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To cite this Article Omae, Amy L. , Solo-Gabriele, Helena M. and Townsend, Timothy G.(2007) 'A Chemical Stain for Identifying Arsenic-Treated Wood Products', Journal of Wood Chemistry and Technology, 27: 3, 201 — 217 To link to this Article: DOI: 10.1080/02773810701700836 URL: <http://dx.doi.org/10.1080/02773810701700836>

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Journal of Wood Chemistry and Technology, 27: 201–217, 2007 Copyright \odot Taylor & Francis Group, LLC ISSN 0277-3813 print/1532-2319 online DOI: 10.1080/02773810701700836

A Chemical Stain for Identifying Arsenic-Treated Wood Products

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Abstract: Convenient and rapid detection of arsenic in treated wood products is necessary when evaluating possible exposure risks from the product during inservice use and disposal. For this study, a modified stannous chloride stain capable of specifically identifying arsenic in preservative-treated wood was developed by causing the over-reduction of molybdenum with stannous chloride prior to sample addition. This reduced the stain's sensitivity to the background phosphate levels in the wood and permitted the detection of elevated arsenate concentrations. The modified stain was confirmed through field testing with weathered wood samples. Alternative application techniques, such as wipes, were further explored.

Keywords: Arsenic, treated wood, CCA, molybdenum, stannous hloride, stain

Funding for this project was received from the Bill Hinkley Center for Solid and Hazardous Waste Management. The research team gratefully acknowledges Florida Wood Recycling in the provision of recycled C&D wood, Dr. William L. Purcell, Dr. Carl D. Hoff, Dr. Tomoyuki Shibata, and Colleen Block for their assistance and advice on the project.

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ARSENIC-TREATED WOOD

Arsenic is a component of several chemical preservatives, mainly chromated copper arsenate (CCA), used to treat wood to reduce biological deterioration. Studies determined that arsenic from wood treated with arsenical-based preservatives may be transferred onto other surfaces that come in contact with the treated wood, $\left[1-3\right]$ and risk assessments showed an increased risk to children who play on arsenic-treated wood playgrounds because of their frequent hand-to-mouth behavior. $[4-7]$ Although CCA was the dominant treated wood on the market, a U.S. voluntary ban effective January 2004 prevents arsenictreated wood from being manufactured for residential uses.^[8] Canada^[9] and Australia^[10] issued phase-outs and restrictions shortly thereafter. Although several European countries had phased-out CCA-treated wood previously, the European Union officially phased-out CCA-treated wood in 2004.^[11] Use of arsenic and chromium in treated wood in Japan has been essentially restricted since 1996.^[10]

Identification of arsenic in treated wood is important not only for inservice use of wood, but in the disposal sector as well. Most arsenic-treated wood structures have an anticipated service life of 10 to 35 years; therefore, many in-service structures constructed in the 1980s and 1990s are, or will soon need to be, disposed.^[12-16] Typical means of wood disposal, such as recycling, incineration, and landfilling, may present additional problems. Recycling CCA-treated wood may re-introduce it into residential areas in the form of mulch^[17,18] or panelboards.^[19,20] Incineration concentrates the metals in the ash and appropriate pollution control devices are needed to capture volatilized metals. $[21-23]$ Disposal of CCA-treated wood in unlined landfills may potentially contaminate groundwater through metals that may leach from the wood.^[24-27]

Visual identification of CCA-treated wood is difficult because its green color tends to fade over time. The green color associated with CCA is due to the copper; the more CCA preservative impregnated into the wood the more intense the green appearance. The most common formulation of the CCA preservative is CCA Type C. The highest typical retention level of CCA—Type $C^{[28]}$ at 40 kg/m³ (kg of CCA/m³ of wood) containing about 19,000 mg /kg (mg of As per kg of wood) appears green even after weathering. However, when wood treated at lower retention levels $(4.0 \text{ kg/m}^3 \text{ CCA} - \text{Type C containing about } 1,900 \text{ mg/kg})$ undergoes weathering, the wood appears similar to weathered untreated wood. Furthermore, the increased production of non-arsenical treated wood has made it difficult to identify arsenic-treated wood based on visual colors because most non-arsenical treatments also contain copper, which imparts a green color. In this study, experimentation was mostly performed on Southern Yellow Pine (SYP) with various types of chemical treatment because SYP is employed for about 80% of all treated wood in the United States.

COLORIMETRIC IDENTIFICATION AND OBJECTIVES

Because of perceived risks associated with CCA and considerations needed during its disposal, this research was directed toward the development of a chemical stain for the identification of arsenic-treated wood. Other chemical stains, such as PAN (1-(2-pyridylazo)-2-naphthol) indicator stain,^[29] which turns a magenta color when positive and orange when negative, are able to identify copper in treated wood but not arsenic. Because there are now many copper-organic treatments on the market, PAN indicator is not able to identify CCA based on the presence of copper. Colorimetric identification methods that are commonly used for the analysis of phosphate in water may hold some promise for identifying arsenic in wood as phosphate $(PO₄³)$ is highly similar in structure and chemical behavior to arsenate $(AsO₄³ -)$, the dominant arsenic species that leaches from CCA-treated wood.^[30]

These colorimetric phosphate identification methods involve the formation of molybdenum blue or molybdenum yellow, which when further reduced results in molybdenum blue. Molybdenum blue, in this case, is a 13-molecule molybdenum complex with phosphate as its central molecule that radiates a blue color. The formation of molybdenum blue is directly related to the concentration of phosphate present. The exact oxidation state of the complex $(+6 \text{ and }$ $+5$) is dependent on the reducing agent used in the reaction, which in turn determines the sensitivity of phosphate detection. Common reducing agents include vanadium, stannous chloride, and ascorbic acid. Preliminary experimentation with these reducing agents found stannous chloride to be more promising because of its increased reagent stability (unlike ascorbic acid) and the formation of molybdenum blue without the intermediate formation of molybdenum yellow (unlike vanadium).

The main objective of this study was to develop an arsenic-specific stannous chloride stain. Once developed, a series of confirmation tests were performed with various types of wood samples. Practical uses of the stain are discussed.

MATERIAL AND METHODS

This study was separated into three primary tasks. The first and most in-depth task focused on developing the procedure by establishing a consistent testing technique, preventing phosphate interference, and optimizing the stain. Optimization of the stain included desensitizing the stain to remove interferences from naturally occurring phosphate in untreated wood and minimizing the reaction time. The second task focused on performing confirmation tests on the optimized stain using different types of treated wood and weathered samples collected from a wood recycling center and from wooden playgrounds. The third task focused on evaluating alternative application

techniques for using the stain and included experiments that utilized surface wipes instead of sawdust samples, and focused on the direct application of the stain to whole wood.

Development of Method

Establishment of Testing Technique

The arsenic-specific stain was developed through modifications of a standard colorimetric phosphate identification procedure^[31] Standard Methods, Method 4500-P D) that utilizes 20.2 mM ammonium molybdate and 110.8 mM stannous chloride reagents. This procedure, although developed for the analysis of phosphate in water, was modified for the analysis of wood by implementing a "dissolution technique" whereby sawdust samples were immersed in distilled water.

Preventing Phosphate Interference

Eliminating false positives from natural phosphate in wood was addressed by decreasing the sensitivity of the original stain. In Standard Methods,^[31] eight parts of the ammonium molybdate reagent (by volume) is added to the sample first. One part of the stannous chloride reagent is added separately to reduce the molybdate molecules already complexed around phosphate. If phosphate was present, the formation of molybdenum blue would occur and the phosphate concentration would be proportional to the intensity of the blue color as determined using a spectrophotometer. However, an overreduction of the molybdenum and a decreased sensitivity to phosphate and arsenate can be accomplished by reducing the molybdate molecules with stannous chloride before it is added to the sample. Therefore, by mixing the two reagents together before sample addition, the sensitivity of the stain will be decreased, which should thus eliminate false positives from background phosphate naturally present in untreated wood and could result in the detection of arsenate from the preservative treatment. The mixture of the two chemicals into a single combined reagent prior to sample addition is termed here as a "modified stain," and this combination of the chemicals was the key for preventing the interference from phosphate naturally present in wood.

Consequently, all experiments were conducted with the modified stain and the dissolution technique. Nine drops (about 0.45 mL) of the modified stain were added to a reaction vessel (20-mL scintillation vial) containing 10 mL of distilled water resulting in an ammonium molybdate and stannous chloride concentration of 0.77 mM and 0.53 mM, respectively. Approximately 0.5 g of sawdust sample was then added to the reaction vessel containing distilled water and modified stain. The reaction vessel was capped and

Table 1. Visual description of blue color, the corresponding spectrophotometric absorbance at wavelength 690 nm, and approximate reaction time for 4.0 kg/m^3 CCA-treated wood tested ($n = 50$) with the modified stain dissolution technique

Visual description	Absorbance at $\lambda = 690$ nm	Approximate reaction time for 4.0 kg/m^3 CCA -treated wood ^{a} (hours:minutes:seconds)
None	0 to 0.025	0:00:00
Faint blue	0.026 to 0.070	0:15:00
Light blue	0.071 to 0.220	0:31:40
Medium blue	0.221 to 0.399	0:53:30
Blue	0.400 to 1.149	2:30:00
Intense blue	>1.150	5:30:00

^aReaction time is the length of time that begins when the wood sample is added to DI water in the dissolution technique and ends when a light blue color develops (absorbance 0.071 at $\lambda = 690$ nm).

shaken. The reaction time, defined as the time between the addition of the wood sample and the formation of a light blue color in the solution (absorbance >0.070 at $\lambda = 690$ nm, Hach Spectronic 20, Milton Roy Company), was recorded. Color descriptions and associated absorbance are shown in Table 1.

Detection limits of the modified stain method and the quantities of phosphate and arsenate that leached from selected wood samples were measured to confirm that the phosphate interference was removed. Detection limits were established by preparing phosphate and arsenate standard solutions (concentrations starting at 0.1 mg/L with increasing increments of 0.1 mg/L) and analyzing them colorimetrically. Leachates from untreated SYP were evaluated for phosphate using the procedure as stated in Standard Methods.^[31] Arsenate in the CCA-treated wood (4.0 kg/m^3) leachates was measured with an atomic absorption spectrometer (AA) with flame atomization (Perkin Elmer Model AA800, Wellesley, MA).

Optimization of Stain

Two sets of experiments were conducted to optimize the modified stain. These experiments included evaluating the optimum volumetric ratio of ammonium molybdate to stannous chloride reagents and evaluating the effects of mixing time to document stain performance. The volumetric ratios of ammonium molybdate to stannous chloride (in ratios of 1 to 1; 4 to 1; 8 to 1; 12 to 1; 16 to 1) were evaluated to increase the intensity of the blue color for arsenic-treated wood and to shorten the reaction time for the blue color to form. Of note is that Standard Method recommends the addition of these reagents separately in an 8 to 1 ratio. Wood samples were tested by the

dissolution technique and included untreated-, $4.0 \text{ kg/m}^3 \text{ CCA}$ -, 9.6 kg/m^3 CCA-, and 40 kg/m^3 CCA-treated wood.

A standard mixing time, defined as the time for the ammonium molybdate and stannous chloride reagents to mix prior to the addition of this combined reagent to distilled water, was evaluated to ensure that the phosphate interference was prevented. The mixing time was to be sufficient to allow for the overreduction of molybdenum by the stannous chloride reagent so the stain's sensitivity was decreased and would not result in a positive reaction for phosphate with untreated wood. In order to determine the required mixing time for the ammonium molybdate and stannous chloride reagents, the ammonium molybdate and stannous chloride reagents were measured out at the optimum volumetric ratio (as evaluated earlier) and the modified stain was tested at mixing times of 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 30, and 45 min on untreated SYP and 4.0 kg/m^3 CCA-treated wood samples.

Confirmation Tests

Non-Arsenical Treated Wood

Other types of treated wood were tested to determine the modified stain's effectiveness for identifying CCA-treated wood from non-arsenical treated wood. The dissolution technique and the optimized modified stain (8 to 1 volumetric ratio) were used to evaluate untreated SYP and $4.0 \text{ kg/m}^3 \text{ CCA-treated}$ wood. In addition to these wood types, non-arsenical wood treatments were evaluated including wood treated with alkaline copper quat (ACQ), copper boron azole (CBA), copper citrate (CC), copper dimethyldithiolcarbamate (CDDC), and borate. All these samples corresponded to preservatives used for residential applications because CCA was voluntarily removed.

Field Test

Field tests were performed to determine if the stain was effective on weathered wood, because previous experiments were mostly performed on new wood. Sawdust samples were collected by drilling holes in pieces of whole wood. Two sets of field samples were evaluated: recycled construction and demolition (C&D) dimensional wood samples and wood samples collected from various playgrounds.

The recycled C&D wood samples (A through I) were analyzed using the PAN indicator stain and an X-ray fluorescence (XRF) unit.^[32-35] The XRF instrument (Innov-X Systems, Inc., Woburn, MA, Model #I-3000C) has the capability to quantitatively evaluate arsenic, chromium, and copper independently by radiating a primary X-ray that causes a secondary X-ray to be emitted from the target atoms. This secondary X-ray, or fluorescence, has a characteristic wavelength specific to different types of elements allowing

the detector to determine which element is present. The results from the modified stain dissolution technique were compared with the results from the PAN indicator and XRF unit.

For the playground samples, analysis included digesting the samples^[36] (Method 3050B) and then analyzing the digestates using an AA spectrometer. The arsenic concentrations were determined in mg of arsenic per kg of wood. The results from the modified stain dissolution technique were compared with the arsenic concentrations from the AA spectrometer.

Alternative Application Techniques

Alternative application techniques evaluated methods that circumvent the need to collect a sawdust wood sample and included the collection of wipe samples or applying the stain directly onto whole wood. Wipe samples can be used to evaluate the amount of arsenic residue potentially transferred onto other surfaces (e.g., hands) that come in contact with the treated wood.^[3,5,7] Applying the stain directly onto whole wood would be an optimal stain application technique because it would prevent the need for collecting samples and for the reaction vessels containing water. During experimentation, the development of a blue color was noted and the reaction time (the time required to develop a visible blue color in solution or on the wood) was recorded.

Testing Sample Wipes

Dry polyester cloths (12×12 cm) were used to collect wipe samples from the wood. The whole wood was repeatedly wiped in the direction of the grain to prevent splintering of the wood or shredding of the wipe. Whole wood samples tested included untreated-, 4.0 kg/m^3 CCA-, and ACZA-treated wood. The wipe was cut to remove excess cloth that did not come in contact with the wood, leaving a small border (0.5 to 1 cm) of noticeably clean wipe. The trimmed wipe was placed at the bottom of the reaction vessel containing 10 mL of distilled water and the modified stain. The side of the wipe that had made contact with the wood was kept on the outside as it was placed inside the reaction vessel.

Direct Application to Wood

The modified stain required dilution before directly testing whole wood samples because of an apparent false positive as the modified stain was a dark blue color. Upon application to the wood in an undiluted form, the dark blue color would remain regardless of the original chemical treatment of the wood sample. A 2 to 1 volumetric ratio of modified stain to water was used to keep a high concentration of the modified stain and change its color to yellow. This diluted modified stain (ammonium molybdate and

stannous chloride concentrations of 12 mM and 8.2 mM, respectively) was applied directly onto whole wood with a dropper applying no more than one drop of diluted modified stain per square inch. Experiments were conducted using untreated- and $4.0 \text{ kg/m}^3 \text{ CCA-treated wood.}$

RESULTS

Development of Method

Establishment of Testing Technique

When implementing the dissolution technique, the solutions of both untreated SYP and CCA-treated wood samples turned blue. CCA-treated wood turned a deeper blue because it contained both phosphate in the wood matrix and arsenate from the chemical treatment of the wood. Thus, false positives were observed in untreated wood with the stannous chloride stain using the Standard Methods procedure because of the naturally occurring phosphate that also leached out of the wood into solution.

Preventing Phosphate Interference

The interference caused by the low levels of naturally occurring phosphate was overcome by mixing the ammonium molybdate reagent and stannous chloride reagent into the modified stain before adding it to the sample. Only the 4.0 kg/m^3 CCA-treated wood samples developed a light blue color in the solution, thus indicating the presence of arsenic-treated wood. The reaction time for the wood sample to form this light blue color in the solution was around 20 min. The untreated wood samples did not form a light blue color.

Further experimentation determined that the modified stain was capable of detecting low concentrations of phosphate and arsenate with a minimum detection limit (MDL) of 0.3 mg /L without the presence of wood. However, the yellow color imparted to the distilled water by the wood sawdust increased the detection limit to 3 mg/L . (A 3 mg/L concentration in solution typically required the wood to contain an arsenate concentration of 300 mg / kg-sapwood, which is well below the lowest concentration in the treated wood zone of CCA-treated wood). The background phosphate concentration that leached from untreated wood within 30 min was around 0.725 ± 0.03 mg/L (95% confidence interval), whereas the arsenate concentration that leached from 4.0 kg/m³ CCA-treated wood was 5.5 ± 0.04 mg/L (95% confidence interval). The background phosphate concentration that leached from the wood was not enough to cause a blue color formation, but the arsenate concentration leaching from 4.0 kg/m^3 CCA-treated wood was more than enough to develop the blue color that allows the modified stain to specifically detect CCA-treated wood. False positives are possible in unusual

cases of wood containing abnormally high phosphate levels ($>$ 3 mg/L leached to solution).

Optimization of Stain

Efforts to optimize the stain focused on minimizing the reaction time while providing an intense blue color for arsenic-treated wood, and no color change for untreated wood. Deviating from the 8 to 1 volumetric ratio for ammonium molybdate to stannous chloride as recommended by Standard Methods did not exhibit a more intense color or shorter reaction time (Table 2). The modified stain began to form a blue color, indicating a positive reaction, with untreated wood as the ratio of ammonium molybdate to stannous chloride reagents increased in the 12 to 1 and 16 to 1 formulations. The reaction time was longer when the ratio was decreased to 1 to 1 and 4 to 1 formulations. The 8 to 1 modified stain formulation had the shortest reaction time and did not react with untreated wood.

The required mixing time for the ammonium molybdate and stannous chloride solution was evaluated to be a minimum of 4 min as the untreated wood sample showed a positive reaction at mixing times of 0, 1, 2, and 3 min, but did not react for mixing times of 4 to 45 min (Table 3). The shortest reaction time with 4.0 kg/m^3 CCA-treated wood occurred at a mixing time of 7 min; however, there was not a large difference between reaction times from the 7 ± 2 min mixing times. Therefore, the modified stain should be able to correctly identify arsenic-treated wood within a reasonable reaction time as long as the ammonium molybdate and stannous chloride reagents are mixed for at least 5 min prior to adding it to the sample being tested.

Confirmation Tests

Non-Arsenical Treated Wood

The modified stain formed a blue color with the CCA-treated wood sample only (Figure 1a). The untreated and non-arsenical (ACQ, CBA, CC, CDDC, and borate) treated wood samples did not form a blue color with the stain, and these samples were therefore negative for the presence of arsenate.

Field Test

The field tests were performed on the two sets of weathered wood samples (recycled C&D dimensional wood samples and wood collected from various playgrounds) largely supported the capability of the modified stain dissolution technique to identify arsenic-treated wood. The results of the recycled C&D dimensional wood samples (A through I) showed that samples H and I were positive for arsenate according to the modified stain dissolution technique

Volumetric ratio	Sawdust samples; reaction time (hours:minutes:seconds)					
(ammonium molybdate to stannous chloride)	Untreated	CCA	4.0 kg/m^3 9.6 kg/m ³ 40 kg/m ³ Weathered CCA	CCA	CCA	
1 to 1						
	>2:00:00	>2:00:00	>2:00:00	>2:00:00	>2:00:00	
4 to 1						
	>2:00:00	0:21:52	0:09:40	0:06:40	0:19:55	
8 to 1						
	0:47:00	0:10:00	0:07:00	0:04:30	0:10:20	
12 to 1						
	0:32:00	0:13:00	0:08:00	0:05:00	0:15:30	
16 to 1						
	0:22:30	0:14:00	0:08:30	0:06:00	0:13:00	

Table 2. Pictures of sample solution color and time of sample reactions for establishing the composition ratio of the modified stain dissolution technique

Figure 1. CCA-treated wood samples are 4.0 kg/m^3 , unless stated otherwise. a) Modified stain dissolution method for sawdust; b) Modified stain for wipe samples; c) Stain performance on whole wood (Top—No stain, Middle—PAN indicator, Bottom—Diluted modified stain).

Table 3. Mixing time for combined reagent and subsequent reaction time in untreated- and 4.0 kg/m^3 CCA-treated wood

Mixing time a	Reaction time ^b (minutes:seconds)			
(minutes)	Untreated	$4.0 \text{ kg/m}^3 \text{ CCA}$		
0	00:10	00:15		
1	02:11	02:43		
2	26:00	10:58		
3	40:30	12:40		
4	NC ^c	11:09		
5	NC	11:19		
6	NC.	10:55		
7	NC	09:34		
8	NC	10:52		
9	NC.	10:52		
10	NC	11:35		
30	NC	12:09		
45	NC	12:59		

^aMixing time is defined as the length of time the ammonium molybdate and stannous chloride reagents are combined prior to addition to DI water.

 b Reaction time is the length of time that begins when the wood sample is added to DI water in the dissolution technique and ends when a light blue color develops (absorbance 0.071 at $\lambda = 690$ nm).

 ${}^{c}NC = No$ color change.

(Table 4). The XRF instrument also confirmed that samples H and I were CCAtreated wood. The PAN indicator stain tested positive for copper in samples C through I; however, samples C and D were determined to be untreated wood by the XRF instrument. The false positives observed with samples C and D may be due to the wood being dirty and contaminated with other elements, such as zinc or tin, which may react with the PAN indicator.^[37] This field test demonstrated the inability for the PAN indicator stain to specifically identify arsenic-treated wood because samples E, F, and G were treated with copper, but not arsenic. Additionally, it is reasonable to assume that sample H contained a higher arsenate concentration than sample I because sample H had a shorter reaction time than sample I. The higher arsenic concentration in sample H was confirmed by the XRF instrument.

Of the 24 sawdust samples collected from various playgrounds, 21 samples developed a blue color (absorbance > 0.070 at $\lambda = 690$ nm). whereas the remaining 3 samples did not show a noticeable blue color. For the 3 samples that did not react, the total arsenic concentrations determined by AA analysis were 149, 159, and 220 mg/kg wood, respectively. Taking into consideration that an AA measures the total arsenic concentration in

	PAN		Elements detected by XRF unit ^{a}		Determined chemical	Reaction time of modified stain dis-
Sample	indicator $(+/-)$	Cr	Cu	As	treatment preservative	solution technique (minutes: seconds)
А		$<$ 216.3 174.7		< 10	Borate ^b	NC ^d
B		< 205.3 < 35.7		< 9.3	Borate ^b	NC.
C	$^+$	< 284	< 34	< 10.3	Untreated	NC
D	$^{+}$	\leq 241.7 \leq 51.3		< 11.7	Untreated	NC.
E	$^{+}$	< 261.3	10 248	< 9.7	Copper	NC
F	$^{+}$	$<$ 253.3	1481	< 18	Copper	NC.
G	$\overline{+}$	< 236	6013	<10	ACO ^c	NC
H	$^{+}$	9194	5412	6431	CCA	17:24
Ι	$^+$	2526	1418	1476	CCA	37:42

Table 4. Results from field tests of recycled C&D wood. Each sample was tested using PAN indicator stain, XRF, and the modified stain dissolution technique

^aXRF values were taken from an average of three trials for each sample.

 b Borate-treated wood was determined due to the aqua green color of wood, which is</sup> most likely a dye added in many borate treatment processes to specify that the wood is treated with a chemical preservative.

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

 ${}^{d}NC = No$ color change.

the sample after digesting with nitric acid, whereas the modified stain dissolution technique is only able to react with the arsenate that leaches out of the wood sample, it is reasonable to assume that the arsenate concentrations leached from these 3 samples, which were all characterized by less than 300 mg-As/kg-wood, were not above the modified stain's MDL of 3 mg/L. However, the 21 samples that did test positive with the modified stain had measured total arsenic concentrations of 384 mg/kg-wood and above, as indicated by the AA spectrometer. Consequently, the modified stain dissolution technique is able to accurately identify arsenic-treated wood that has a minimum arsenate concentration of roughly 300 to 400 mg/kg-wood. This level of detection is considered adequate for identifying unweathered CCA-treated wood (lowest manufactured concentration in the U.S. is 1,900 mg/kg) and also highly weathered wood that has lost up to 80% of the chemical preservative.

Alternative Application Techniques

Testing Sample Wipes

The modified stain was able to specifically identify sample wipes from arsenic-treated wood, but with a longer reaction time (Figure 1b). The wipe

sample from weathered untreated wood did not react. The wipe sample used on the weathered 4.0 kg/m³ CCA-treated wood showed a light blue color in approximately 3 h and achieved a maximum color intensity in about 12 h, as opposed to the sawdust wood samples that typically react to form a light blue color in 30 to 45 min and achieve maximum color intensity in 5 h. The weathered 40 kg/m³ CCA-treated wood wipe sample reacted in approximately 50 min also achieving a maximum color intensity around 12 h, when the sawdust samples typically reacted in 10 to 20 min and achieved maximum color intensity in 5 h. The longer reaction time was expected and most likely due to the lower amount of arsenic that is transferred onto the wipe versus the amount within the sawdust matrix. A positive reaction was also observed with the ACZA wipe in 17 min with a maximum color intensity around 5 h.

Direct Application to Wood

The diluted modified stain applied directly to wood was able to identify new 4.0 kg/m^3 CCA-treated wood (Figure 1c) with an average reaction time of 30 to 60 min. Unfortunately, the diluted modified stain did not work well in the field when directly applied to weathered wood. Exposure to sunlight caused all wood samples to react to a dark brown or black color within 15 min. Additionally, weathered wood samples have an excessive amount of dirt and other discolorations on their surface that makes identifying a possible blue color on the wood surface difficult. Consequently, the diluted modified stain may identify CCA-treated wood in a controlled environment when directly applied to new wood, but use of the diluted modified stain to detect CCA-treated wood in the field would not be reasonable.

SUMMARY AND DISCUSSION

The development of an arsenic-specific stain was facilitated through this study by combining ammonium molybdate and stannous chloride (8 to 1 volumetric ratio) for at least five minutes before sample addition. This procedure was capable of detecting the elevated arsenate concentrations in wood from arsenical-based wood preservatives and prevented the detection of background phosphate present in the wood matrix.

Options currently available to homeowners for minimizing the risk from existing structures include the application of coatings, such as stains, paints, polyurethane coatings, and water-repellant finishes.^[5,38,39] Risks from hand-to-mouth ingestion can be most readily evaluated through the analysis of wipe samples.^[3] A service has existed for the analysis of wipe samples; $\left[5\right]$ however, it requires sending a wipe sample to a centralized facility for the analysis of the wipe by AA, which can take days to weeks. Of interest would be to compare the sensitivity of the wipe analysis between the AA and the modified stain developed through the current study. Although AA would have lower detection limits and would be quantifiable, the modified stain may be sensitive enough to detect the arsenic for uncoated structures.

Given the amount of preparation and time needed for the detection of arsenic using the modified stain with the dissolution technique, the stain is not considered practical for identifying many hundreds of wood pieces in short periods of time, as would be necessary at wood recycling facilities if each individual piece of wood was to be evaluated. If several thousands of pieces of wood are to be identified rapidly, other technologies such as XRF and laser-induced breakdown spectroscopy (LIBS) may be implemented;^[40] however, these technologies are characterized by high capital costs (handheld XRF units cost around U.S. \$20,000 whereas more automated systems have been estimated to cost in excess of U.S. \$100,000). An arsenic test kit comprised of the modified stain would cost an estimated U.S. \$15 to 35 and would be capable of analyzing on the order of 100 samples. Given the relatively low cost, those within the disposal sector may find the modified stain useful for a small number of tests, which can serve as a means to spotcheck select loads or for confirming visual or XRF/LIBS sorts on selected samples within the disposal sector.

Overall this study provides a new procedure for identifying wood treated with arsenical-based preservatives. The modified stannous chloride stain with the dissolution technique was found to perform well on sawdust and wipe samples. Laboratory experiments on new wood showed potential for the diluted modified stain to be used by direct application to the wood surface; however, more research is required before the direct application method can be implemented for samples in the field.

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