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**A Chemical Stain for Identifying  
Arsenic-Treated Wood**

**(FINAL)**

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## LIST OF ABBREVIATIONS AND ACRONYMS

As	Arsenic
AA	Atomic Absorption
AAC	Alkyl Ammonium Compound
ACC	Acid Copper Chromate
ACQ	Ammoniacal Copper Quat
ACZA	Ammoniacal Copper Zinc Arsenate
BB	Below Baseline
BDL	Below Detection Limit
CBA	Copper Boron Azole
CC	Copper Citrate
CCA	Chromated Copper Arsenate
CDDC	Copper Dimethyldithiolcarbamate
C&D	Construction and Demolition
CPSC	Consumer Product Safety Commission
Cr	Chromium
Cu	Copper
DI	De-ionized
FCSHWM	Florida Center for Solid and Hazardous Waste Management
FDEP	Florida Department of Environmental Protection
LIBS	Laser Induced Breakdown Spectroscopy
MDL	Minimum Detection Limit
nc	No Change
P	Phosphorous
PAN	1-(2-pyridylazo)-2-naphthol
TAG	Technical Awareness Group
UF	University of Florida
UM	University of Miami
USEPA	U.S. Environmental Protection Agency
XRF	X-ray Fluorescence Spectroscopy

## UNITS OF MEASURE

%	Parts per hundred
µg	Microgram
°C	Degrees Celsius
g	Grams
kg/m <sup>3</sup>	Kilograms of chemical per cubic meter of wood. Chemical typically refers to CCA on an oxide basis.
L	Liter
mg	Milligrams
mg/kg	Milligrams of chemical per kilogram of wood
mg/L	Milligrams per liter
mL	Milliliter
nm	Nanometer
pcf	Pounds of chemical per cubic foot of wood. Chemical typically refers to CCA on an oxide basis.
pH	Measure of the hydrogen ion activity
ppm	Parts per million

## ABSTRACT

From the 1980s through 2003, wood treated with arsenical preservatives dominated the treated wood market. A phase-out of arsenic-treated wood was implemented in January 2004 that prevents it from being manufactured for use in residential areas. This phase-out coupled with increased public awareness has increased the demand for methods to identify As-treated wood. Existing methods used to identify As-treated wood are either characterized by high capital costs (e.g. X-ray), are difficult for use by the home user (e.g. commercially available arsenic test kits), or are not overly accurate (e.g. visual inspection or use of stains that react with copper-based preservatives). Therefore, the main objective of this study was to develop a simple, inexpensive, and accurate stain which could identify arsenic-treated wood such as chromated copper arsenate (CCA) and ammoniacal copper zinc arsenate (ACZA).

The approach focused on evaluating colorimetric-based methods that are able to detect phosphate. This approach was chosen because the similarity in structure and chemical behavior between arsenate and phosphate. All phosphate colorimetric methods evaluated suffered from interference reactions due to the natural low level phosphate concentrations found in untreated wood. One of these stains, the stannous chloride stain, was successfully modified to reduce this interference. The successful experimental testing procedure, based upon a dissolution method, allowed the stain to produce a noticeable blue color (absorbance of 0.145 at a wavelength of 690 nm) in 30 to 45 minutes and an intense blue color (absorbance of 1.150 at a wavelength of 690 nm) in approximately 5 hours. The stain has a minimum detection limit (MDL) of 2 mg/L in the leachate, and has been successfully field tested using various samples collected from in-service wood structures and from wood found within the waste stream.

The dissolution method developed as part of the modified stannous chloride stain requires the immersion of a sawdust sample into water. Other simpler applications were evaluated including the immersion of wipes, which worked well as long as the amount of arsenic released into solution was above the stains minimum detection limit of 2 mg/L. Applications directly on the wood were met with inconsistent results due to the heterogeneity of wood. Analysis of ash samples with the stain was not successful because the color of the ash masked the color formation of the stain. Overall, an arsenic-specific stain was developed from this study using a dissolution pre-processing method. This method works for both sawdust and wipe samples. The method developed is suitable for analyzing a few wood samples in the field. The method is easy to use and provides on-site results within an hour.

**CHAPTER I**  
**BACKGROUND, MOTIVATION, AND OBJECTIVES**

# CHAPTER I

## BACKGROUND, MOTIVATION, AND OBJECTIVES

This chapter focuses on describing the background (Section I.1), motivation (Section I.2), and the project objectives (Section I.3) for this study.

### I.1 BACKGROUND

Most wood used in outdoor settings is pressure-treated with chemical preservatives in order to reduce biological deterioration. There are two wood preservative formulations that contain arsenic: chromated copper arsenate (CCA) and ammoniacal copper zinc arsenate (ACZA). CCA is a waterborne chemical that was developed in the 1930s and gained widespread commercial use in the U.S. during the 1970s. There are several formulations of CCA preservative depending on the relative proportions of metals, the most common being Type C containing 47.5%  $\text{CrO}_3$ , 18.5%  $\text{CuO}$ , and 34.0%  $\text{As}_2\text{O}_5$  (AWPA, 2005). The chromium acts as a fixing agent in order to bind the arsenic and copper to the wood. The other type of As-treated wood is ACZA containing 50.0%  $\text{CuO}$ , 25.0%  $\text{ZnO}$ , and 25.0%  $\text{As}_2\text{O}_5$ . In ACZA-treated wood, the insoluble copper arsenate is fixed to the wood after the ammonia and water evaporates.

Along with CCA and ACZA, there are other types of waterborne chemical treatments available that also reduce biological deterioration. These alternative types of preservatives usually contain copper but not arsenic. Some alternative copper-based preservatives are ammoniacal copper quat (ACQ), and copper boron azole (CBA) [Figure I.1]. Boron-treated wood does not contain copper or arsenic, but the formulations used for treating dimensional wood leach easily and are not typically used in outdoor settings.



Figure I.1: Photograph of New Untreated, Boron, 4.0  $\text{kg/m}^3$  CCA, 40  $\text{kg/m}^3$  CCA, ACQ, and CBA-Treated Wood

Untreated wood is naturally characterized by a yellow hue, but when treated with a preservative, it takes on the color associated with that particular chemical. Copper formulations when applied to wood usually impart a shade of green. Additionally, increasing the amount of chemical added or “retention level” will cause a more distinct color change as can be seen in Figure I.1. Retention levels are usually expressed in units of either kilograms of chemical per cubic meter of wood ( $\text{kg/m}^3$ ) or pounds of chemical per cubic foot of wood (pcf). Typical manufacturing retention levels for CCA-treated wood range between 4.0  $\text{kg/m}^3$  (0.25 pcf) and 40  $\text{kg/m}^3$  (2.5 pcf). Wood treated at the higher retention level of 40  $\text{kg/m}^3$  CCA is mostly used for marine and industrial applications and is characterized by a strong green color. Wood treated at the lower retention level of 4.0  $\text{kg/m}^3$  CCA was mostly used for residential applications, prior to

2004, and is characterized by a subtle olive color. When the wood has undergone weathering, wood treated at lower retention levels will often fade and look similar to that of weathered untreated wood. The higher retention levels of CCA-treated wood will often maintain the green color after weathering as shown in Figure I.2. Although ACZA does contain copper, the color of ACZA-treated wood is often a dark brown. This is due to a chemical reaction that occurs during treatment of the wood. ACZA preservative is mostly used in the western US to treat Douglas Fir. Douglas Fir contains a naturally occurring compound, called taxifolin, which reacts with the ammoniacal copper solution to produce a dark brown color (Ruddick and Xie 1994). In addition, Douglas Fir is so dense that incisions must be made in order to allow the ACZA preservative to penetrate into the wood [Figure I.3]. Boron-treated wood does not usually cause a color change, but some manufacturers of boron-treated wood may intentionally add a dye in order to identify it as treated wood. For example, the dye added to boron-treated wood by the trade name N-Durz® imparts an aqua green color to the wood.

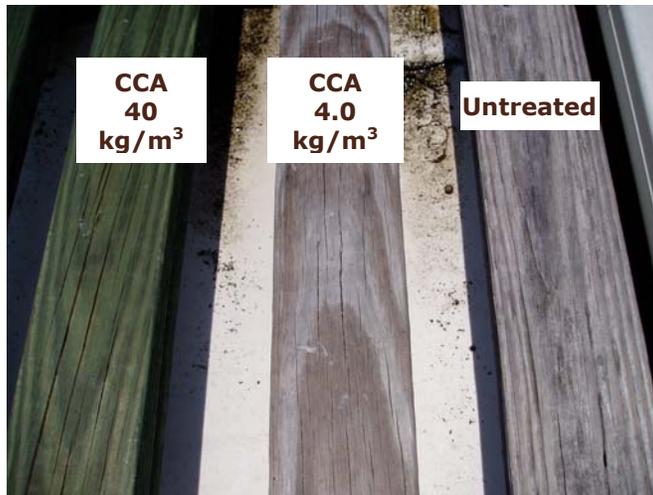


Figure I.2: Photograph of Weathered 40 kg/m<sup>3</sup> CCA, 4.0 kg/m<sup>3</sup> CCA, and Untreated Wood

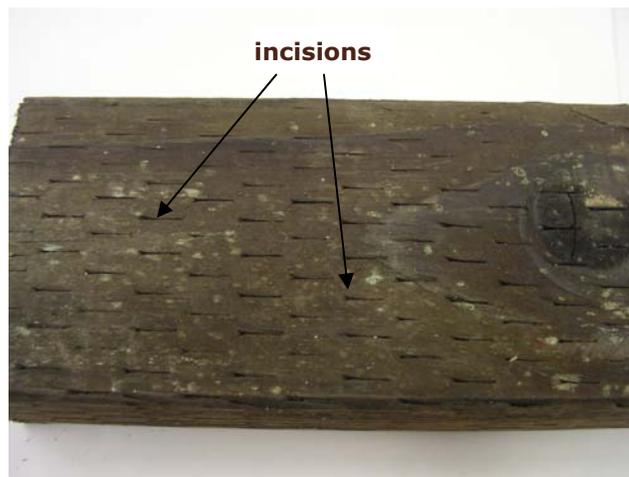


Figure I.3: Photograph of ACZA-Treated Wood Incisions

## I.2 MOTIVATION

From the 1980s through 2003, CCA was the dominant type of chemical used to pressure treat wood in order to increase its longevity (AWPA 2005). The recent phase-out of As-treated wood in January 2004 (USEPA, 2002; US CPSC, 2003) prevents it from being manufactured for use in residential areas in attempts to minimize human contact with As-treated wood; however, the phase-out does not affect pre-existing As-treated wood structures in residential areas, including playgrounds, picnic tables, fences, decks, etc. Due to increasing public awareness of As-treated wood and the associated health effects from arsenic, there has been an increasing demand for methods to identify As-treated wood.

Additionally, most As-treated wood structures have an integrity period of 10 to 35 years (Alderman et al. 2003; McQueen and Stevens 1998; Stalker 1993; Cooper, 1993; Solo-Gabriele and Townsend, 1999). Therefore, many in-service As-treated wood structures that were constructed in the 1980s and 1990s will soon need to be disposed. This will further increase the demand for identifying As-treated wood to determine how wood is to be processed upon disposal. Options for wood disposal include landfilling, composting, energy recovery, and recycling as mulch or wood-cement composites (Solo-Gabriele and Townsend 1999). Each of these options have thresholds for the relative proportion of arsenic-treated wood that would be acceptable. For example, if the goal is to produce an ash that does not fail hazardous waste criteria, less than 5% of the wood burned to produce the ash can be CCA-treated (Solo-Gabriele et al. 2002). Mulch must be essentially free from CCA-treated wood (<0.05%) if it is to meet Florida guidelines used to evaluate land application of recycled materials. Landfill disposal will be strongly affected by the dilution available from other waste materials. If landfill disposal is chosen as the disposal method of choice, ideally such a landfill should be characterized by a bottom liner designed to capture leachate. Unfortunately, in the State of Florida, inadvertent mixing of treated wood with untreated wood at construction and demolition (C&D) processing facilities results in the disposal of some treated wood within C&D landfills (Solo-Gabriele and Townsend 1999; Tolaymat et al. 2000), which are generally unlined within the State. Such landfills do not possess a means to capture leachate making the groundwater located beneath them more vulnerable to contamination.

Furthermore, current government and public initiatives suggest the increasing necessity of identifying As-treated wood in existing structures. The U.S. Environmental Protection Agency (USEPA) and U.S. Consumer Product Safety Commission (CPSC) are currently sponsoring studies to identify coatings that may be applied to existing wood structures to minimize exposure from arsenic found on the surface of treated wood (USEPA 2005). Environmental groups have also submitted a petition to the USEPA to remove the hazardous waste exemption provided to As-treated wood upon its disposal. If this exemption were removed, the cost for As-treated wood disposal would dramatically increase due to the need for disposal of the wood within hazardous waste facilities. Finally, the State of Florida Department of Environmental Protection (FDEP) is currently working on developing new regulations intended to minimize the recycling of As-treated wood into consumer mulch and minimize the disposal of As-treated wood into unlined landfills. All of these developments, if they come into affect, would serve to further increase the demand for methods to identify As-treated wood.

Because ACZA-treated wood has a dark brown color resulting from the chemical reaction

that occurs during treatment and required incisions during the treatment process, it is relatively easy to identify ACZA by the naked-eye. Unfortunately, visual identification of CCA-treated wood is not as obvious and most methods used to identify CCA-treated wood are inaccurate, expensive, dangerous, or time-consuming. Visual identification of CCA-treated wood's green color is the easiest and most common, but it is often inaccurate because wood treated with CCA at a lower retention level and untreated wood look similar, in particular after the wood has weathered. In addition, wood treated with alternative chemical preservatives are more popular and may also have a green color associated with them. Another option is to utilize 1-(2-pyridylazo)-2-naphthol (PAN) indicator, which is a chemical stain specific for copper. This will identify wood treated with copper-based preservatives, but it is unable to distinguish CCA-treated wood from other copper-based alternative treated woods. Other available technologies that can accurately identify CCA-treated wood include x-ray fluorescence (XRF) technology, laser induced breakdown spectroscopy (LIBS), atomic absorption (AA) analysis, and arsenic test kits. XRF technology and LIBS are very rapid methods providing results within a matter of seconds or less. However, these units are characterized by high capital costs. For example commercially available hand-held XRF units typically cost between \$20,000 to \$35,000. AA analysis is also expensive costing tens of dollars per analysis and unable to provide results on-site. Arsenic test kits are characterized by low capital costs, but usually involve the formation of hazardous arsine gas, which makes its use of concern due to safety concerns; the reaction time for these arsenic test kits is approximately 45 minutes (Solo-Gabriele et al in press). Wiping kits are another type of arsenic test kit (Maas et al. 2004), but they do not provide results on-site and are time-consuming because the wipe sample must be sent to a lab where the wipe is processed and the resultant extract from the wipe is then analyzed by an AA spectrometer. The complications involved in using these methods to identify the chemicals contained in wood may diminish the enthusiasm for some to test their wooden structures, but it does not diminish the necessity.

### **1.3 OBJECTIVES**

The overall goal of this study was to develop an As-specific stain that is able to discern CCA-treated and ACZA-treated wood from wood that is not treated with arsenic, including untreated and alternative-copper treated wood. The As-specific stain was to be based on similar stains used to identify phosphate in water, mainly the ascorbic acid and stannous chloride methods. Focus was placed on removing the interferences observed with untreated wood and reducing the time required for the stain to identify CCA-treated wood. A series of experiments were performed in attempts to best meet these concerns and simplify the testing procedure for the consumer.

The sawdust, shredded wood, and whole wood used for this project were obtained from new wood purchased at common retail establishments, unless otherwise stated as weathered (used or old) wood. Most experiments were conducted using CCA-treated wood at the lowest retention level of 0.25 pcf (4.0 kg/m<sup>3</sup>) to ensure that the As-specific stain was able to detect the lower levels of CCA.

The organization of this report is consistent with the objectives of this study. Chapter II includes a brief description of the chemical reaction involved in the As-specific stain and the experiments designed to develop the resulting stain and its testing method. The report closes with a summary, conclusions, and a set of acknowledgments (Chapter III).

## **CHAPTER II**

# **DEVELOPMENT OF A CHEMICAL STAIN FOR IDENTIFYING ARSENIC-TREATED WOOD**

## CHAPTER II, DEVELOPMENT OF A CHEMICAL STAIN FOR IDENTIFYING ARSENIC-TREATED WOOD

This chapter is separated into five sections. The first section (Section II.1) focuses on the application of phosphate colorimetric methods stains for identification of arsenate in wood. The second section (Section II.2) discusses the chemical packaging required to properly preserve the integrity of the stain. Subsequent sections describe the results associated with whole wood application (Section II.3) and other attempted stain applications (Section II.4). The final formulation and application instructions for the stain are presented in Section II.5.

### II.1 APPLYING PHOSPHATE STAINS TO ARSENATE STAINS

The dominant arsenic species in CCA-treated wood is arsenate ( $\text{AsO}_4^{3-}$ ), which is highly similar to phosphate ( $\text{PO}_4^{3-}$ ) in structure and chemical behavior. There are several colorimetric methods for detecting phosphate that rely on the formation of a color complex involving molybdenum. These phosphate detection methods result in either molybdenum blue or molybdenum yellow, which when reduced further results in molybdenum blue. Arsenate is often listed as an interference for phosphate chemical identification methods; likewise, phosphate is often listed as an interference for arsenate chemical identification methods. Unfortunately, CCA-treated wood contains both naturally occurring phosphate in the wood matrix and impregnated arsenate chemical. This section presents some background on the intended formation of molybdenum blue (Section II.1.a), the development of a standard dissolution method for testing (Section II.1.b), and the method used to remove interferences associated with naturally-occurring phosphate in untreated wood (Section II.1.c).

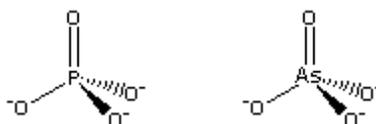
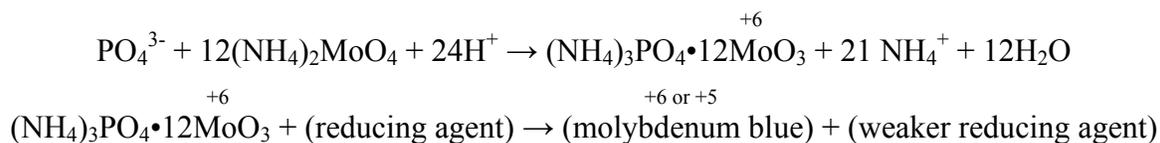


Figure II.1: Molecular Structure of Phosphate (left) and Arsenate (right)

#### II.1.a Background on Molybdenum Blue

Many phosphate and arsenate identification methods involve the formation of molybdenum blue, which in this case is a sensitive, large 13-molecule complex with phosphate or arsenate as its central molecule. However, molybdenum blue is a somewhat loose term used to describe any molecular complex involving molybdenum that radiates a blue color. The blue color emitted is often due to the reduction of some of the molybdenum atoms in the complex from a +6 oxidation state to a +5, or some other oxidation state in between. This changes the mean oxidation state of the entire complex from a +6 to a lower mean oxidation state between +6 and +5. The chemical reaction is as follows:



Because of this and the fact that molybdenum is able to participate in complexes involving over a hundred molecules, the number of possible molybdenum blue combinations is practically infinite.

Although it was first uncovered in the late 18<sup>th</sup> century, achieving an actual understanding of the structure of molybdenum complexes only began in the 1990s. Molybdenum is highly sensitive to any changes in composition, pH, and temperature. The sensitive nature of this reaction causes the resulting mean oxidation state among the molybdenum blue complex to be different with differing reducing agents. In other words, different reducing agents create different types of molybdenum blue.

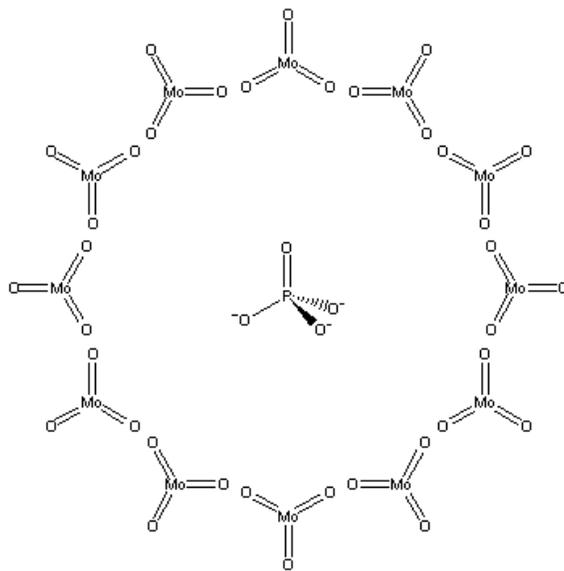


Figure II.2: Molybdenum Blue with Central Phosphate Molecule (conceptual, not actual structure)

The most well-known phosphate colorimetric identification stains include stannous chloride, ascorbic acid, and vanadomolybdophosphoric acid. The stannous chloride and ascorbic acid methods result in the formation of molybdenum blue, which is directly related to the concentration of phosphate present. The stannous chloride and ascorbic acid reagents act as the reducing agent for the molybdenum complex. The differing strength of the two reducing agents subsequently cause the different types of molybdenum blue. The vanadomolybdophosphoric acid method forms molybdenum yellow, which when reduced results in molybdenum blue. Each of these methods as described in *Standard Methods* (APHA, 1995) were examined for their potential to design a stain that would detect arsenate in treated wood.

### II.1.b Establishing a Standard Experimental Testing Method

The stannous chloride, ascorbic acid, and vanadomolybdophosphoric acid methods were all originally intended to detect phosphate in water samples. Attempting to use these methods on the surface of a piece of wood introduced too many variables that were difficult to control, such as the density, chemical concentration, porosity, absorption, etc. In order to successfully achieve the objectives of this study a consistent experimental testing method was required to minimize these variables. Experimentation showed that the resultant blue color was best achieved when the wood sample was immersed in the chemical solution. By doing so, some of the components, such as phosphate or arsenate, contained inside the wood diffused into solution where it was able to freely interact with molybdenum oxides to form molybdenum blue. In order to evaluate this, a 20-mL sample (scintillation) vial was filled with approximately 10 mL of solution. Addition of about 0.5 g of untreated wood to the solution was enough to develop an intense blue color, indicating the presence of phosphate. The reaction time, or the time required for the solution to develop a

noticeable blue color, was just under two minutes using the original formulation of the stannous chloride stain. The process of submerging the sawdust sample into water is called through the current study as “the dissolution method.” When the dissolution method was repeated with CCA-treated wood, a more intense blue color was observed due to the presence of phosphate and the added arsenate from CCA.

Similar results were achieved when applying the dissolution method to the ascorbic acid phosphate identification method. The ascorbic acid method successfully identified the presence of phosphate in untreated wood with a reaction time of approximately six minutes, and the presence of phosphate and arsenate in CCA-treated wood with a reaction time of approximately 15 minutes. The vanadomolybdophosphoric acid phosphate identification method, however, was not preferred because of the yellow color (from the molybdenum yellow complex formed using this method) that indicates the presence of phosphate. The sample wood, already having a yellow hue, made it difficult to positively determine whether any yellow color was due to the wood or phosphate detection. *Standard Methods* stated that arsenate is a potential interference to the vanadomolybdophosphoric acid phosphate identification method if the sample was heated. Heating the sample in a water bath for 30 minutes caused the faint yellow color in the 4.0 kg/m<sup>3</sup> CCA-treated wood sample to change to faint gray-blue. Investigation of developing an As-specific stain using the vanadomolybdophosphoric acid phosphate identification method was discontinued because only a slight color change occurred and the labor required to produce this change was too intensive for any realistic testing by the lay public for As-treated wood.

### **II.1.c Eliminating Interferences with Untreated Wood**

In the ascorbic acid and stannous chloride phosphate identification methods, both untreated and As-treated wood reacted to develop a blue color. This failed to fulfill the objective of developing an As-specific stain to only identify As-treated wood. Untreated wood reacted because of the presence of phosphate, not arsenate. Wood naturally contains phosphate because phosphorous is an essential nutrient that is required by plants and is thus ingrained in the wood matrix; therefore, the positive reaction seen with untreated wood when tested with the stannous chloride and ascorbic acid methods was because of this natural phosphate. The blue color that formed with As-treated wood was due to the presence of both phosphate in the wood matrix and arsenate from the chemical treatment of the wood.

Experimenting with the ascorbic acid phosphate identification method did not give any compelling results or further belief that ascorbic acid would be able to only identify arsenate. A noticeable blue color developed in untreated wood around two minutes and in CCA-treated wood around six minutes. The ascorbic acid method would detect phosphate in any wood sample and be unable to specifically identify As-treated wood. After examination into the reagents used for the ascorbic acid method, there was no indication that changing the reagents could result in a stain that was able to distinguish As-treated wood from all other types of wood. Furthermore, the chemicals used in the ascorbic acid stain are characterized by a short shelf life (about one week). It was thus decided to discontinue the examination of using ascorbic acid to specifically identify arsenate.

In *Standard Methods*, the procedure for the stannous chloride phosphate identification method requires eight parts of ammonium molybdate reagent be added to the sample first and one part stannous chloride reagent added second. However, by first combining the ammonium molybdate and stannous chloride reagents together in the same ratio, CCA-treated wood still reacts

with a noticeable blue color appearing in approximately 30 to 45 minutes, but untreated wood does not change color at all. An intense blue color developed in approximately 4 to 5 hours depending on the concentration of CCA in the wood sample. *In combining the reagents, molybdenum atoms are more reduced than they would be if added to the sample first. It is this over-reduction of molybdenum that lowers the sensitivity to phosphate and gave way to the successful development of a chemical stain to identify CCA-treated wood. This stain formed by combining the reagents is called the modified stannous chloride stain.* The minimum detectable concentration of the stannous chloride method in *Standard Methods* was about 3  $\mu\text{g}$ -phosphorous per liter. Using the modified method of combining the ammonium molybdate and stannous chloride reagents together to cause an over-reduction of the molybdenum atoms, the minimum detectable concentration changed to approximately 2 mg-P/L in order to cause a similar degree of color change. This means an increase in the minimum detectable concentration of phosphate by over 66,000%. In other words, the blue color formation was inhibited in untreated wood by causing the minimum detection limit (MDL) of the stain for phosphate to be above the actual concentration of natural phosphate in wood. Therefore, any blue color resulting from the stain with a wood sample would only be caused by the exceptionally high arsenate concentration from the chemical treatment of As-treated wood.

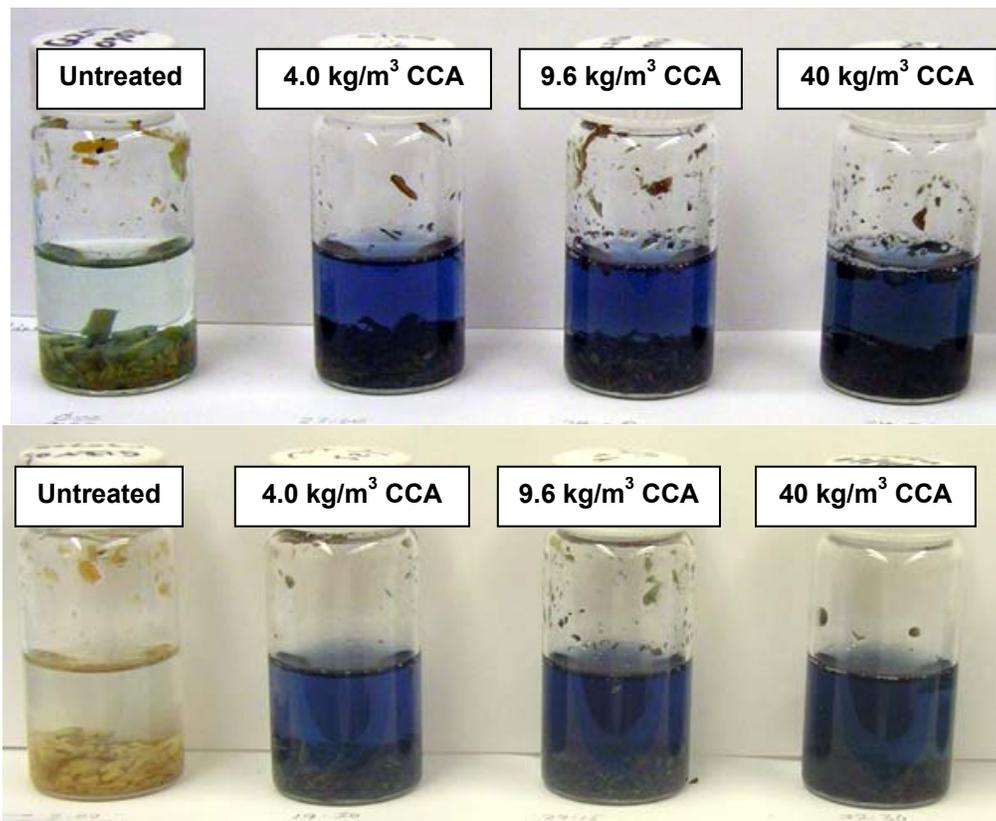


Figure II.3: Pictures of Original Stannous Chloride Stain Phosphate Identification Method (top) and Modified Stannous Chloride Stain (bottom) on New Wood at Reaction Time 5 Hours

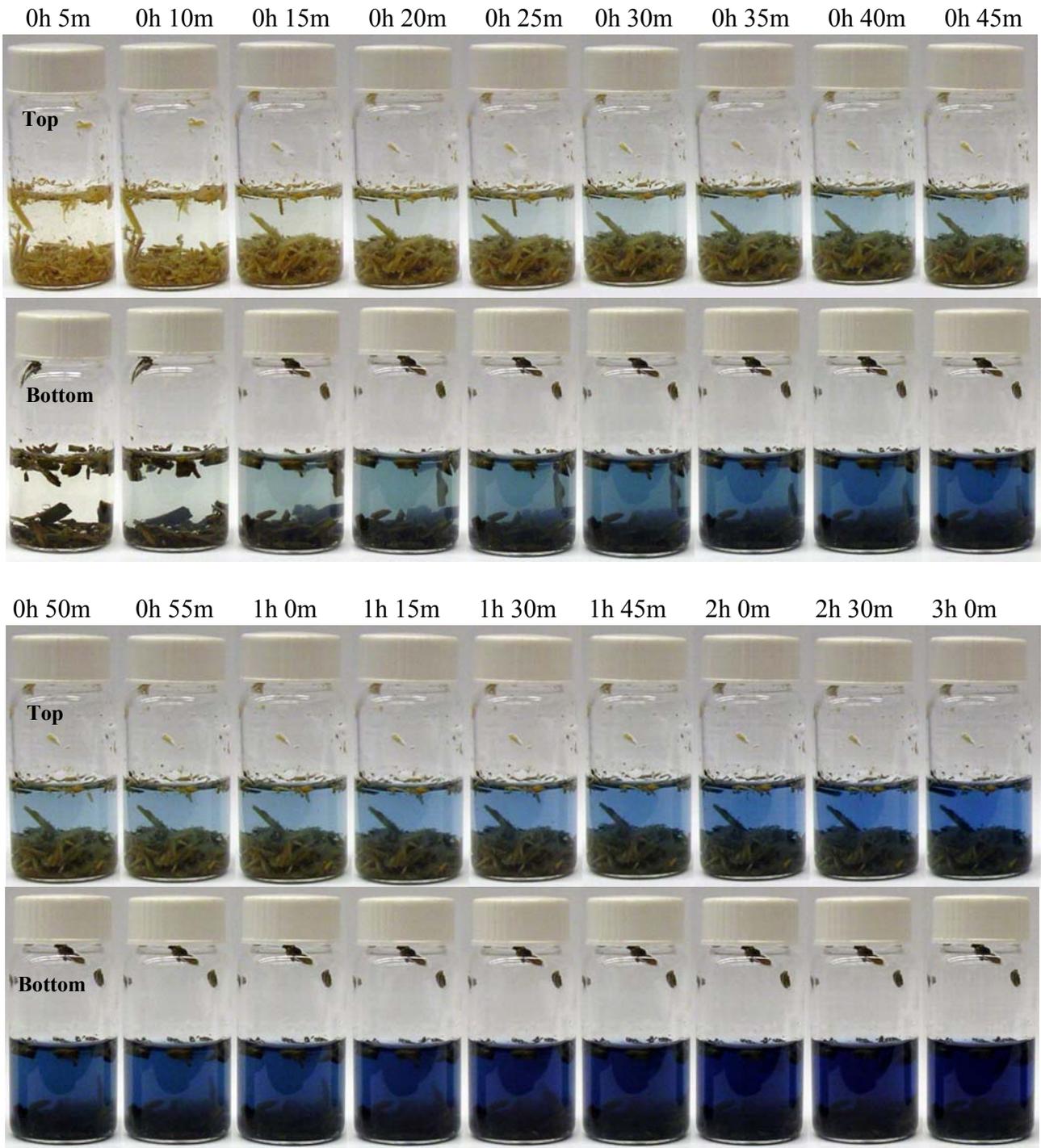


Figure II.4: Stannous Chloride Stain Progression of Color Change for New  $4.0 \text{ kg/m}^3$  (top) and  $40 \text{ kg/m}^3$  (bottom) CCA-Treated Wood (h=hours; m=minutes)

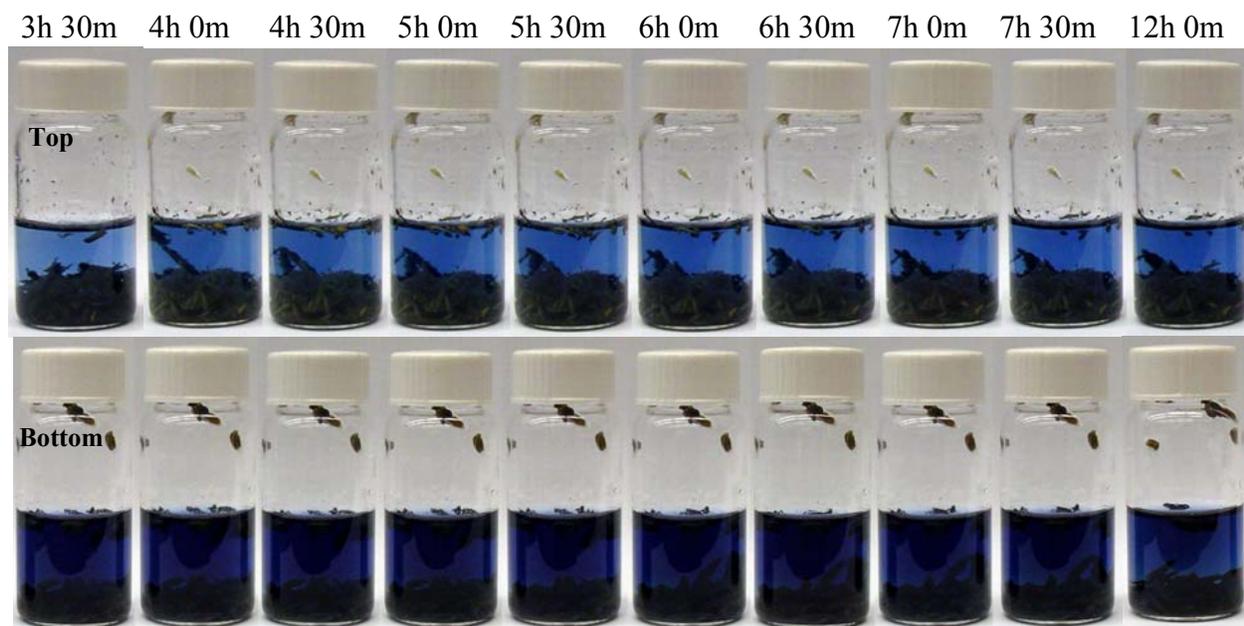


Figure II.4 (con'd): Stannous Chloride Stain Progression of Color Change for New 4.0 kg/m<sup>3</sup> (top) and 40 kg/m<sup>3</sup> (bottom) CCA-Treated Wood (h=hours; m=minutes)

Spectrophotometric analysis of the actual wavelength emitted by the blue color from the stannous chloride stain dissolution method with CCA-treated wood was performed to quantitatively express the terms used to describe the different shades of blue used in these experiments. Table II.1 expresses the visual description of the blue color (faint blue, light blue, medium blue, blue, dark blue, intense blue) used in the experiments to its corresponding absorbance at a wavelength of 690 nm. The selected wavelength was chosen because this was the advised wavelength for the stannous chloride method in *Standard Methods*. It is noted that some of the samples gave a maximum absorbance around 830 nm, which is characteristic of heteropoly acids, such as molybdenum blue (usually having a range between 700 to 840 nm for various elements) (Sandell and Onishi, 1978).

Visual Description	none	faint blue	light blue	medium blue	blue	intense blue
Absorbance at 690 nm	0 to 0.025	0.025 to 0.070	0.071 to 0.220	0.221 to 0.399	0.400 to 1.149	>1.150
Approx. Reaction Time for 4.0 kg/m <sup>3</sup> CCA-Treated Wood (h:mm:ss)	0:00:00	0:15:00	0:31:40	0:53:30	2:30:00	5:30:00

Table II.1: Visual Description of Blue Color, the Corresponding Spectrophotometric Absorbance at Wavelength 690 nm, and Approximate Reaction Time for 4.0 kg/m<sup>3</sup> CCA-Treated Wood

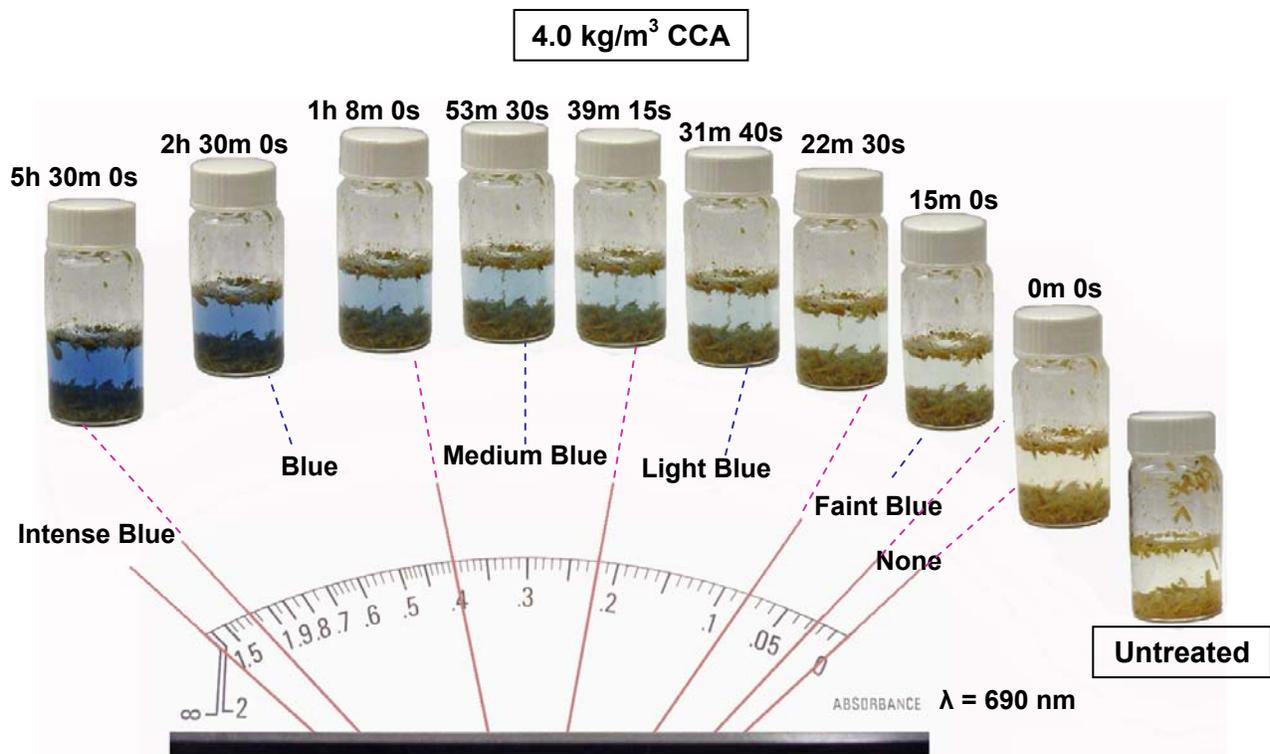


Figure II.5: Pictorial Representation of Blue Color Development with 4.0 kg/m<sup>3</sup> CCA-Treated Wood

Although the modified stannous chloride stain does not allow an untreated wood sample to develop a blue color, a high enough concentration of phosphate in the sample may cause some development of a blue-green color. The MDL of the stain for phosphate added in solution is approximately 0.8 mg/L, but the yellow hue of wood in solution prevents a noticeable blue color from forming even at 0.8 mg/L. This allows the stain to handle a higher concentration of phosphate of approximately 2 mg/L. The natural concentration of phosphate in the wood that leaches into solution is approximately 0.7 mg/L and so the amount of phosphate leached from untreated wood is below the detection limit of the modified stannous chloride stain. The MDL for arsenate is also approximately 2 mg/L. The arsenate concentration that leaches from CCA-treated wood at the lower retention level of 4 kg/m<sup>3</sup> is approximately 5 mg/L. Consequently, any formation of a blue color with a wood sample is due to the presence of arsenate.

## II.2 A POTENTIAL ARSENIC-TEST KIT

This section addresses the parameters needed for possibly marketing the stannous chloride stain as an arsenic-test kit. The ammonium molybdate and stannous chloride reagents must be stable and the stannous chloride stain must produce consistent results. If, over time, the stannous chloride stain gave erratic results, then producing it for widespread use would be unreasonable. This section discusses reagent storage (Section II.2.a), the required mixing time (Section II.2.b), using Whirl Pak bags as the reaction vessel (Section II.2.c), the progression of the stannous chloride stain shelf life test (Section II.2.d), and the results from the stain's field test (Section II.2.e).

### II.2.a Storage of Ammonium Molybdate and Stannous Chloride Reagents

The stannous chloride stain is highly sensitive to its chemical composition, and the quality of the ammonium molybdate and stannous chloride reagents that comprise the stain must be maintained over time. A shelf life test of the stain was performed that combined the reagents in an 8 to 1 ratio of ammonium molybdate to stannous chloride and were subsequently stored as a single combined reagent. This would reduce the complexity and labor required in order to use the arsenic-test kit.

Unfortunately, the first attempt at performing a shelf life test of the stannous chloride stain with the reagents combined and then stored showed that its integrity decreases with time when the ammonium molybdate and stannous chloride reagents were combined into a single reagent. The reaction time increased dramatically and the stain developed a light blue color instead of an intense blue with As-treated wood; untreated wood still had no positive reaction with the stain. Following addition of more ammonium molybdate reagent, an intense blue color did evolve, which may have been evident of excess stannous chloride. However, attempts to change the 8 to 1 ratio of ammonium molybdate to stannous chloride reagents did not yield better results in reaction time and color intensity.

**CONCLUSION:** The ammonium molybdate and stannous chloride reagents comprising the stannous chloride stain must be stored separately to maintain its effectiveness.

### II.2.b The Required Mixing Time

The time allowed for the ammonium molybdate and stannous chloride reagents to be combined, labeled the "mixing time," was determined in order to evaluate how long the two reagents may interact without having detrimental affects on the reaction time, color intensity, or accuracy of the stannous chloride stain. Mixing the ammonium molybdate and stannous chloride reagents must be performed in a specific way to ensure that molybdenum is reduced enough not to detect low levels of phosphate in untreated wood. The ammonium molybdate reagent must be added to the stannous chloride reagent in an 8 to 1 ratio.

The reagents were mixed together well and then let stand for at least five minutes. These five minutes reduce enough molybdenum to guarantee that untreated wood will not cause a positive reaction with the stannous chloride stain. Letting the mixture stand for less than five minutes still permits untreated wood samples to react and form a blue color, which gives a false positive. However, letting the combined reagents stand for longer than approximately one hour reduces the integrity of the stain by dramatically increasing the reaction time and reducing the color intensity in

As-treated wood as witnessed in the first attempt at the shelf life experiment.

**CONCLUSION:** The mixing time for the ammonium molybdate and stannous chloride reagents to be combined must be no less than five minutes and no more than one hour.

### II.2.c Whirl Pak Bags as the Reaction Vessel

Although the 20-mL sample (scintillation) vials were used to test the stannous chloride stain dissolution method, it could potentially cause increased labor because it requires having a sample of wood small enough to fit inside the small container. Therefore, Whirl Pak bags were explored to see if they could serve as an alternate reaction vessel when it was desired to test larger wood samples that would not fit inside of the 20-mL sample vials. Additionally, Whirl Pak bags cost less than the 20-mL sample vials. The main concern with using Whirl Pak bags was interference from any possible phosphate already existing inside the Whirl Pak bag because it could not be acid washed prior to use.

The standard stannous chloride stain dissolution method was utilized by increasing the volumetric ratios of the ammonium molybdate reagent, stannous chloride reagent, and DI water with the sample weight. Only untreated and 4.0 kg/m<sup>3</sup> CCA-treated wood were tested. The CCA-treated wood formed a noticeable blue color in approximately 17 minutes and its maximum intensity occurred around 5 hours. The untreated wood sample did not react to form a noticeable blue color, indicating that any phosphate that may have already been present inside the Whirl Pak bag was not detected.

**CONCLUSION:** Whirl Pak bags may be used as the reaction vessel in place of the 20-mL sample (scintillation) vials as long as the stannous chloride stain dissolution method is performed in the same proportions.

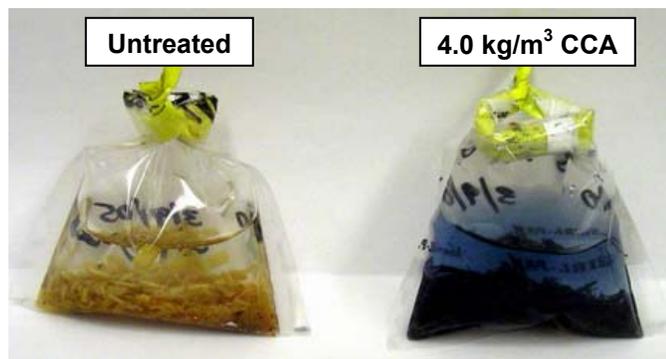


Figure II.6: Picture of Stannous Chloride Stain with Whirl Pak Bags on Untreated and 4.0 kg/m<sup>3</sup> CCA-Treated Wood

### II.2.d Shelf Life of the Stannous Chloride Stain

Once it was determined that the ammonium molybdate and stannous chloride reagents must be stored separately, a revised shelf life test of the stannous chloride stain was performed. The stannous chloride stain was tested every two weeks for six months. Untreated and 4.0 kg/m<sup>3</sup> CCA-treated wood were tested every two weeks by the stannous chloride stain dissolution method. Alternative treated wood, including borate, ACQ, and CBA, was tested every four weeks, and the

last shelf life test on the stain was performed on untreated, borate, ACQ, CBA, CC, CDDC, 4.0 kg/m<sup>3</sup> CCA, 40 kg/m<sup>3</sup> CCA, and ACZA-treated wood.

The ammonium molybdate and stannous chloride reagents were stable throughout the shelf life period of six months when stored at room temperature. The stannous chloride stain continued to be effective at identifying As-treated wood and the reaction time remained in a reasonable time period of 30 to 45 minutes, as shown in Table II.2. Table II.3 shows that the time required to reach maximum intensity continued to be around five hours.

**CONCLUSION:** The ammonium molybdate and stannous chloride reagents that comprise the stannous chloride stain can be stored for a period of six months without affecting the stain's effectiveness or reaction time.

<b>Weeks</b>	<b>Average Reaction Time</b>
*0	19:21
*2	30:20
*4	29:16
6	30:37
8	32:15
10	40:43
12	42:27
14	43:42
16	34:43
18	43:45
20	35:26
22	33:44
24	17:19
26	20:15
NOTE: mm:ss *Experiment week repeated.	

Table II.2: Progression of stannous chloride stain with 4.0 kg/m<sup>3</sup> CCA-treated wood during shelf life test

<b>Weeks</b>	<b>Approx. Time of Max. Intensity (hours)</b>
*0	5
*2	5
*4	5
6	4
8	5
10	5
12	5
14	5
16	5
18	5
20	5.25
22	5
24	5
26	5
NOTE: *Experiment week repeated.	

Table II.3: Progression of Stannous Chloride Stain's Approximate Time of Maximum Intensity during Shelf Life Test

## II.2.e Field Test of the Stannous Chloride Stain

The modified stannous chloride stain dissolution method was field tested using recycled C&D dimensional wood samples and wood samples collected from various playgrounds. Almost all of the experiments using the stain, prior to the field test, were performed on new wood, so a field test would determine if the stain was still effective on weathered wood, which is mainly how it would be used.

The recycled C&D wood samples were analyzed using the PAN indicator stain and an XRF unit (Blassino, et. al., 2002; Solo-Gabriele, et. al., 2004). The wood was then drilled to create a representative sample that would be introduced to the stain using the dissolution method. As shown in Table II.4, the field test proved that the modified stannous chloride stain was specific to identifying As-treated wood even in weathered wood samples. Although the PAN indicator may be used to identify wood treated with copper-based preservatives, the XRF unit is generally more accurate at identifying the presence of certain metals; therefore, the accuracy of the modified stannous chloride stain's ability to identify As-treated wood was compared to the readings from the XRF unit. Samples A-I were tested with the PAN indicator, XRF unit, and modified stannous chloride stain. Samples H and I tested positive for arsenate with the modified stannous chloride stain by resulting in a blue color. Additionally, because sample H reacted with the modified stannous chloride stain more rapidly than sample I, it is reasonable to assume that sample H contained a higher arsenate concentration than sample I. This is because the blue color intensity of the modified stannous chloride stain is dependent on the arsenate concentration in the sample, which would result in a lower reaction time (the time required to achieve a noticeable blue color) and an increase in color intensity. The readings from the XRF unit support this hypothesis. Another interesting observation is the higher accuracy of the modified stannous chloride stain than PAN indicator. The PAN indicator tested positive for samples C and D, which were determined to be negative for copper by the XRF unit. The successful field test of the modified stannous chloride stain on recycled C&D wood supports the idea that producing an arsenic-test kit involving the modified stannous chloride stain would be practical and accurate if the consumer desired to analyze certain structures for the presence of As-treated wood.

Sample	PAN indicator (+/-)	Elements Detected by XRF Unit (Average, ppm)			Determined Chemical Treatment Preservative	Reaction Time of Stannous Chloride Stain (min:sec)
		Cr	Cu	As		
A	-	<216.3	174.7	<10	*Borate	nc <sup>a</sup>
B	-	<205.3	<35.7	<9.3	*Borate	nc
C	+	<284	<34	<10.3	Untreated	nc
D	+	<241.7	<51.3	<11.7	Untreated	nc
E	+	<261.3	10248	<9.7	Copper	nc
F	+	<253.3	1481	<18	Copper	nc
G	+	<236	6013	<10	†ACQ	nc
H	+	9194.3	5412.3	6431.7	CCA	17:24
I	+	2526.3	1418.7	1476.3	CCA	37:42

NOTE: XRF values were taken from an average of three trials for each sample; mm:ss

\*Borate treated wood was determined due to the aqua green color of wood, which is most likely a dye added in many borate treatment processes to specify that the wood is treated with a chemical preservative.

†An identifying tag was still attached to Sample G indicating it was ACQ-treated wood.

<sup>a</sup>nc=No Change.

Table II.4: Results of Field Test of Recycled C&D Wood from PAN Indicator, XRF, and Modified Stannous Chloride Stain Analysis

Wood samples collected from various playgrounds were also examined in a blind study. The modified stannous chloride stain dissolution method was performed on each of the 24 total playground samples. Twenty-one samples developed an intense blue color; the remaining three samples showed a faint blue color, but not enough to be noticeable to the untrained eye. All the samples were separately analyzed using an AA spectrometer and the arsenic concentrations were determined. In the three samples that did not react, the total arsenic concentrations achieved in the digestate of the samples with nitric acid were 1.54, 1.54, and 2.2 mg/L [Table II.5]. Taking into consideration that an AA analysis measures the total arsenic concentration in the sample, while the modified stannous chloride stain is only able to react with the arsenate that leaches out of the wood sample, it is reasonable to assume that these three samples did not leach enough arsenate to be above the modified stannous chloride stain's MDL of 2 mg/L. This may be due to excessive weathering of the wood sample, not receiving a representative sample of the wood, or outside contamination. However, the 21 samples that did test positive with the stannous chloride stain had measured total arsenic concentrations within the digestates of 3.97 mg/L and above and corresponding total arsenic concentrations of 380 mg/kg or greater, as indicated by the AA spectrometer. Consequently, the modified stannous chloride stain dissolution method is able to accurately identify As-treated wood that has a minimum arsenate concentration of roughly 380 mg/kg in the wood matrix.

Sample Name	AA (mg/kg)	AA Avg. Digestate Conc. (ppm)	Intense Blue with Stannous Chloride Stain
FHRP 2	149	1.5	NO
Briar Bay Lake 3	159	1.5	NO
Clover Leaf 1	220	2.2	NO
Bunche 2	384	4.0	YES
Clover Leaf 3	387	4.0	YES
Serena Lakes 4	513	5.4	YES
Briar Bay Lake 1	521	5.6	YES
Serena Lakes 1	578	5.8	YES
Briar Bay Lake 2	643	6.5	YES
FHRP 1	652	7.0	YES
Colonial Drive 2	742	8.1	YES
Devonaire 3	1012	10.0	YES
Clover Leaf 2	1224	12.2	YES
Colonial Drive 1	1167	13.1	YES
Water Oaks 1	1287	13.3	YES
Indian Hammock 2	1399	16.4	YES
Devonaire 2	1498	16.5	YES
Colonial Drive 3	1679	18.0	YES
Indian Hammock 1	1670	18.7	YES
Serena Lakes 2	1795	19.1	YES
Serena Lakes 3	2384	25.5	YES
Amelia Earhart 1	3013	30.4	YES
Bunche1	3229	34.8	YES
Devonaire 1	4852	47.3	YES

Table II.5: Results from Field Test of Playground Samples from AA and Modified Stannous Chloride Stain Analysis

## II.3 WHOLE WOOD APPLICATION OF THE MODIFIED STANNOUS CHLORIDE STAIN

With the success of the modified stannous chloride stain using the dissolution method, the stain was examined for the possibility of identifying CCA-treated wood by applying the stain directly onto whole wood. This section discusses changing the initial modified stannous chloride stain color through dilution in order to prevent confusion between a positive reaction and the color of the combined reagents (Section II.3.a). The method of applying the stain to the wood is discussed in order to let the blue color appear in a reasonable amount of time (Section II.3.b). The stannous chloride stain test was performed on whole wood directly exposed to sunlight in attempts to make the blue color appear quicker and more intense (Section II.3.c).

### II.3.a Changing the Initial Color of the Stannous Chloride Stain

When the ammonium molybdate and stannous chloride reagents are combined to make the stannous chloride stain, a very dark, intense blue emerges. The color of the stannous chloride stain appears almost black. The stain could not be applied directly onto a wood surface because the stain is already a blue color and the observer is unable to determine if a positive reaction indicating the presence of arsenate is causing the blue color or if the blue color is due to the original color of the stain.

By diluting the modified stannous chloride stain with water, the dark blue dissipates to a yellow color. The more diluted, the lighter the yellow color appears. Therefore, by testing a diluted stannous chloride stain on a wood surface, a positive indication of arsenate is more easily witnessed because it is easier to determine the development of a blue color. Unfortunately, the more diluted the stain becomes, the less intense the blue color that develops due to a decrease the concentration of the stain. This is expected since the stain is directly dependent on the concentration of arsenate available to form molybdenum blue and on the molybdenum oxide atoms required to produce the blue color. A 2 to 1 ratio of the stannous chloride stain and distilled water is dilute enough to change the color of the stain to a deep yellow but still able to give the most intense blue color for a positive sample of CCA; this was labeled the diluted stannous chloride stain [Figure II.7].

**CONCLUSION:** If the stain is to be applied directly to wood, the combined stannous chloride stain should be diluted with DI water in a 2 to 1 ratio, which will change the color of the stannous chloride stain from a dark blue to a deep yellow.



Figure II.7: Picture of Modified Stannous Chloride Stain (left) and Diluted Stannous Chloride Stain (right)

The diluted stannous chloride stain on whole wood has a longer reaction time than the dissolution method, and it is more difficult to discern a positive reaction in whole wood application. The longer reaction time is largely due to the time required for the stain to absorb into the wood. Unlike the PAN indicator stain, the diluted stannous chloride stain must be absorbed into the wood where it may interact with arsenate molecules to form molybdenum blue. Again, it must be kept in mind that the intensity of blue color depends on the concentration of arsenate. Also, when the wood is wet by the stain the color change is even more difficult to determine as the wet appearance darkens the color of the wood. Many times, it was only after the wood dried that a blue color was obvious. Although CCA-treated wood reacted to form a blue color, untreated wood samples turned brown or gray over time where the stain was applied.

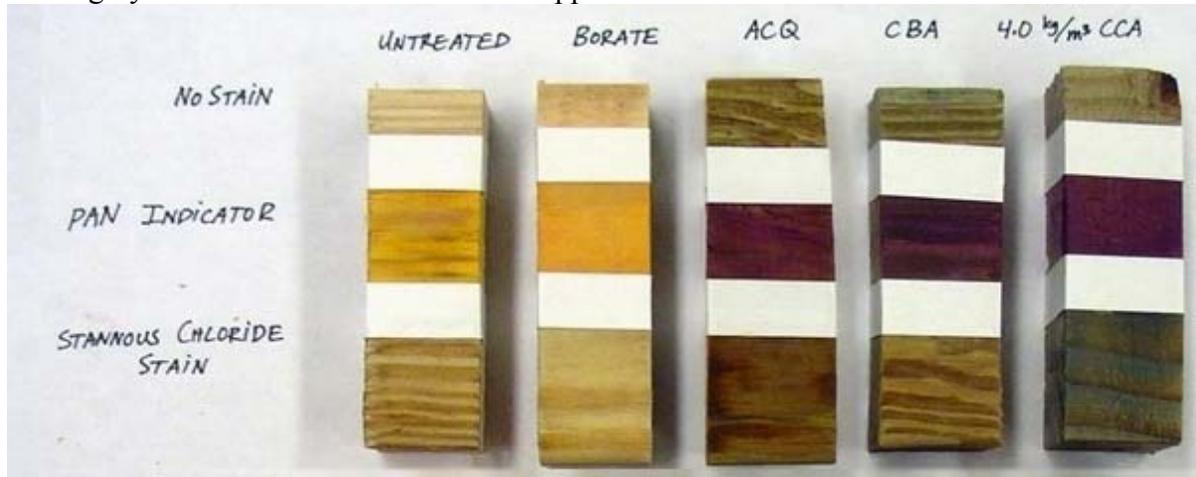


Figure II.8: Picture of PAN Indicator and Diluted Stannous Chloride Stain on New Untreated, Borate, ACQ, CBA, and 4.0 kg/m<sup>3</sup> CCA-Treated Wood

### II.3.b Whole Wood Application Method

Various methods of applying the diluted stannous chloride stain to whole wood were tested, including the use of a dropper, a wipe, and a spray. These methods were chosen in order to address the absorption and saturation of the whole wood with the stain. Because of the difficulty in determining the blue color apart from the dark brown color associated with the color of wet or saturated wood, it was desirable for the diluted stain to be applied in such proportion that there was enough stain to react with any available arsenate but not to cause the saturated wood to retain the dark brown color for a long period of time.

Unfortunately, none of the tested application methods reduced the reaction time of the diluted stannous chloride stain nor did they reduce the possible confusion in discerning the various colors of blue, gray, and brown. The dropper method was, however, the easiest to utilize. The wipe method was not effective because color determination was too difficult and not enough stain absorbed into the wood. The spray method was unproductive because the amount of stain required to be sprayed on the wood in order to witness a reaction was the same as that discharged by the dropper method. In addition, the spray bottle mechanism was difficult to clean and may have been damaged by the high acidity of the stain.

**CONCLUSION:** For direct application to wood, the diluted stannous chloride stain gives the most desired results when applied using a dropper method, applying no more than one drop of diluted stannous chloride stain per square inch.

### **II.3.c Effects of Sunlight**

Since efforts to improve the diluted stannous chloride stain's absorption and reaction time were ineffective, the time it takes for the wood to dry was considered as another factor that may possibly reveal the blue, gray, or brown color faster. By reducing the drying time, there would be less confusion in the color of the stain.

When the diluted stain was applied to whole wood using the dropper method in direct sunlight, all the whole wood samples, including untreated, borate, ACQ, CBA, CC, CDDC, and CCA-treated wood, reacted and eventually developed a dark brown or black color. The results of the stain were affected by the exposure to direct sunlight because of molybdenum blue's large sensitivity in the temperature difference in the experimental environment. This reinforced the necessity to perform testing using the stannous chloride stain at room temperature (20 to 25°C).

**CONCLUSION:** The diluted stannous chloride stain must be applied to whole wood in a controlled room temperature (20 to 25°C) environment.

## II.4 OTHER ATTEMPTED STAIN APPLICATIONS

Focus was placed on various applications of the modified stannous chloride stain dissolution method because the whole wood method could not provide distinct and reproducible color differences and had a longer reaction time. The dissolution method was used to determine if the stain could identify CCA-treated wood when a wipe sample was taken of the wood (Section II.4.a) and in samples of ash (Section II.4.b).

### II.4.a Wipes

The process for arsenic test kits involving wipes requires the consumer to take a wipe sample of the wood, send it in to a laboratory where it may be analyzed using an AA spectrometer, and the results are sent back to the consumer. The dissolution method was used to determine if the modified stannous chloride stain was able to identify wipe samples from CCA and ACZA-treated wood. Although the dissolution method was proven very effective on wood samples of sawdust or shredded wood, a wipe sample would require less labor and would be representative of the degree of arsenate that may rub off on a human hand. The wipes used for sample collection were made of a dry polyester cloth. Two methods were used to collect the wipes, each of these methods provided very different results.

The first method used to collect the wipes is a standardized method as described by Shibata et al. (2006) and U.S. CPSC 2003. When the wipe samples were collected from new CCA-treated wood using the standard method, the effectiveness of the dissolution method for wipes was similar to that of sawdust or shredded wood. The stain only developed a blue color for wipes collected from CCA-treated wood and the reaction time was approximately 30 minutes to achieve a noticeable blue color. However, the stain was not as effective when the standard wipe method was used to collect wipes from weathered (used) wood. The weathered wood samples were exposed to the natural environment for about 2.5 years. The reaction time of the stain when applied to a wipe collected from an old  $4.0 \text{ kg/m}^3$  CCA-treated wood sample was approximately 24 hours, and the time required to reach maximum intensity was 48 hours. This maximum intensity was a gray color instead of blue. The gray color usually signifies the transition from colorless to blue. Even when the stain was tested on a wipe collected from a weathered  $40 \text{ kg/m}^3$  CCA-treated wood sample, the time required to achieve a noticeable blue color was approximately 2.5 hours with a maximum intensity time still at 48 hours. This reaction time of the stain when tested on wipe samples collected using standard methods was much longer on weathered wood than on new wood.

Due to the deficiencies of using the standard wipe procedures to collect arsenate on wipes from weathered wood samples, a second attempt was made to collect wipe samples; however, this time the standardized wipe method was not used. In this case, the wipe sample was collected from an area of the wood where it was the “cleanest,” so as to minimize the collection of dirt. While collecting the wipe sample, the site was wiped repeatedly in the direction of the grain to prevent splintering and shredding of the wipe. The excess wipe that did not contact the wood was cut off and then discarded. The portion of the wipe where the sample was collected was placed inside the vial so the sample is on the outside of the wipe. The vial was subsequently analyzed using the stannous chloride stain dissolution method. The same weathered wood was used for wipe sample collection. The untreated wood still did not react. The  $4.0 \text{ kg/m}^3$  CCA-treated wood reacted in approximately 3 hours with a maximum intensity time around 12 hours [Figure II.9]. The  $40 \text{ kg/m}^3$  CCA-treated wood reacted in approximately 1 hour with a maximum intensity time around 12

hours. With this new method of wipe sample collection, the stannous chloride stain dissolution method was able to detect CCA-treated wood with a longer, but still reasonable, reaction time. Wipe samples collected from new ACZA-treated wood reacted in approximately 18 minutes with a maximum intensity time around 5 hours. Weathered ACZA-treated wood was unavailable, and therefore not tested.



Figure II.9: Picture of Wipe Samples from Weathered Untreated,  $4.0 \text{ kg/m}^3$  CCA, and  $40 \text{ kg/m}^3$  CCA-Treated Wood with the Stannous Chloride Stain

#### II.4.b Ash

The stannous chloride stain dissolution method was also used to determine if it was able to identify arsenate in ash because incineration is one of the methods used for disposing of wood and for a fuel source. Incineration concentrates the metals found in wood and a previous study performed by Khan et al. (2004) determined that approximately half of the arsenic species found in CCA ash were in the form of arsenate. Accidental inhalation or consumption of CCA ash can be hazardous to one's health. This concern was expressed by an environmental group with respect to Huntington Beach, California. A common practice at this beach is to create bonfires at night. Some research at this beach has shown that the ash residues from some of these bonfires were contaminated with CCA residues, resulting in the need to clean-up the contaminated ash sites. An arsenic specific stain would be very helpful in this situation to identify ash sites requiring remediation.

Unfortunately, the use of the stain's dissolution method was ineffective at identifying CCA ash because the color of the ash was so intense that it masked any possible molybdenum blue color that developed. However, a potential connection between the pH level of the ash and the percentage of CCA-treated wood that made up the ash was witnessed. This is believed to be due to the chemicals impregnated into the wood that increase the wood's longevity in the environment. The solution that carries the desired chemicals into the wood for most types of alternative treatments is basic, while the chemical solution for CCA-treated wood is acidic (AWPA 2005). One type of alternative treated wood that is impregnated by acidic chemicals is acid copper chromate (ACC); however, the use of ACC is uncommon (Solo-Gabriele et al. 2000). Alkyl ammonium compound (AAC) also is an acidic chemical, but AAC is often used as one of the components of alkaline copper quat (ACQ), which would result in a net increase the pH of the preserved wood. Unfortunately, the pH of ACZA-treated wood was unavailable, but it is assumed to be a basic solution because of its ammonia component. When the chemicals were concentrated in the ash due to incineration, the observed pH levels somewhat depended on the type of wood composing the ash [Figure II.10]. However, further study is needed to determine if the relationship

is genuine and the actual significance of this connection.

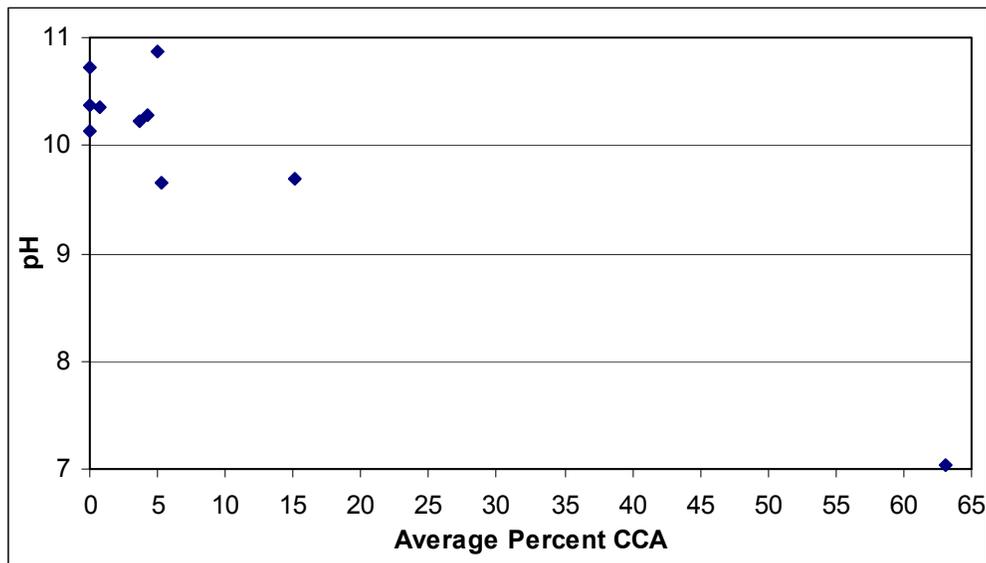


Figure II.10: Graph of Ash pH vs. Average Percent CCA-Treated Wood

## II.5 RESULTING STAIN TO IDENTIFY ARSENIC-TREATED WOOD AND METHODS OF TESTING

From the various results achieved during this study, a chemical stain based on a modified stannous chloride method was developed that can detect arsenic in treated wood. The modified stannous chloride stain did not react with untreated or alternative-treated wood. A noticeable blue color appeared within 30 to 45 minutes, and an intense blue color was achieved in approximately 5 hours. The MDL of the stain is approximately 2 mg/L of arsenate, and the background phosphate concentration of the sample must be less than 2 mg/L to maintain the stain's integrity. If the stain was formulated into an arsenic-test kit, then the cost of the stain would be similar to other arsenic-test kits involving wipes or arsine gas formation. The hazardous formation of arsine gas is avoided by using the modified stannous chloride stain, but the stain still requires caution in handling the acidic chemicals. If marketed, the complexity of the testing procedure would be minimized for the consumer. In addition, the stain continues to be effective for at least six months when stored properly.

### II.5.a Dissolution Method with MDL

The modified stannous chloride stain is composed of two reagents: ammonium molybdate reagent and stannous chloride reagent. These reagents must be stored separately, and all glassware must be acid washed. The composition of each reagent is the same as described in *Standard Methods* (1995), Method 4500-P D, shown below.

*Ammonium molybdate reagent I:* Dissolve 25 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in 175 mL distilled water. Cautiously add 280 mL conc  $\text{H}_2\text{SO}_4$  to 400 mL distilled water. Cool, add molybdate solution, and dilute to 1 L.

*Stannous chloride reagent I:* Dissolve 2.5 g fresh  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  in 100 mL glycerol. Heat in a water bath and stir with a glass rod to hasten dissolution.

These reagents are combined to form the stannous chloride stain, using eight parts ammonium molybdate reagent and one part stannous chloride reagent. The combined reagents are mixed well and then let stand for five minutes before testing. The reagents should only be combined immediately prior to testing. If the stain is allowed to sit for an extended amount of time (over one hour) before testing, then the time required to observe a noticeable blue color and the time required for maximum color intensity will increase. In addition, the maximum intensity of the blue color may decrease.

The modified stannous chloride stain is most effective when testing a sample using the devised dissolution method. The dissolution method uses a 20-mL sample (scintillation) vial to which 10 mL of distilled water is added. Nine drops of the combined stannous chloride stain is added to the sample vial (within the appropriate timeframe described previously of 5 minutes to 1 hour). Approximately 0.50 g of the sawdust or shredded wood sample is added to the sample vial. The vial is then shaken and the start time is noted.

The sample vial should be placed on a white background to better discern any change in color. The observer may shake the sample vial occasionally, but allow the sawdust or shredded wood enough time to settle in order to observe the color of the solution. Any development of a blue

color indicates that the sample wood contains arsenate and is most likely CCA-treated wood. The appearance of an intense blue color is gradual over a period of approximately 5 hours; however, a noticeable blue (light blue) color appears in approximately 30 to 45 minutes. If the observer is uncertain about the appearance of a blue color, then s/he may choose to wait a longer time frame. If there is no observed change in color, then the sample wood is not treated with arsenic.

If marketed to the consumer, the modified stannous chloride stain arsenic-test kit will contain a 20-mL sample vial with 10 mL distilled water, a dropper vial containing ammonium molybdate reagent, a dropper vial containing stannous chloride reagent, and an empty dropper vial to be the mixing container. Written instructions, including example pictures and a color key, will also be provided to ensure the consumer will not reach an erroneous conclusion. The resulting stannous chloride stain arsenic-test kit will be effective at identifying arsenate concentrations as low as 2 mg/L, simple to use, results acquired in a reasonable amount of time, less dangerous, and cost-effective. Figure II.11 is representative of instructions that can be included in the stannous chloride stain arsenic-test kit to be followed by the consumer.

# Arsenic Test Kit

**WARNING:** Acidic chemicals are used in the test. Handle all chemicals carefully. Review the Safety Information unpacking, setting up, or operating this equipment.

**Scope and Application:** For wood

## Section 1 Safety Information

Please read this entire manual before unpacking, setting up, or operating this equipment. Pay attention to all danger and caution statements. Failure to do so could result in serious injury to the operator or damage to the equipment.

To ensure that the protection provided by this equipment is not impaired, do not use or install this equipment in any manner other than that specified in this manual

### 1.1 Use of Hazard Information

**DANGER:** Indicates a potentially or imminently hazardous situation which, if not avoided, could result in death or serious injury.

**CAUTION:** Indicates a potentially hazardous situation that may result in minor or moderate injury.

**Note:** Information that requires special emphasis.

#### 1.1.1 Precautionary Labels

Read all labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed.

	This symbol, if noted on the instrument, references the instruction manual for operation and/or safety information.
	This symbol, if noted on the product, indicates the need for protective gloves.
	This symbol, if noted on the product, indicates the need for protective eye wear.

Figure II.11: Stannous Chloride Stain Arsenic-Test Kit Consumer Instructions (Modified from instructions developed by Hach Chemical, 2004)

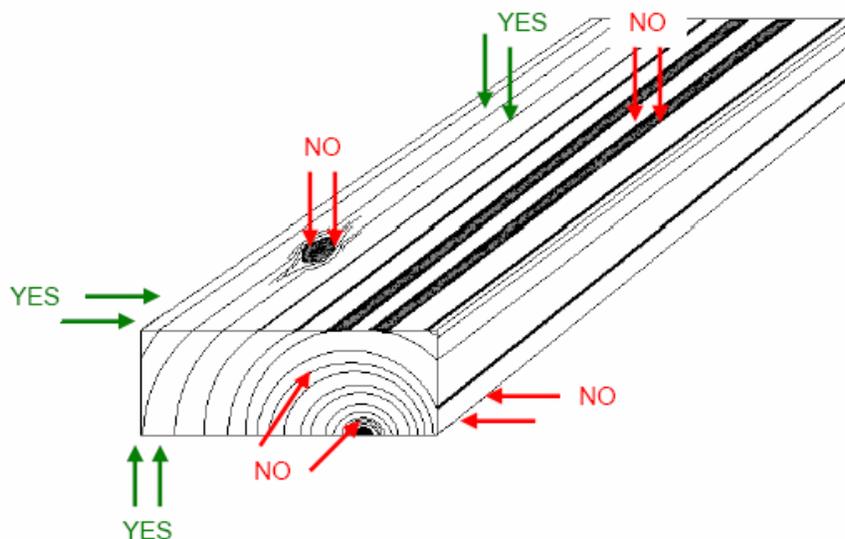
## Section 2 General Product Information

### 2.1 Introduction

This Arsenic test kit provides a simple way of determining the “presence” or “no presence” of arsenic-treated wood. This kit uses easy-to-handle reagents packaged in unit doses. There is no formation of gas.

#### 2.1.1 Tips and Techniques

1. The sawdust or shredded wood sample must be collected before beginning “Step 1” of arsenic test.
2. If the sawdust or shredded wood sample must be collected from a piece of whole wood, the use a drill to make holes where the highest concentration of chemical preservatives may be located, such as along the side of the whole wood piece, and collect the sawdust. Avoid collecting the wood sample from the center of the wood or near knots in the wood. [See diagram below.]



3. All steps are to be performed immediately following each other in sequence.

#### 2.1.2 Reagent Description

*Reagent 1:* 8 mL ammonium molybdate

*Reagent 2 with dropper cap:* 1 mL stannous chloride

*Reaction Vessel (RV):* 20-mL sample vial containing 10 mL distilled water

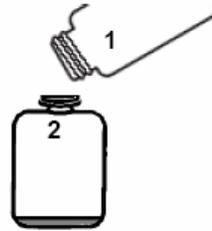
Figure II.11 (con'd): Stannous Chloride Stain Arsenic-Test Kit Consumer Instructions (Modified from instructions developed by Hach Chemical, 2004)

## 2.2 Procedure

1. Remove the Reagent 1 cap and the Reagent 2 dropper cap.



2. Carefully pour all of Reagent 1 into Reagent 2.



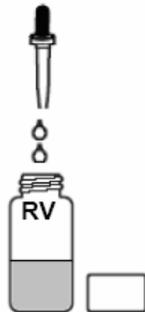
3. Replace the Reagent 2 dropper cap and swirl to mix for 20 seconds.



4. Let Reagent 2 stand for 5 minutes.



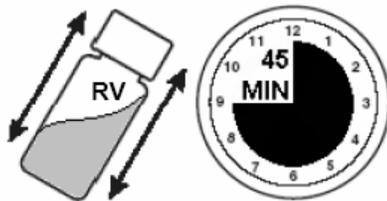
5. After 5 minutes, remove the reaction vessel cap and add 9 drops of Reagent 2 into the reaction vessel.



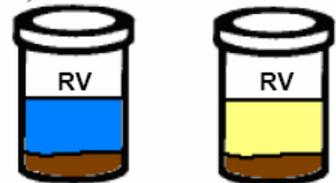
6. Add 0.5 grams (about 1/3 teaspoon) of sample sawdust or shredded wood to the reaction vessel.



7. Replace reaction vessel cap, shake reaction vessel to mix, and let stand. Allow reaction to occur for 45 minutes.



8. There are two possible results. Any blue color indicates an arsenate concentration above 2 mg/L (arsenic-treated wood is present). A clear, yellow, brown, or beige color indicates an arsenate concentration below 2 mg/L (unlikely arsenic-treated wood is present).



POSITIVE

NEGATIVE

*Note: If you are unsure if a blue color is present, then wait another 2 hours and re-examine the color. If blue, then an arsenate concentration above 2 mg/L (arsenic-treated wood is present). If clear, yellow, brown, or beige, then an arsenate concentration below 2 mg/L (unlikely arsenic-treated wood is present).*

Figure II.11 (con'd): Stannous Chloride Stain Arsenic-Test Kit Consumer Instructions (Modified from instructions developed by Hach Chemical, 2004)

**CHAPTER III,  
SUMMARY, RECOMMENDATIONS, AND  
ACKNOWLEDGMENTS**

## **CHAPTER III, SUMMARY, RECOMMENDATIONS, AND ACKNOWLEDGMENTS**

### **III.1 SUMMARY & RECOMMENDATIONS**

The stannous chloride stain, which was originally intended to detect phosphate, has been successfully altered so that it will only detect arsenate in arsenic-treated wood. By causing an over-reduction of the molybdenum and using the dissolution method, wood not treated with arsenic does not react with the stain. The stain radiates a noticeable blue color (absorbance of 0.145 at a wavelength of 690 nm) in 30 to 45 minutes; an intense blue forms in approximately 5 hours (absorbance of 1.150 at a wavelength of 690 nm). The modified stannous chloride stain developed through this study can be packaged in a fashion that is very easy for consumer use and represents an available test kit that does not form arsine gas.

Aside from testing As-treated wood using the modified stannous chloride stain dissolution method, the stain was also tested using other methods. The whole wood application method, which is most desired, was tested using a diluted stannous chloride stain. Unfortunately, the whole wood application's success in a laboratory setting on new wood was not replicated in the field on co-mingled C&D recycled wood. This was largely due to the increased number of variables that were introduced when considering the application of the stain onto whole wood, such as heterogeneity of the wood, surface dirt/contamination, stain sensitivity, and difficulty in identifying the molybdenum blue color. The dissolution method, on the other hand, was successful at identifying As-treated wood within recycling C&D wood, but it would be considered time consuming and labor intensive if attempting to separate many pieces of wood at recycling facilities. Collecting wipe samples of wood and subsequently analyzing the wipes with the modified stannous chloride stain dissolution method has also been effective at identifying As-treated wood because the arsenate concentration in the leachate from the wipe sample was above 2 mg/L. The stannous chloride stain dissolution method could not be applied to ash samples to identify possible arsenic contamination because of the masking color caused by the ash.

Overall, the development of a stain capable of identifying As-treated wood was successfully completed. This stain is based upon a dissolution method incorporating a modified stannous chloride stain. The modified stannous chloride stain was successfully utilized using wood sawdust and wipes. Although the stain was unable to be used for identifying arsenate in ash, the relationship between the pH level of the ash and the percentage of CCA-treated wood that made up the ash may be examined further. If the relationship was held to be true, then an ash sample's acidic character may indicate the presence of arsenate.

## III.2 ACKNOWLEDGMENTS

Funding for this project was received from the Florida Center for Solid and Hazardous Waste Management. The dedicated staff from the FCSHWM helped to maintain the web page for this project ([www.ccaresearch.org](http://www.ccaresearch.org)) and also handled numerous information requests associated with this research. The authors gratefully acknowledge the project's technical awareness group (TAG) and TAG meeting participants for their guidance and feedback. A list of the most recent technical awareness group (TAG) members along with minutes of the TAG meetings are provided on the web page developed for this project under the “administration” link.

The research team gratefully acknowledges the assistance received from Florida Wood Recycling in the provision of recycled C&D wood for use in this study. The team also gratefully acknowledges Dr. William L. Purcell and Dr. Carl D. Hoff of the UM chemistry department who provided advice on the project, Gary Jacobi who provided ash samples for use in this study, Tomoyuki Shibata who performed AA analyses and provided advice on the project, and Colleen Block who assisted in conducting shelf life experiments of the stannous chloride stain.

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