1. Examples of copper, zinc and arsenic levels in an ACZA treated, unleached Douglas-fir sample at points shown in the photomicrographs.

Figure 4.6.1. B.

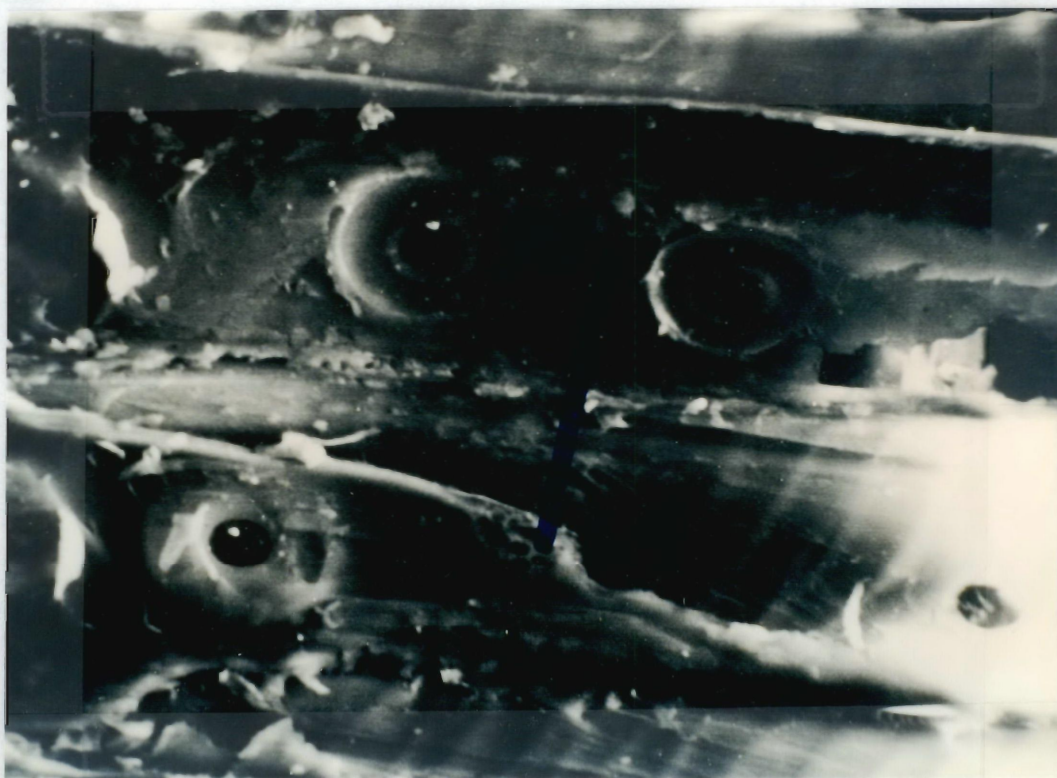
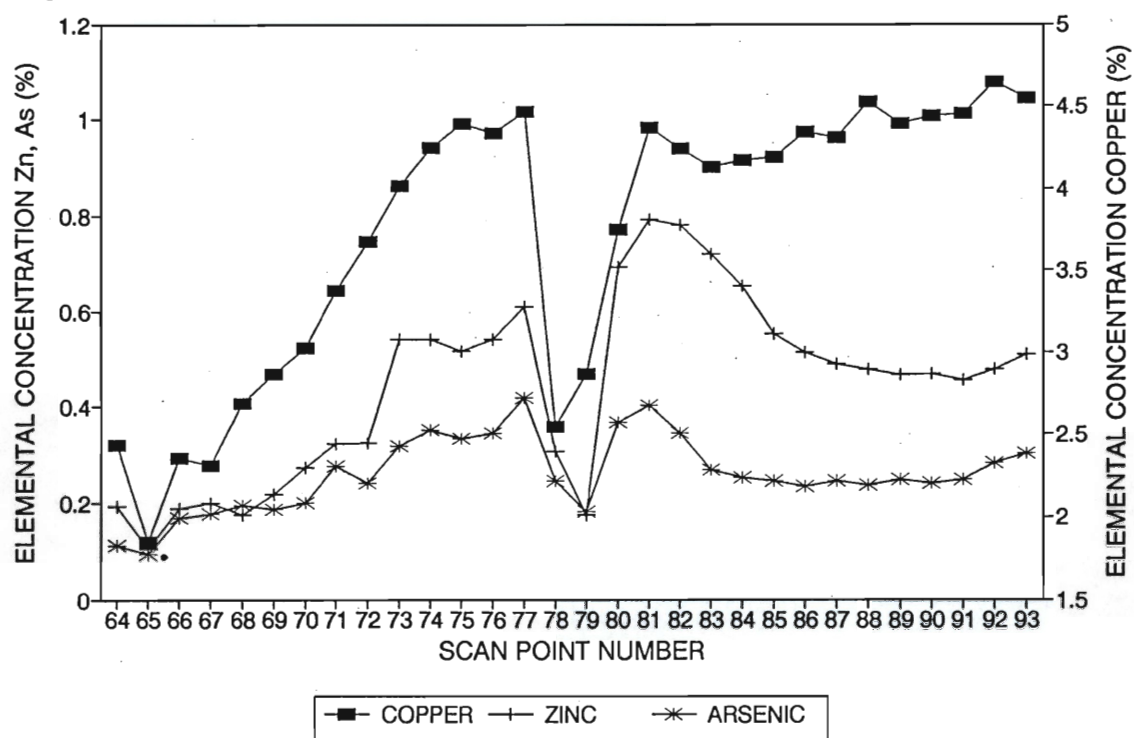


Figure 4.6.1. C.

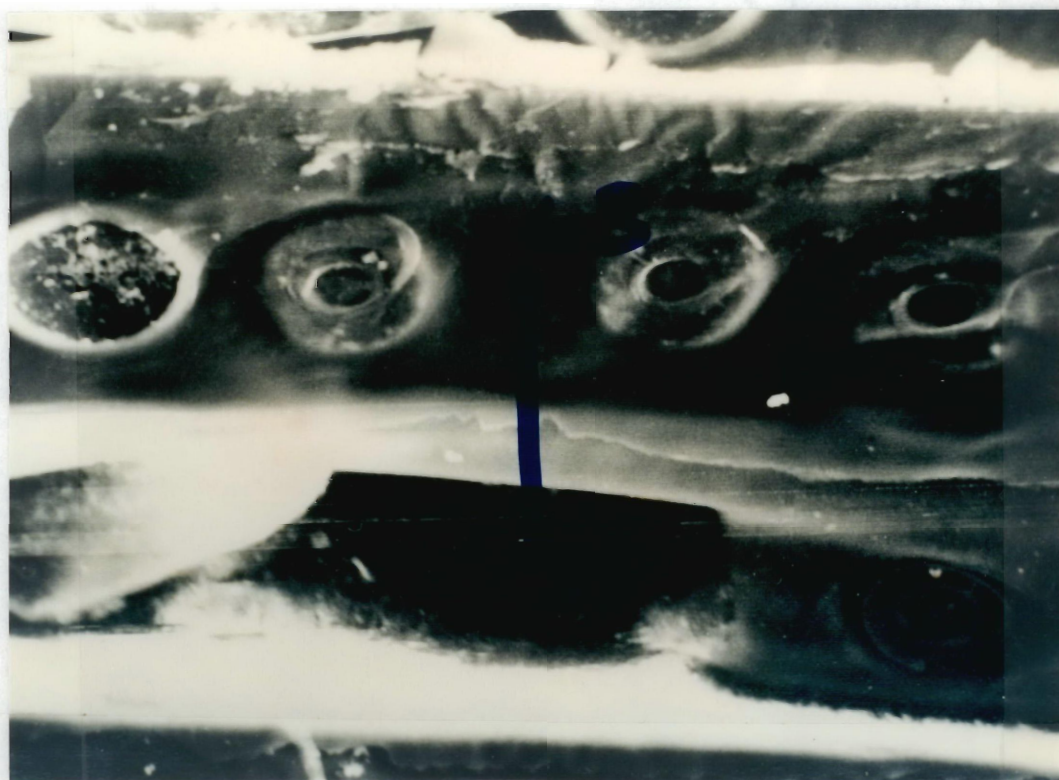
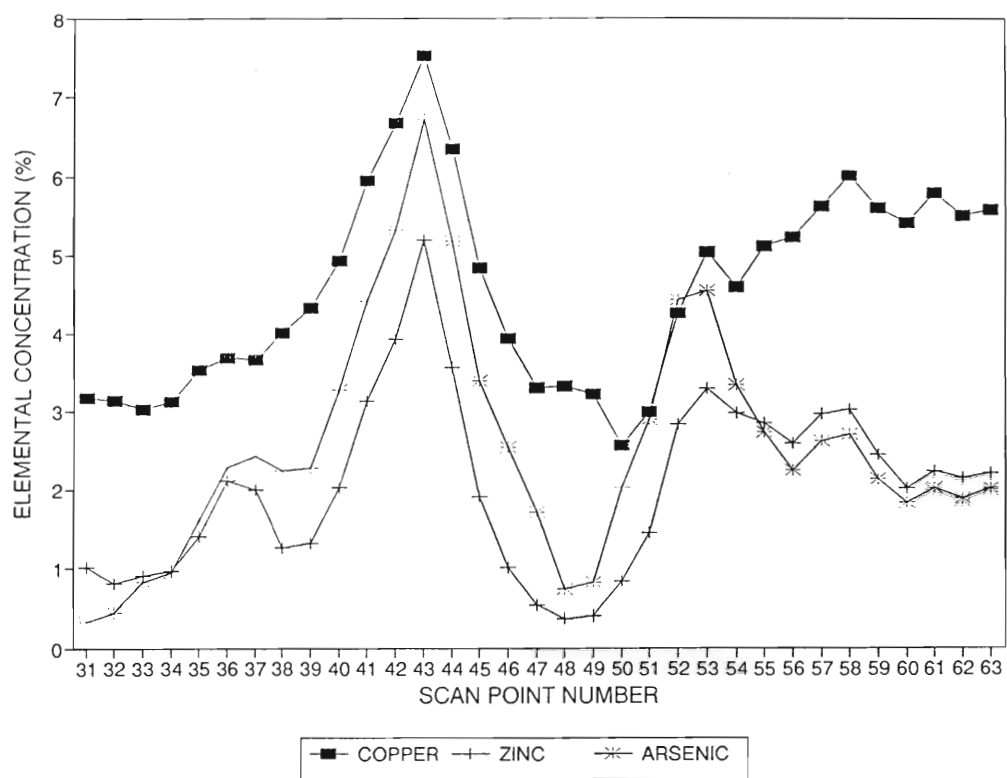


Figure 4.6.1. D.

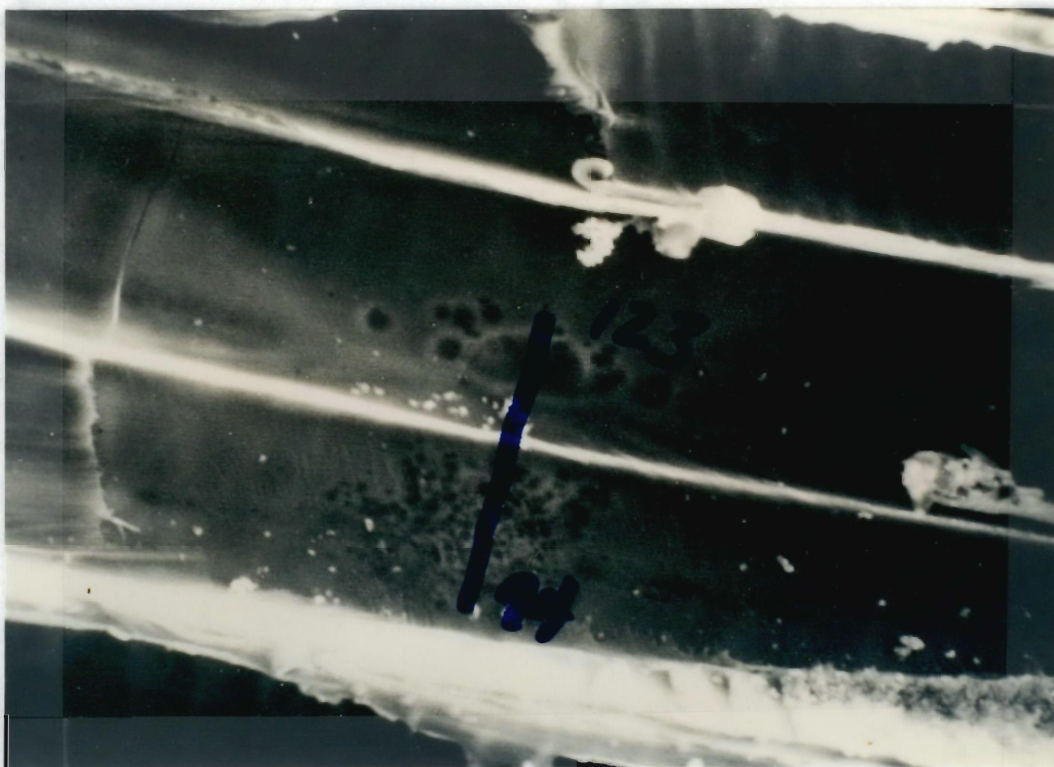
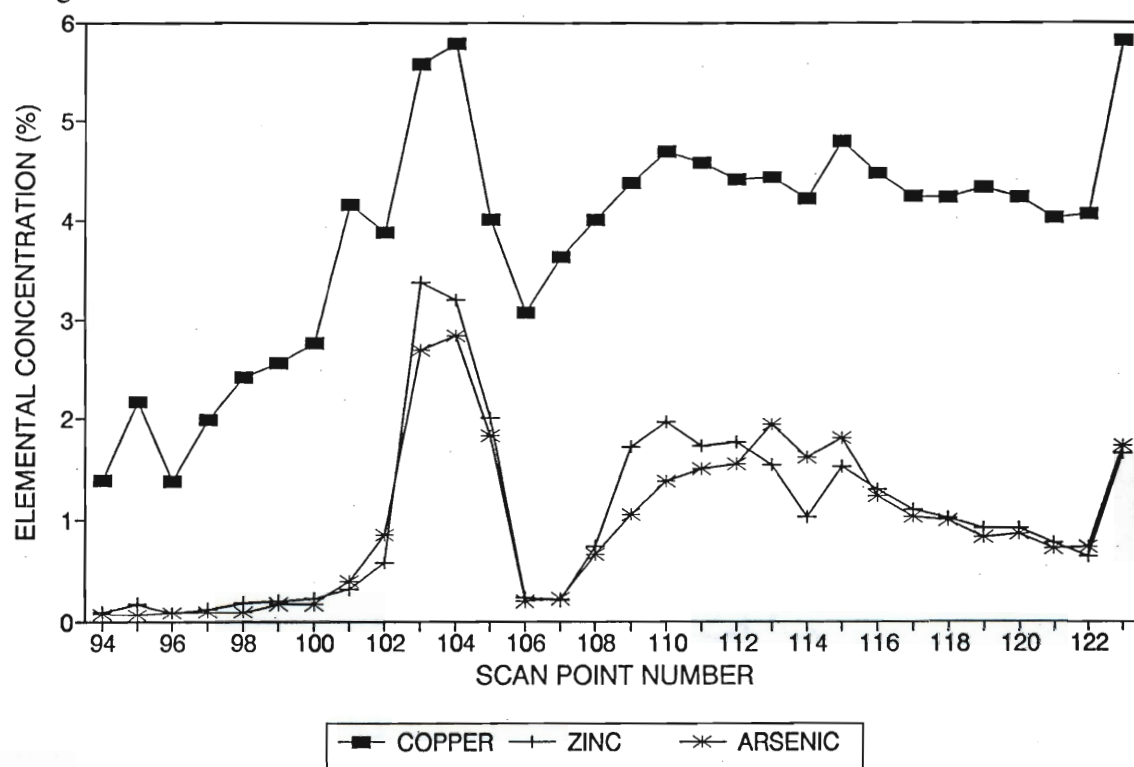


Figure 4.6.2. A.

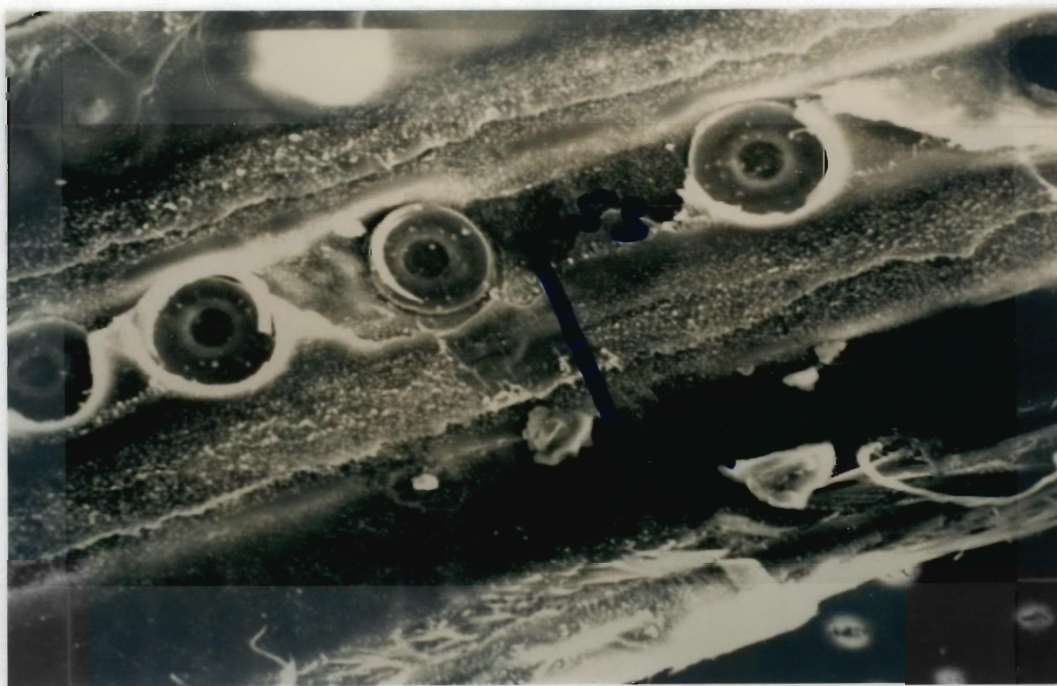
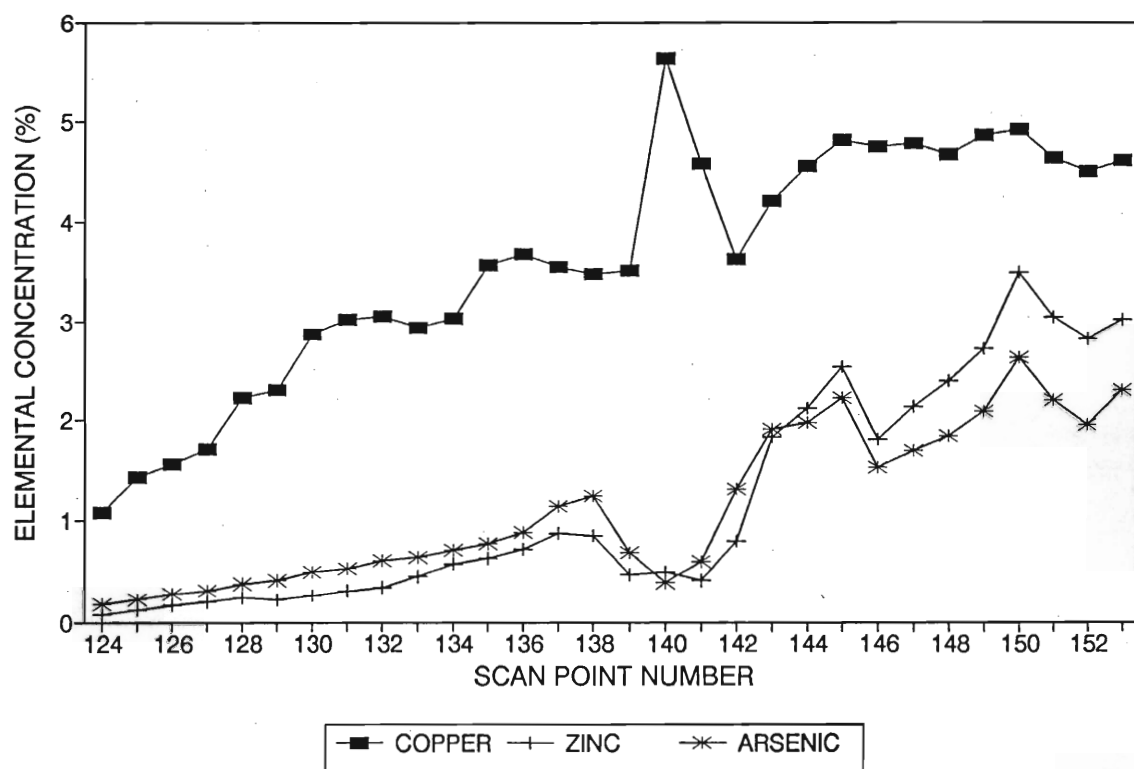


Figure 4.6.2. Examples of copper, zinc, and arsenic levels in an ACZA treated, leached Douglas-fir sample at points shown in the photomicrographs.

Figure 4.6.2. B.

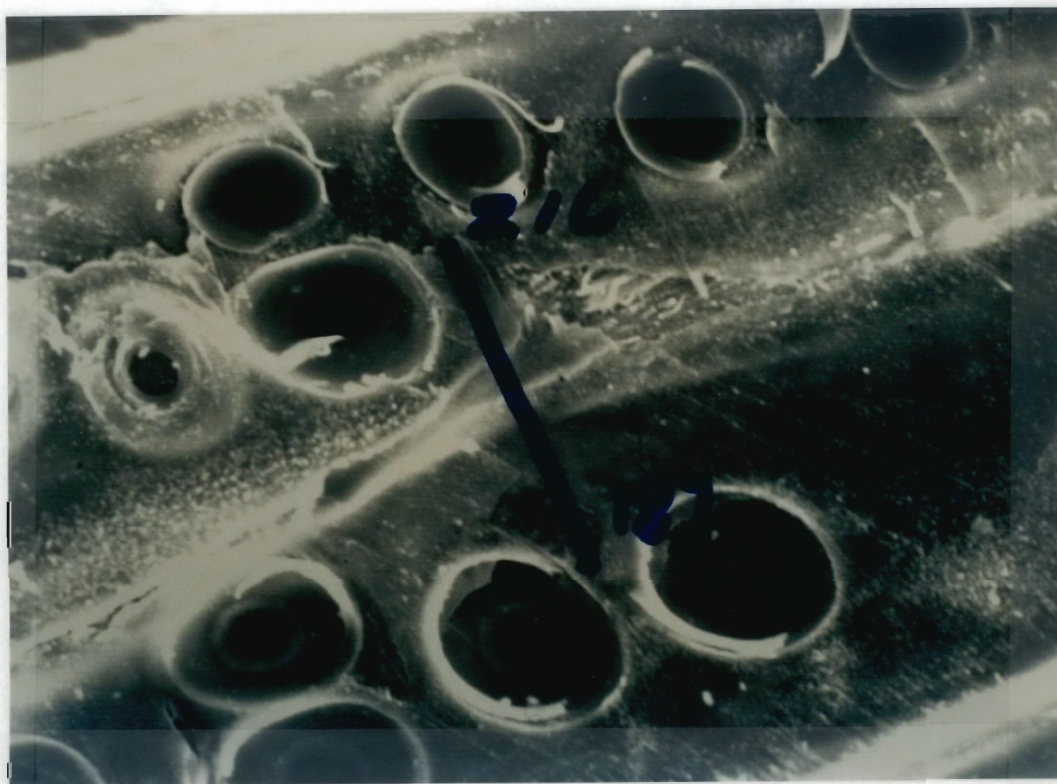
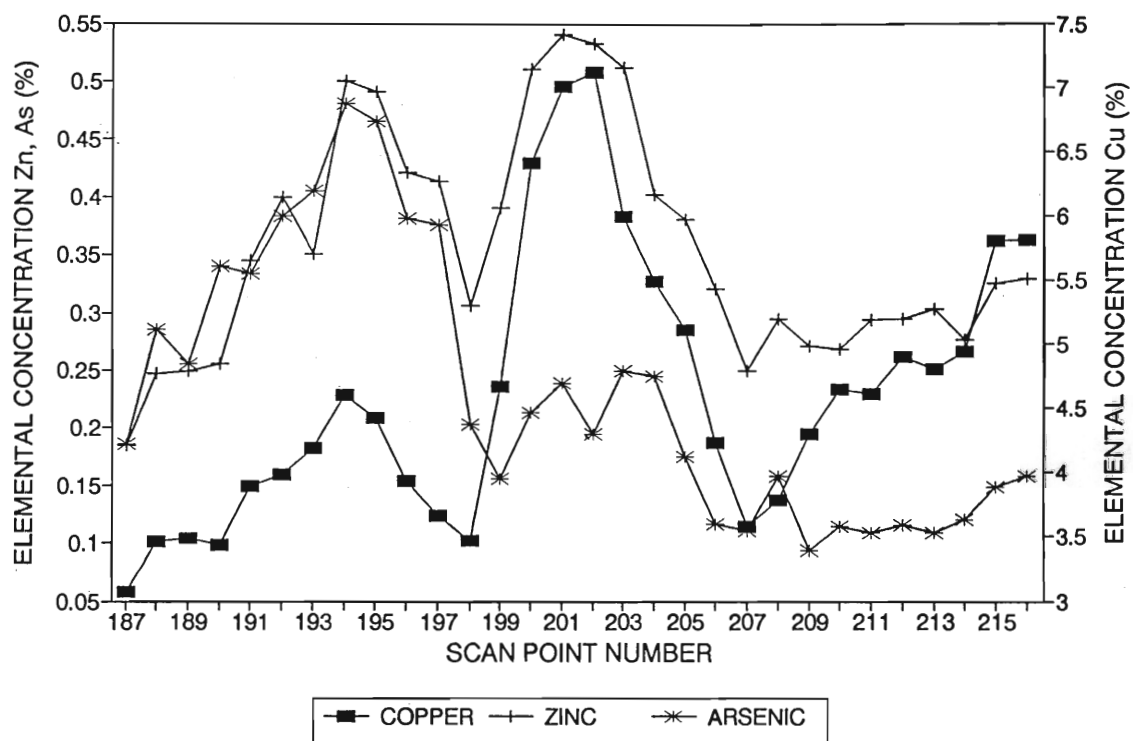


Figure 4.6.2. C.

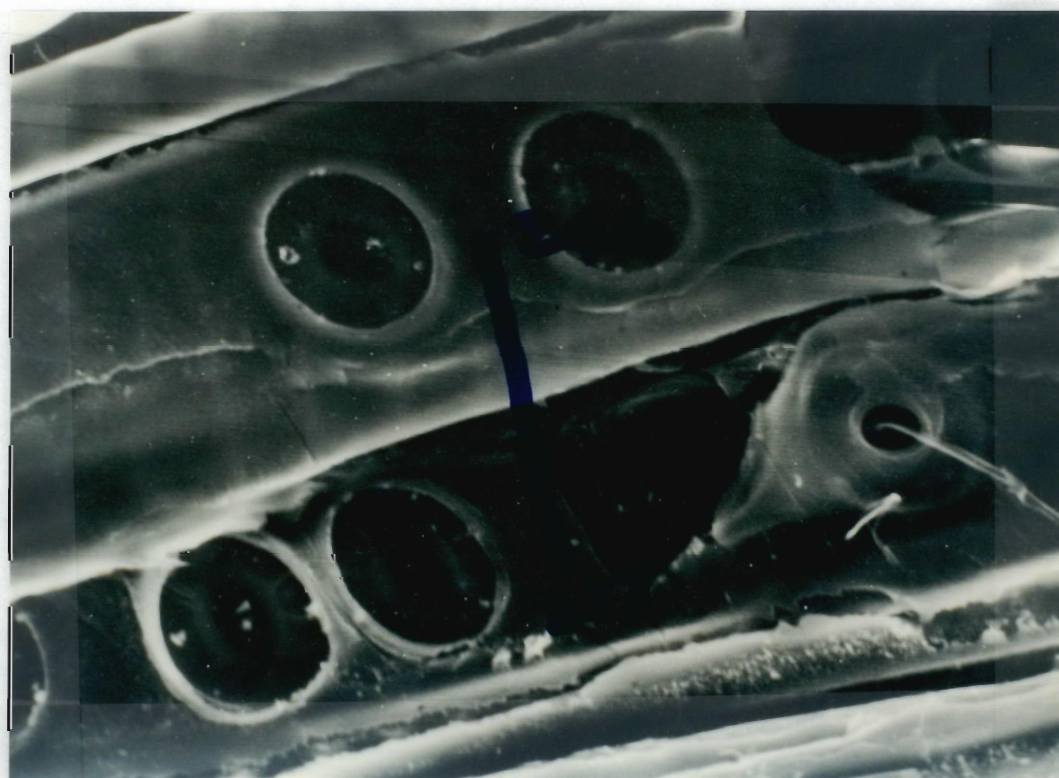
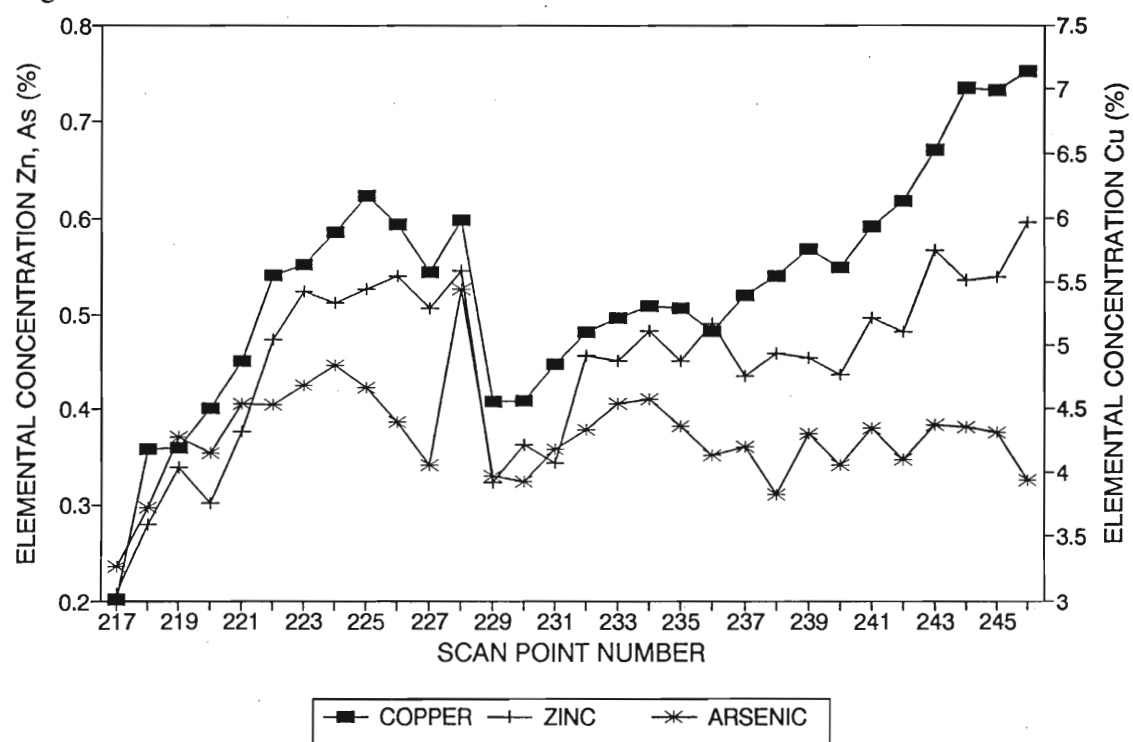
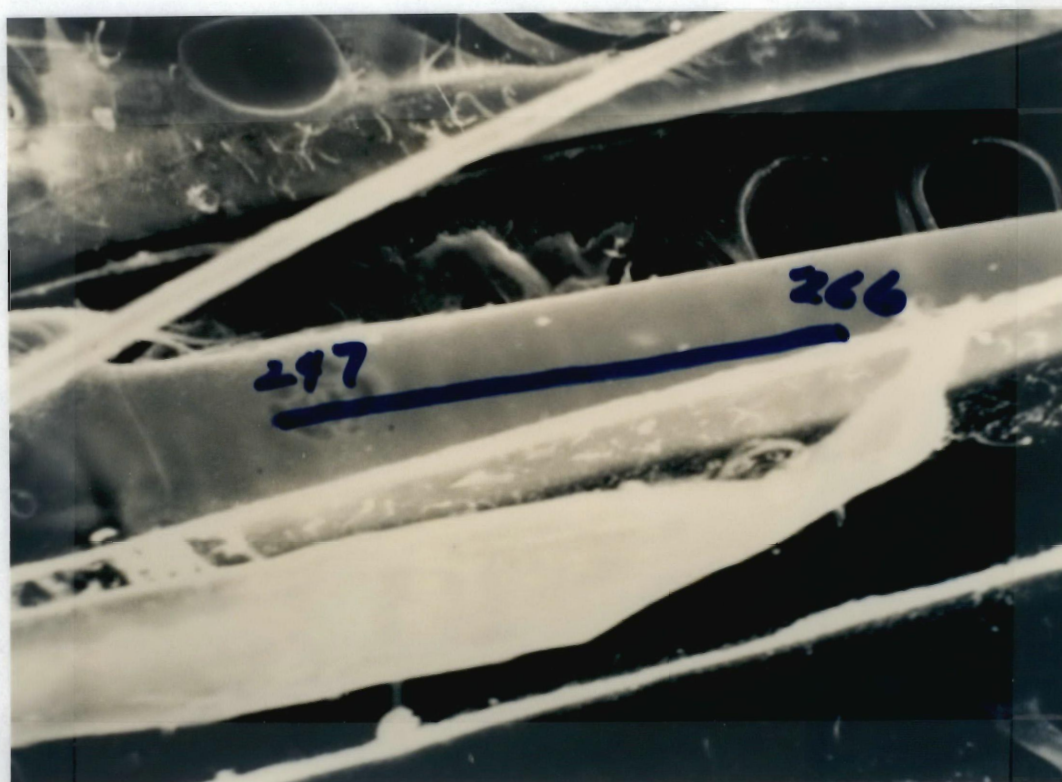
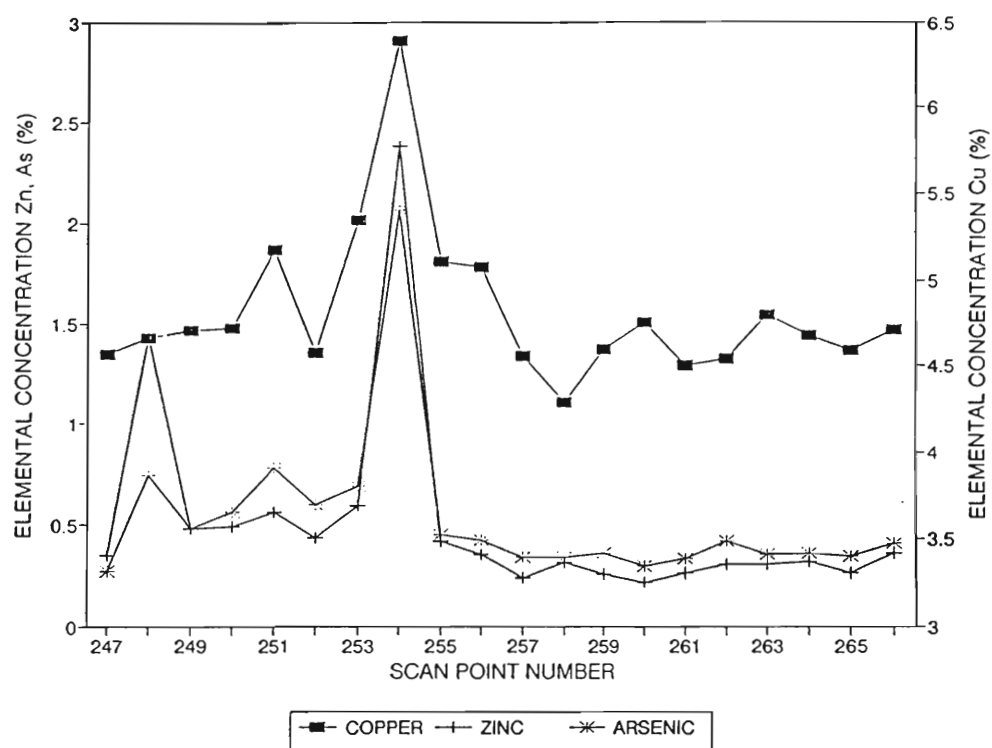


Figure 4.6.2. D.



wall, or at least lignin content, could significantly affect preservative levels if metals adsorbed to phenolic compounds. The effect of crossing the cell wall on chemical levels was quite variable; sometimes causing a dramatic increase in chemical levels, sometimes a decrease, and at other times causing no significant change (Figures 4.6.1., 4.6.2.).

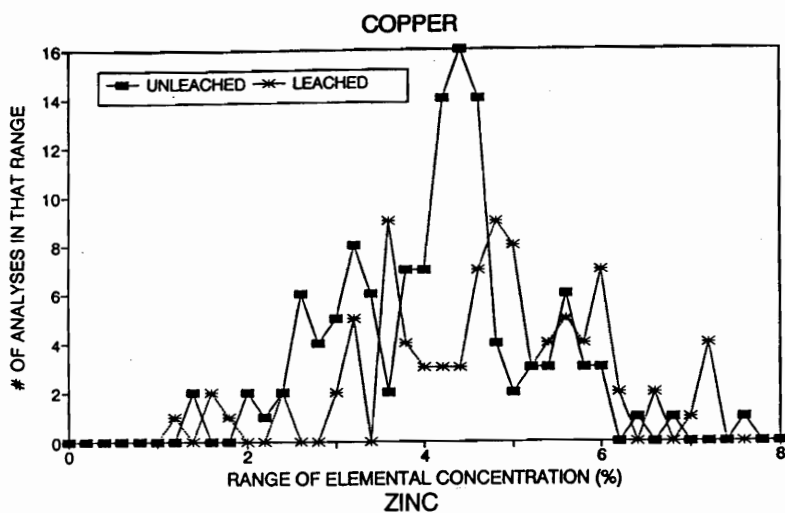
Despite the variability of chemical levels between locations, some interesting trends in the proportions of copper, zinc, and arsenic in the wood as compared to that in the treating solution were noted. For example, the proportion of copper in the wood was often several times higher than that in the treating solution (Figures 4.6.1., b; 4.6.2., b, c, d), while at other times it was the same or even lower than in the treating solution (Figures 4.6.1., a, c; 4.6.2., a). The adsorption of copper by the wood, especially phenolic groups, was noted in an earlier part of this study and may partially explain the increased copper levels in the wood. However, part of the difference in chemical proportions also can be attributed to variations in levels of zinc and arsenic; on a percentage basis their levels varied much more than those of copper (Figure 4.6.3.). It is possible that preservative access occurred by diffusion only within some cell walls, and that zinc and arsenic precipitated out of solution before diffusing into these areas. Previous results in this study (Section 4.3.) suggested that copper was less sensitive to the ammonia content of the preservative solution and precipitated after zinc and arsenic. Thus, copper may diffuse to a greater depth in the wood and achieve a more uniform distribution within the sample.

Also apparent from this analysis was the close relation between levels of copper, zinc and arsenic within a single sample. Levels of all three components fluctuated in the same manner across a single traverse, even though the level of copper was often several times higher than that of zinc or arsenic (Figures 4.6.1., 4.6.2.). The association between levels of zinc and arsenic was particularly close, supporting the earlier suggestion that zinc and arsenic precipitation are related. However, there were also areas within traverses where the zinc levels rose well above those of arsenic (Figures 4.6.1., b; 4.6.2., b, c). In these cases, the copper levels also rose, suggesting that these might be areas where the metals are undergoing adsorption reactions with the wood and were less available to precipitate the arsenic.

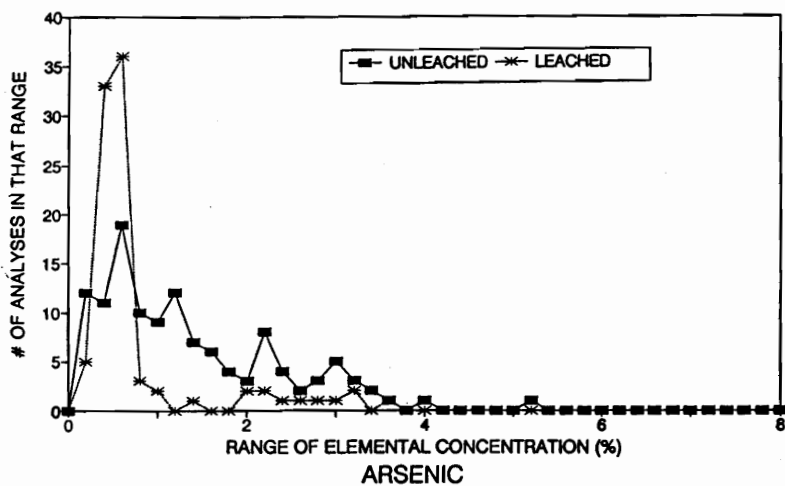
There was little difference in copper levels between traverses on leached and unleached samples, but levels of arsenic, and surprisingly zinc, tended to be lower in leached traverses (Figure 4.6.3.). While lower arsenic levels in the leached samples were expected, earlier work in this study found that very little zinc leached from ACZA treated wood as a result of the low water solubility of zinc. However, high variability in zinc and arsenic levels within different areas of the same sample were noted and the results may reflect traverses through these zones.

In general, the results of the EMMA analysis showed that the distribution of copper, zinc, and arsenic within ACZA treated wood was extremely variable, even within individual cells. In addition, the proportion of copper in the treated wood was much higher than that in the treating solution, providing further evidence for

A.



B.



C.

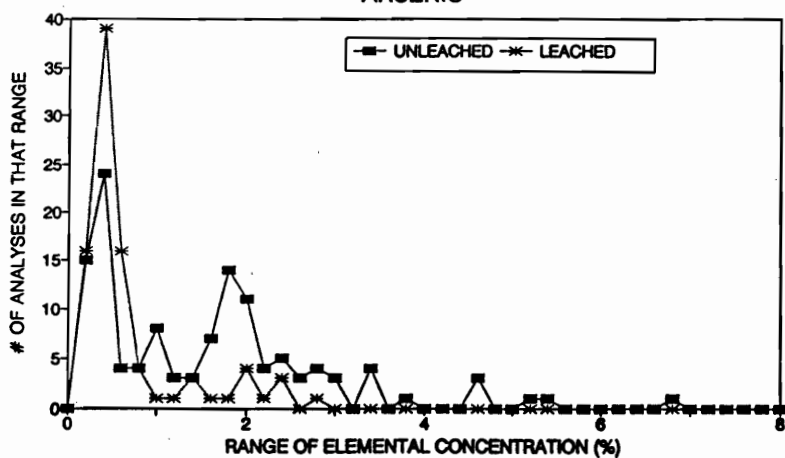


Figure 4.6.3. Range of elemental levels of A.) copper, B.) zinc, or C.) arsenic in unleached and leached samples.

the selective adsorption of this cation. Also of interest was the very close association between levels of zinc and arsenic throughout the wood, reinforcing the hypothesis that much of the arsenic is "fixed" through reactions with zinc.

4.7. Bonding Environment of Copper

4.7.1. Introduction

Other parts of this paper have attempted to explain fixation mechanisms based on the effect that metal adsorption reactions had on the treated substrate. Another approach is to examine the bonding environment of the metal itself, using a technique such as electron paramagnetic resonance spectroscopy (EPR) (also called electron spin resonance spectroscopy (ESR)). In this technique, materials which contain unpaired electrons, such as copper, are subjected simultaneously to a varying microwave frequency magnetic field as well as a static magnetic field. The unpaired electron interacts with these two magnetic fields, absorbing energy. The presence of other magnetic forces, such as those caused by bonding of the copper atom, cause changes in the electron's energy absorption pattern, thus providing information about the atom's molecular environment. The absorption pattern is often described by a proportionality constant, "g", which is frequency independent. The value of g is 2.002 for an unpaired electron if its environment is free of magnetic fields other than that created by the electron spin (Plackett, et al., 1987). Because copper atoms in a solid cannot rotate freely about all axes, two types of absorption are observed, corresponding to parallel or perpendicular orientation of the magnetic field to the rotational axis of the copper atom. The g-value for copper in the parallel section of the spectrum typically varies between 2.08 - 2.42, and that in the perpendicular part of the spectrum between 2.04 - 2.06, depending on the nature of copper's molecular environment (Plackett, et al., 1987).

4.7.2. Materials and Methods

The EPR tests were conducted on lignin because it appears to adsorb copper more strongly than other wood components. Spruce lignin was treated with either ACZA, a solution of copper oxide in dilute ammonium hydroxide, or a solution containing only dilute ammonium hydroxide. For the ACZA treatment, 7.97 grams of lignin were combined with 85.3 grams of 0.008% ACZA (0.004% CuO, 0.002% ZnO, and 0.002% As₂O₅) in a 125 milliliter Erlenmeyer flask, agitated for 15 minutes, and then allowed to precipitate for 5 minutes. The ACZA solution was then poured off and the precipitate washed 5 times with 50 mls of distilled water which had been adjusted to pH = 9.8 with ammonium hydroxide. A similar process was carried out using 8.12 grams of lignin agitated with 81.30 grams of a 0.004% CuO solution or 8.11 grams of lignin agitated with 81.02 grams of a 0.25% ammonia (from ammonium hydroxide) solution. The washing procedure was used to maximize the proportion of copper in the wood which was fixed due to adsorption reactions.

The washed lignin from these procedures was stored in plastic bags for 24 hours to retard drying and simulate conditions in treated wood. The samples were then air-dried at room temperature for 5 days, and analyzed for copper, zinc, and arsenic using X-ray fluorescence techniques. The ACZA treated lignin contained 0.042% CuO, 0.028% ZnO and no detectable arsenic, while the CuO treated lignin

contained 0.052% CuO. EPR analysis was conducted at the Oregon Graduate Center, Beaverton, Oregon, using a Varian EPR Spectrophotometer.²

4.7.3. Results and Discussion

Comparison of the spectra of the ammonia treated lignin to that treated with ACZA or CuO reveals the alterations due to the presence of Cu²⁺ (Figure 20). The spectra of ACZA and CuO treated lignin were very similar, with g-parallel and g-perpendicular values of 2.405 and 2.046 for the ACZA treatment and 2.392 and 2.043 for the CuO treatment, respectively. The g-parallel values determined in this study are higher than values reported in previous work which examined pine sapwood impregnated with an ammoniacal copper complex (g-parallel < 2.25) (Hughes, et al., 1992). The proportion of adsorbed copper was presumably much lower in that study, as whole wood was treated and no effort was made to wash out unfixed copper. There is a tendency for the g-parallel value to increase as the distortion of copper from a tetrahedral configuration increases (Hughes, et al., 1992), as might occur if copper becomes bonded to more bulky substituents such as lignin. The nonhomogeneous broadening of peaks in the g-parallel region of both spectra indicated that copper species were present in more than one molecular environment, but that at least one of the environments involved some type of bonding. The uneven hyperfine splitting in the g-perpendicular region also demonstrated the presence of more than one copper species. This type of hyperfine

²The author is indebted to Dr. Ninian Blackburn, Oregon Graduate Center, for his assistance in performing the EPR analysis as well as interpreting the spectra.

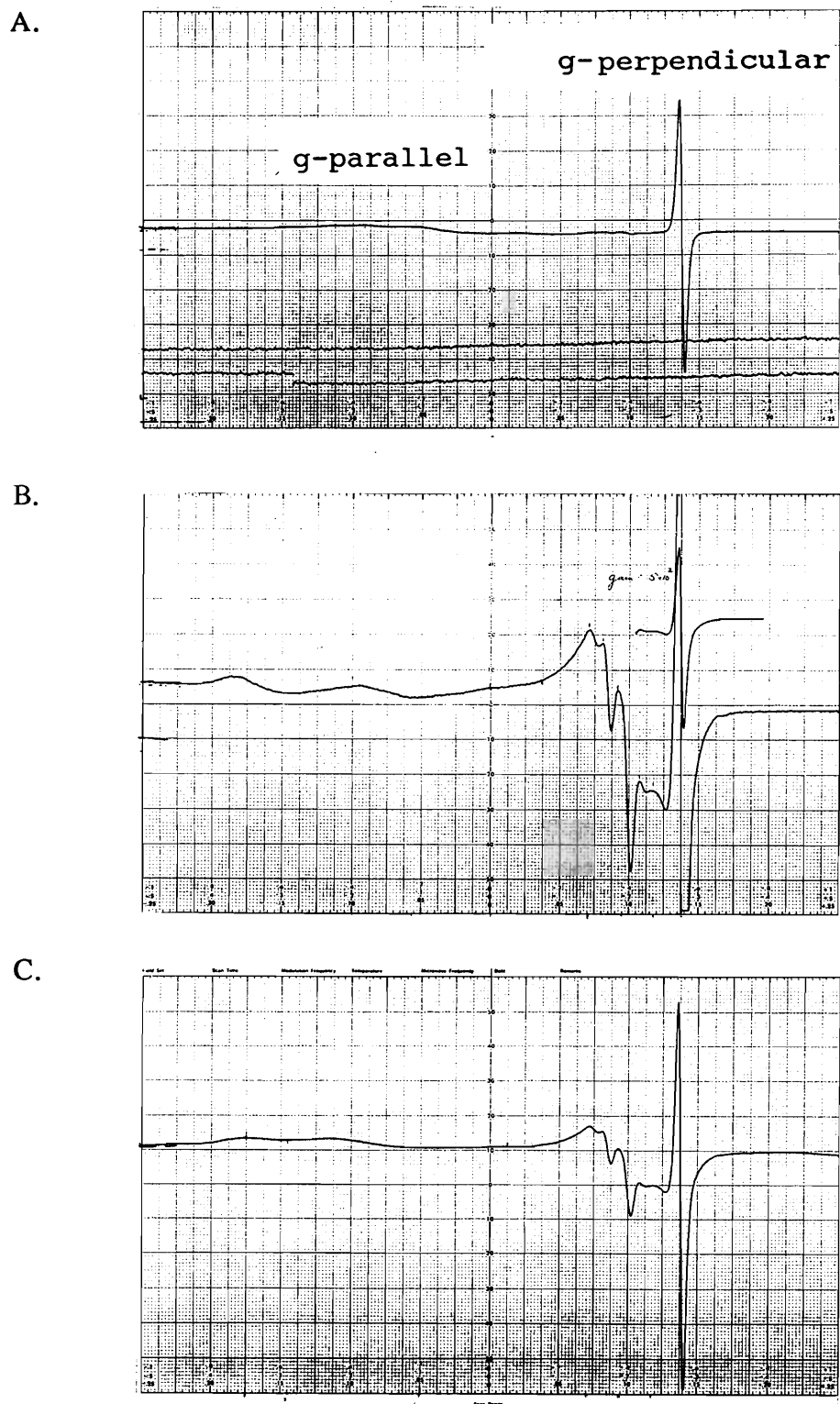


Figure 4.7.1. EPR spectra of spruce organosolve lignin after A.) ammonia treatment, B.) CuO treatment, or C.) ACZA treatment.

splitting may be attributable to the bonding of copper to nitrogen atoms, suggesting that some of the copper in the lignin was still bonded to ammonia molecules.

A dominant feature in the spectra was the free radical signal of lignin. Although lignin normally has a strong free radical signal, copper appeared to enhance this signal even further. ACZA treated and CuO treated lignin had free radical signals 1.4 and 1.3 times, respectively, that in lignin treated with ammonium hydroxide. It appears that reactions occurring during the adsorption of copper induce free radical formation, possibly transforming some of the phenolic groups into quinone-type structures. If copper serves as an electron acceptor in these reactions, the presence of Cu^+ would be indicated within the treated wood. However, a dramatic increase in lignin free radical content following treatment with basic sodium has been noted previously (Steelink, 1966). This increase was attributed to alkaline demethylation of guaiacols, which would subsequently be oxidized to orthoquinones and then hydroquinones. These hydroquinones might then form stable radical semiquinone anions under basic conditions (Steelink, 1966).

The generation of free radicals in the wood by ACZA may also influence the manner in which this preservative protects against decay fungi. In previous research, both brown and white rot fungi produced a two to threefold increase in the free radical content of southern pine and sweet gum (Steelink, 1966). This increase was attributed to enzymatic oxidation of phenolic constituents to produce quinone moieties, which in turn would react with other phenolic groups to produce

stable radical anions trapped within the lignin structure (Steelink, 1966). This mechanism is very similar to that described for reaction with basic metal salts (Steelink, 1966), and it is possible that ACZA treatment interferes with this pathway for fungal degradation of wood.

The intensified free radical peak, combined with the g-perpendicular hyperfine splitting, was consistent with the presence of copper in a square planer configuration; perhaps bonded to two oxygens from a lignin phenolic group and two ammonia molecules. However, the spectra also suggested that copper was present in several forms, making other types of lignin-copper bonding possible.

5.0.

SUMMARY

This paper has described a series of experiments conducted to improve our understanding of the mechanism of ACZA fixation in Douglas-fir. The results of these experiments suggest that several types of interactions take place within the preservative and between the preservative and the wood.

The adsorption of copper by wood components or functional groups similar to those found in wood has been demonstrated in several experiments. Levels of copper in ACZA treated wood were found to be proportionally much higher than those in the treating solution (Section 4.1.), and copper was selectively depleted from the treating solutions (Sections 4.2., 4.3., 4.5.). This finding agrees with previous studies, which noted copper adsorption from ACZA (Cooper, 1991) or CCA (Dahlgren, 1972; Pizzi, 1982) treating solutions.

Phenolic constituents within the wood appear to provide the majority of the reactive sites for copper adsorption during ACZA treatment. Lignin adsorbed significantly more copper from an ACZA treating solution than did heartwood, sapwood, cellulose or xylan (Section 4.2.). In addition, heartwood adsorbed more copper than sapwood, probably due to the presence of phenolic incrustations and extractives within the heartwood cells. Accordingly, heartwood adsorbed slightly less copper after the extractives had been removed (Section 4.5.2.). Copper also leached at a higher rate from heartwood than sapwood, possibly due to the

formation of water soluble copper/extractive complexes (Section 4.1.). Although adsorption by cellulose was minimal, xylan did adsorb a significant amount of copper, suggesting that copper may also have reacted with the uronic acid groups in hemicellulose.

Tests with lignin model compounds indicated that the phenolic hydroxyl group was a major reaction site during copper adsorption. Aromatic compounds with OH groups appeared to adsorb copper more readily than those with methoxyl groups (Section 4.5.3.), and ACZA treatment altered peaks associated with the hydroxyl group in the FTIR spectrum of vanillin (Section 4.5.6.). Similarly, FAB mass spectrophotometry analysis of ACZA treated vanillin detected mass/charge ratios in agreement with displacement of the hydroxyl hydrogen followed by formation of a bond to a copper or zinc species (Section 4.5.7.).

Examination of the bonding environment of copper within treated lignin also indicated interaction with phenolic hydroxyls (Section 4.7.). The copper treatments increased the free radical content of the lignin, suggesting that copper displaced hydroxyl hydrogens or methoxy methyl groups on catechol-type moieties within the lignin. Multiple species of copper were detected in the ACZA treated lignin, including at least one form that appeared to be associated with ammonia. The bonding environment was consistent with copper situated in a square-planer configuration, perhaps bonded to two phenolic hydroxyl oxygens and two ammonia molecules.

Although copper adsorption appeared to be an important factor in ACZA fixation, less than 40% of copper in the wood was fixed in this manner (Section 4.1.). The remaining copper was still highly leach resistant however (Section 4.1.), probably due to the formation of insoluble precipitates as the ammonia evaporated. This reaction does not require the presence of zinc or arsenic (Section 4.1.), and a large proportion of the copper is probably deposited within the wood as a basic copper salt. Although copper arsenate appeared to be a major precipitate in ACA formulations, this precipitate probably forms in ACZA treatments only when the amount of arsenic exceeds the amount of available zinc.

Zinc appeared to undergo the same type of ion-exchange reactions with wood components as copper, but to a much lesser extent (Sections 4.2., 4.3.). Zinc also adsorbed more readily to lignin than to heartwood, sapwood, cellulose, or xylan, suggesting that the phenolic groups may be a primary reaction site for zinc. However, unlike copper, zinc adsorbed at least as or more readily to xylan than heartwood. It is possible that the nonlignin phenolic reactive sites in the heartwood, such as extractives or cell incrustations, were quickly claimed by copper, or that zinc was more prone to react with the uronic acid groups in xylan.

As with copper, zinc was most readily adsorbed by phenolic compounds which contained hydroxyl, not methoxyl groups (Section 4.5.3.). In addition, FAB mass spectrophotometry of ACZA treated vanillin detected mass/charge ratios in agreement with the loss of a hydrogen and the addition of zinc species. Although most of the changes in the FTIR spectrum of ACZA treated vanillin were probably

attributable to copper adsorption, zinc adsorption may have also played a role in altering the hydroxyl region of the spectrum (Section 4.5.6.).

Although some zinc adsorption was noted, the primary mechanism of zinc fixation appeared to be precipitation as a water-insoluble salt. When the ammonia in the treating solution was allowed to evaporate, zinc precipitated before copper (Sections 4.3., 4.4.), and in direct proportion to the precipitation of arsenic. As arsenic solubility is not dependent on ammonia, it seems likely that zinc precipitates from ACZA as a basic zinc arsenate. However, zinc was also highly leach resistant when wood was treated with solutions containing very little arsenic, indicating that other insoluble precipitates such as basic copper salts form in the absence of arsenic (Section 4.1.).

Arsenic, in contrast to copper and zinc, appeared to interact very little with the wood substrates, or with copper or zinc which were adsorbed to the wood substrates (Section 4.2.). Arsenic depended on the presence of metal cations to become leach resistant, and leached substantially unless the metal oxide:arsenic pentoxide ratio exceeded 2.0 (Section 4.1.). Zinc appeared to improve the leach resistance of arsenic when compared to formulations containing copper as the only cation. Similarly, the majority of the arsenic was precipitated by the zinc when the ammonia was allowed to evaporate (Sections 4.3., 4.4.), and examination of ACZA treated wood revealed that zinc and arsenic levels were closely related within the wood structure (Section 4.6.). The zinc and arsenic precipitated in a nearly 1:1 molar ratio and one possible fixation product is $\text{Zn}_2\text{As}_2\text{O}_7$ (Section 4.4.).

However, when available zinc in the solution is depleted due to adsorption reactions, the remaining arsenic must depend on copper for fixation.

The results of this study generally support the conventional premise that arsenic fixation occurs by precipitation of metal/arsenate complexes as ammonia evaporates from the treated wood. This fixation mechanism requires that sufficient metal cations are present in the treating solution to react with all of the arsenic anions. In contrast, the metal cations are not dependent on arsenic for fixation, since they have low water solubility and undergo adsorption reactions with the wood. However, adsorption reactions can interfere with arsenic fixation by reducing the availability of metal cations in the preservative solution.

The severity of arsenic leaching due to adsorption of metal cations in the wood will vary with treating conditions and wood species. Although the majority of metal adsorption to wood powders in this study occurred within 10 minutes, adsorption may occur over a much longer period in commercial treatments, since preservative components can continue to diffuse through the wood where they may come in contact with new reactive sites. Consequently, longer treating schedules and storage practices which inhibit drying would allow more adsorption to occur before the metals precipitated. Conversely, practices such as long final vacuum periods and kiln drying after treatment might speed ammonia loss and increase the proportion of metals available to precipitate the arsenic. Similarly, increased adsorption might occur in permeable wood species where ACZA components could diffuse rapidly into the cell walls where they would contact more lignin, or in wood

species which contain a high proportion of extractives or other phenolic materials. In addition, the percentage of arsenic susceptible to leaching may increase when low solution concentrations are employed, since a higher proportion of copper and zinc will be adsorbed from the solution. Further research is needed to determine if these treating variables significantly affect ACZA fixation, and if they can be manipulated to minimize arsenic leaching.

Arsenic leaching could be minimized more directly by increasing the proportion of zinc in the original treatment solution. However, the efficacy of the preservative against insects and decay fungi might be adversely affected by such composition changes. More biological testing is needed to determine how the ratios of copper, zinc, and arsenic in ACZA could be altered to minimize arsenic leaching while still providing maximum protection against wood destroying organisms.

ACZA is a proven wood preservative with potential for much greater use in the future. Hopefully, this research, as well as future research projects, will provide the information needed to ensure that ACZA continues to be a safe and effective system for protecting wood against biological degradation.

6.0.

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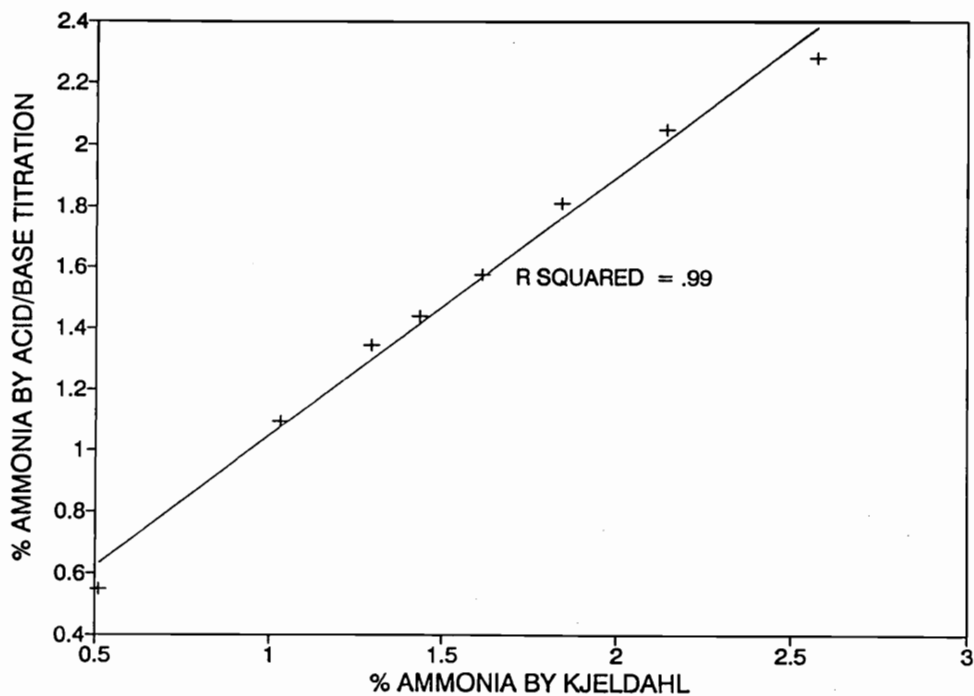
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APPENDIX

7.1.

Appendix A

A.



B.

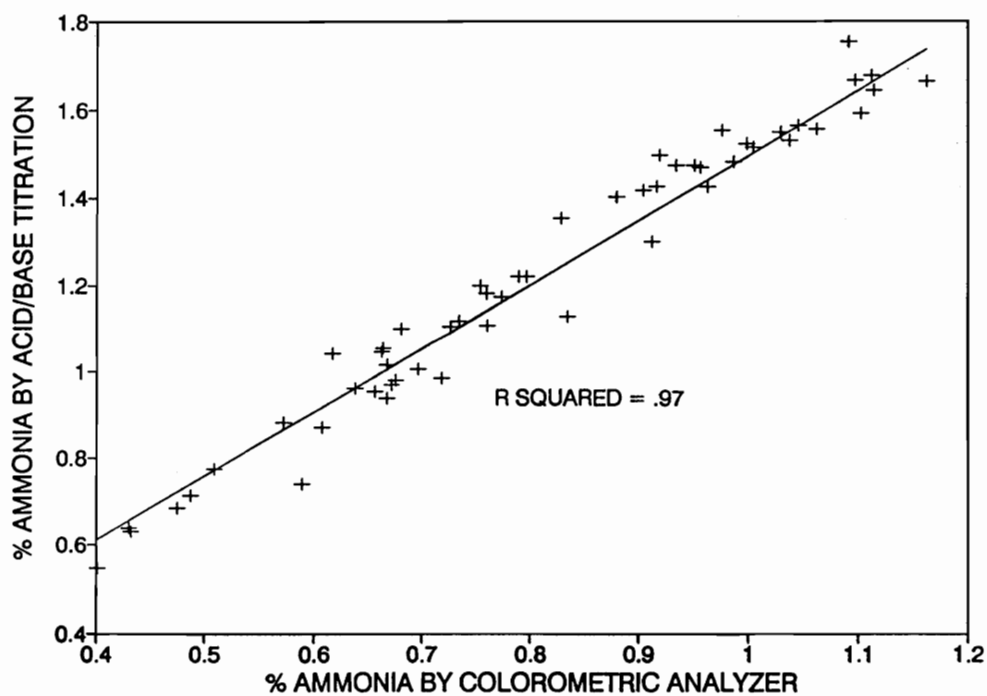


Figure 7.1. Correlation between acid/base titration method and A.) Kjeldahl analysis or B.) Alpkem RFA-300 colorimetric analysis for determining ammonia content in ACZA.