INTERNSHIP AT THE UNIVERSITY OF TENNESSEE; KNOXVILLE

EMPLOYMENT REPORT

The use of small samples for assessing treated wood conformance

performed at the course of studies

Forest Products Technology and Management

Salzburg University of Applied Sciences / Kuchl Campus

submitted from

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Salzburg, December 15, 2016

Acknowledgements

I wish to express my sincere gratitude to Dr. Adam M. Taylor for his support and encouragement throughout my internship and for helping me within the process of this report. Furthermore, I would like to thank him for providing me with the opportunity to do my internship at the University of Tennessee in Knoxville USA.

Also, I would like to thank Prof. Timothy Young, organizing the collaboration between University of Tennessee and University of Applied Sciences Salzburg making it possible to do my internship in Knoxville.

Special thanks to Jeff Lloyd, Jae-Woo Kim and Karson Guardado from Nisus Corporation in Rockford, Tennessee, to Kim Merritt from Southern Pine Inspection Bureau Pensacola, Florida and Angel Tarrier from Viance Treated Wood Solutions Charlotte, North Carolina letting me use their laboratories and facilities and giving me support with any questions during my studies.

Funding for this project was provided by the Austrian Marshall Plan Foundation as a scholarship. With this scholarship, I could cover all main financial expenses within this trip to the US as well as my stay in Knoxville. Thanks a lot, to the Austrian Marshall Plan Foundation for providing this scholarship.

Finally, I would like to express my deep gratitude to FH-Prof. Univ. Prof. Dr.-Ing. Dr. Prof. C.M. Barbu for the opportunity, support, all the work and efforts he has put into making this internship possible for me.

Abstract

In order to determine the function or performance of wood – preserving chemicals in research, small samples in wood-treating industry or laboratory conditions help to analyze a product quality and function. Sometimes the use of small samples for assessing treated wood conformance is just a part of the whole determination, but in fact still an important one. In this case, it is about two different conformances:

- In prior research creosote, was recovered from used railroad ties. Small impregnated wooden block samples have been put into a degradation test with decay - fungi to determine the threshold of effective retention of recovered creosote.
- Companies having variance problems within their treated lumber. The use of standard cup size requires a lot of samples to be mixed with the effect of a great variance within the analyzed data. The use of small volume cups in XRF – Analyzing using less sample material to improve reliability and minimize variance problems.

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Introduction

Evaluation of treated wood samples is being used in industry or research for assessing treated wood conformance. For industry to be assured their products reach the standards as well as for research to be assure they can approve their hypothesis and provide correct data for the industry. The two projects in this report aim to fulfill these goals.

First part is a small sample wood decay fungi test following AWPA (American-Wood-Protection-Association) Standard E 10, as a smaller side project within research investigating the reuse of creosote extracted from used railroad ties. The task is to test recovered creosote to treat new ties: the recovered creosote is being used to evaluate the minimum creosote retention to prevent decay under laboratory conditions against a range of standard decay organisms according to American Wood Protection Association standards (such as AWPA E 10).
Creosote is an effective preservative for sawn and peeled timber productions. The research at the Centre of Renewable Carbon is about to recover the creosote from used railroad ties. One smaller part within this project was a fungi-test orientated on the E10-12 “Standard method of testing wood preservatives by laboratory soil-block cultures”. The test should help to evaluate the performance of the recovered vs. commercial creosote and determine its threshold. The report describes the method how the test has been done and shows data that has been collected till the time this report has been finished.

Second part of this report shows the work done to prove a hypothesis by Patricia K. Lebow, Prof. Adam M. Taylor and Prof. Timothy M. Young to show the possibility to use small volume cup sizes with less material within XRF-Analysis for “accurate and precise results”[1]. Because preservative retention in wood varies within and between boards, subsequent sampling of a charge may produce higher or lower retentions than the initial measurement. This has caused some concern with the wood treating industry, and there is interest in better understanding how much variability can be expected when a charge is measured multiple times. Measuring is done by XRF – Analysis with Oxford or Asoma or other machines. These machines use cups to hold wood flour from ground cores for sampling with opening diameters of 24mm or 29mm. This leads into the possibility samples from of boards with lower retentions combined with cores from higher retentions. As a result of such a variability within a batch of treated wood, charges which have been found acceptable at the treating plant or laboratory are sometimes reported to be inadequately treated during a subsequent inspection. If the cores were grouped into a few subsamples, rather than into one sample, the variability within the charge could be estimated. To enable the use of subsamples with only a few cores of wood, different cup sizes with smaller openings than the standard cup have been identified as a potential tool.

[1] Taylor A. M., et Al. (2015): *Reduced volume wood sampling method*, Forest Products Journal

Research Hypotheses

This research should show the use of small samples for assessing treated wood within two different kind of projects. The hypotheses in this studies are:

1. **Project: Efficacy of Creosote recovered from treated wood via thermal desorption: A comparison of new and recovered creosote in a standard laboratory decay test**

- Recovered creosote has the same properties as wood-preservative like commercial creosote.
- Which threshold and retention is necessary to reach reliable properties from recovered creosote.

2. **Project: Use of small volume cups in XRF - Analyses**

- Splitting core samples and using smaller cups with smaller opening diameters can be used on XRF – Analyzers
- It provides precise data and avoids lower retentions to get onto the market.

Objectives

Objectives "Efficacy of Creosote recovered from treated wood via thermal desorption":

Defining threshold and retention and showing effectiveness and performance of recovered vs. commercial creosote by fungi decay-test (from AWPA E10).
Impregnated test – blocks been set up for a fungi decay test

Objectives "Use of small volume cups in XRF – Analyses":

Wood treating industry is testing their samples at a facility within the company or it is being tested by external laboratories. The use of Oxford X 3500 and Asoma Ametek 200 Benchtop Analyzers in this process requires a cup size which hold up to 20 cores for testing.
For this project, many samples and runs on Oxford and Asoma XRF – Analyzers have been done with standardized material to collect an amount of data to prove the thesis using smaller volume cup-sizes with smaller opening diameters and less testing material can be used on these machines with reliable outcome of data. The research can influence the whole wood – treating industry to gain more reliable and correct data in their testing process and in long terms rise the quality of their products. Lower retentions than the initial measurement can lead to fatal failure if those low – quality products do not keep their quality and therefore in possible financial disasters for the company. This possible error should be erased by this research.

Report Organization

The report will be organized in two main parts to separate the two projects shown in this report.

For the fungi – test it will first be given a short overview about the recovering – process of creosote from railroad ties.

The report shows results from two projects titled "The use of small samples for assessing treated wood conformance" which I have worked on during the time at the Center of Renewable Carbon. The main part is divided, first presenting "Commercial vs. recovered creosote – fungi test" followed by "XRF-Analyses - Use of small cups for more precise data".

Main Part 1: Efficacy of Creosote recovered from treated wood via thermal desorption: A comparison of new and recovered creosote in a Standard laboratory decay test

Creosote has proven to be an effective preservative for sawn and peeled timber products. It has been used for more than a century for heavy – duty marine, industrial, and railroad structures, because it minimizes both weathering and decay. Wood products treated with creosote (AWPA, P1/P13) and its solutions (P2 and P3) have high durability, are flexible and cost effective, and are easily installed. Wood products treated with these creosotes typically last at least 30 years and have proven to last as long as 100 years. Creosote continues to be the wood preservative of choice for some of the most demanding structural uses of wood, such as marine construction and railroad crossties. For example, treated wood crossties continue to be the rail transportation industry's primary track and rail support of choice; treated wood ties absorb and withstand extreme vertical and lateral loads and maintain rail gauge, surface and alignment.

At the end of their use in any heavy, medium or light duty track application, creosote treated wood products can be recycled and / or reused. Some applications include:

- Energy production in commercial power plants. Recycling used creosote treated wood as a bio – fuel, conserves landfill space and offsets the need for fossil fuels.
- Depending on condition of the crosstie:

    1) Reused in Class 1 secondary track and rail yards,
    2) Sold to short – line railroads for reuse in track

In the US, the total number of railroad ties (crossroad ties or sleepers) in the track accounts for approximately 700 – 800 million. Over 21 million railroad ties are produced per year with approximately 20 million being replaced after providing excellent primary service in railroad track. More than 80% of used ties are consumed as fuel in approved boilers such as timber companies, cement kilns, and co-gasification facilities with proper air permit modifications and, in many cases, little equipment modification. Only a small fraction (0.3 %) is currently landfilled. However, the U.S. EPA following their Non-Hazardous Secondary Material rule (NHSM) in 2014 classified treated wood as "waste". As a result, starting in 2016, most treated wood ties currently used for low CO_2 biomass fuel must be disposed of by incineration, or in landfill, with most likely going to landfill if boiler and gasification facilities do not install costly upgraded fuel oil delivery system with cleaner-burning natural gas. If used ties for fuel are disposed of in landfill, preservative components in the ties are released through soil or water to eventually reach and enter the ground water and take a long time to break down and are consequently toxic to some animals and possibly to humans. As well, they would take up millions of cubic feet of landfill space and approximately 0.3 million tons of preservatives remaining in the used ties will decompose over time, producing 1.65 million tons of greenhouse gases (GHG) annually. Our proposed research, therefore, seeks to alleviate these problems that cause environmental hazards and GHG emission by removal of preservative contaminants found in used ties and more importantly allowing for the valuable re-use of the preservatives. Such an approach could potentially prove to be the most commercially viable option for this solid waste. By recycling the creosote, this proposed research will demonstrate that it is possible to avoid the large environmental impacts associated with landfill, GHG release and fossil fuel use, by eliminating the need to landfill used ties containing creosote, and indeed demonstrate it is commercially desirable to do so.

Recovered creosote by two – step thermal process

Creosote could have been obtained with a bench – scale fixed – bed reactor by a research group at the University of Tennessee in Knoxville at the Departments Center of Renewable Carbon and Biosystems Engineering & Soil Science, together with engineers from Nisus Corporation Rockford – Tennessee.
Creosote – treated Railroad ties from National Salvage & Services Corporation (Bloomington, IN, USA)[2] have been used for the recovery process. The railroad ties been chopped to a fraction size < 0.40 mm with a 20% water content. The material was used in the experiment to finally be able to obtain the recovered creosote.
First step is a thermal desorption with a residence time of 7 – 10 min, 250° C temperature. After second run: Pyrolysis, residence time is set to 72 sec. with creosote (thermal treatment at temperatures: 250°, 280°, 300°, 325° and 350°C) and bio – oil (at 500°C) being collected. Biochar is another side product which can be used for applications like water filtering.

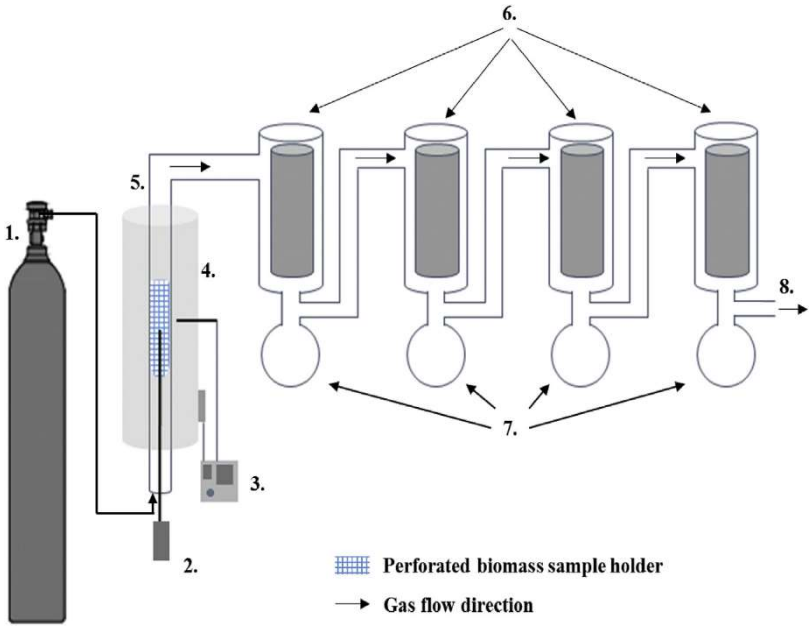


Fig. 1. Schematic representation of the laboratory scale thermal desorption reactor system. **1**. Nitrogen gas cylinder, **2**. Thermocouple measuring biomass bed temperature, **3**. Furnace PID controller, **4**. Tubular furnace, **5**. Quartz tube reactor with porous stainless steel biomass sample holder, **6**. Dewar like condensers filled with liquid nitrogen, **7**. Liquid sample collection and **8**. Outlet gas port.

Figure 1: Schematic representation of the laboratory scale thermal desorption reactor system[2]

Commercial creosote shows a water content of around 4 %, recovered creosote around 8 %. This difference "*should not have any major effect on recovered creosote*" (by Pyoungchung Kim).

[2] Pyoungchung Kim et. al. (2016): Recovery of creosote from used railroad ties by thermal desorption, ElsevierLtd.

Materials and Method

Next chapters describing materials and methods used in the project.

Fungi preparation

For the cultivation of test – fungi a culture material, malt agar substrate was prepared (AWPA E 10, 7.1) to help the growth of fungi to accelerate.

Two wood – decay fungi have been cultivated:

Postia placenta (AWPA E 10, 6.2.1.2)
A brown – rot wood – decay fungi, belonging to the group of filamentous basidiomycetes which is known for a fast decay of cellulose with minor lignin removal, is suitable to use at softwood test blocks

Trametes versicolor (AWPA E 10, 6.3.1.1)
A white rot belonging to the family of polyporaceae is common to be seen on hardwood making it suitable to be used on hardwood test blocks

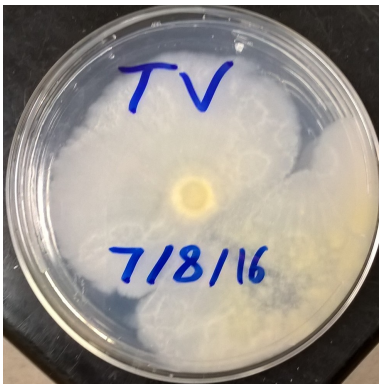


Image 1: Trametes versicolor cultivated in petri dish, Pic.: Stelzer R.

It took between 2 – 4 weeks for the fungi to grow out in around 6 to 8 petri dishes placed in an incubator with a temperature of 82°F / 28°C.

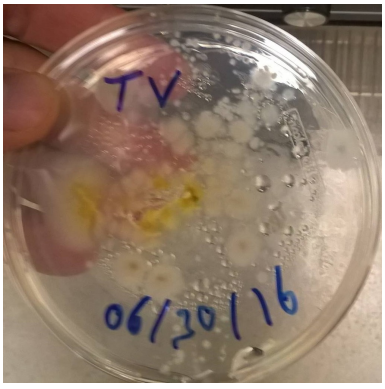


Image 2: Contaminated Trametes versicolor, Pic.: Stelzer R.

First cultivation of *Trametes versicolor* and *Postia placenta* grew out showing contamination. Jae-Woo Kim from Nisus Corporation provided uncontaminated *Postia placenta* which could be applied to the jars with the test – blocks on August 29. 2016 until around three months till mid – November for degradation – test. Results can be seen in Table 4, Table 5 and Table 6.

The prior cultivated *Trametes versicolor* didn´t show any specific indication for contamination was applied to test – jars at same date (August 29. 2016). Actual it showed contamination by mold after some days of incubation. Another new *Trametes versicolor* was cultivated and could have been applied to test jars on October 04. 2016. There have been no results yet for degradation – test of *Trametes versicolor* on gum – block samples by the time this report has been finished.

Wood species for test – blocks

There have been used two different wood species:

- pine (*Pinus* spp.) to be tested for brown – rot and
- sweetgum (*Liquidambar styraciflua L*.) to be used for white – rot

The blocks have been cut into size 17 mm x 17 mm = 4913 mm³ with a weight around 2,75 g.

Image 3:Gum cubes test-blocks, Pic.: Stelzer R.

Calculation of threshold and retention

Test about how much toluene test – blocks incorporate / absorb:

- 5 blocks / pine (*Pinus* spp.*)* and gum (*Liquidambar styraciflua L*.)
- bulk filled with vacuum pump oil (cleans air from toluene to protect air pumps)
- weight test – blocks
- glass treatment beaker put in vacuum desiccator (diameter 250 mm) filled with toluene and blocks pressed down with a weight
- desiccator sealed and process started
- about 20 – 25 min vacuum and 20 min to get the toluene taken up
- blocks weight taken after process directly before toluene is vaporized

Measurement of exposure to toluene in Pine and Gum wood samples					
	Label	Before in g	After in g	Absorption in g	ø
Pine	F1	2,4467	4,6720	2,2253	
	F2	2,4555	4,6170	2,1615	
	F3	3,1852	4,4840	1,2988	
	F4	2,6869	4,5470	1,8601	
	F5	2,7315	4,1551	1,4236	
					1,79386
Gum	G1	2,9255	4,840	1,9145	
	G2	2,7376	4,562	1,8244	
	G3	2,7650	4,418	1,6530	
	G4	2,4784	3,877	1,3986	
	G5	2,7147	4,582	1,8673	
					1,73156

Table 1: Measurement of exposure to toluene on pine and gum wood samples

Actual definition of threshold:

Following calculation was done to define threshold and retention of creosote concentration for the testing blocks.

1 pcf = 16.02 kg/m³

Estimated solution uptake: 500 kg/m³

Cubes with 17 mm, which is: 17 x 17 = 4913 mm³ = 4.913 cm³

actual uptake: $\frac{1,79386}{4,913\ cm^3} * 1000$ = 365.13 kg/m

Fungus	Threshold for creosote			Solutions to prepare, according to fraction of threshold						
	pcf	kg/m3	solution concentration to achieve threshold	0%	25%	50%	75%	100%	150%	200%
P. placenta	0,6	9,612	2,63%	**0**	**0,66%**	**1,32%**	**1,97%**	**2,63%**	**3,95%**	**5,27%**
T. versicolor	0,75	12,015	3,29%	**0**	**0,82%**	**1,65%**	**2,47%**	**3,29%**	**4,94%**	**6,58%**

Table 2: Calculation of threshold for creosote

The calculated solutions been reached by multiplying the "*solution concentration to achieve threshold*" with the estimated "*solutions to prepare, according to fraction of threshold*".

	Target retention (kg/m3)						
	0%	25%	50%	75%	100%	150%	200%
Pine	**0,00**	**2,403**	**4,806**	**7,209**	**9,612**	**12,418**	**19,224**
Gum	**0,00**	**3,004**	**6,008**	**9,011**	**12,015**	**18,023**	**24,030**

Table 3: Target retention in kg/m³ for pine and gum

Table 3 shows target retention in kg/m³ for test blocks to reach at vacuum impregnation. Table 4, Table 5 and Table 6**Fehler! Verweisquelle konnte nicht gefunden werden.** on page 10 / 11 / 12 showing actual retention in kg/m³ and % for impregnated test – blocks.

Vacuum-Impregnation

Calculated concentrations been prepared and the test-blocks been treated by vacuum-impregnation. From each wood species 6 blocks per concentration have been treated with commercial and recovered creosote. Also, one set of 6 blocks each wood-species has been just treated with a 0.0 % concentration as control-medium.

The commercial creosote has been given by Nisus Corporation, Rockford – Tennessee. The recovered creosote has been obtained at the Centre of Renewable Carbon, The University of Tennessee in Knoxville. Preferred choice of recovered creosote for fungi – test was the one obtained at a temperature of 280° C.

Image 4: Preparation of gum test – blocks in 2,47% solution of recovered creosote, pic.: Stelzer R.

Solutions for vacuum impregnation has been prepared according calculated threshold for pine and gum. 6 blocks have been treated in one solution. For each wood species, there have been 6 blocks just treated in 100-% toluene as control-samples. The blocks have been weighed immediately after impregnation and after drying obtaining the concentrations uptake and actual retention for each test – block.

Image 5: Apparatus used for vacuum impregnation, pic.: Stelzer R.

Image 5 showing apparatus used for vacuum impregnation of test – blocks. An air pump (on the right) was used to create a vacuum inside a vacuum desiccator. With a treatment beaker put inside, holding the test – blocks which have been put into the creosote concentration (left side). A flask was connecting the air pump to the vacuum desiccator. It is containing oil to filter the toluene which could harm the air pump.

Preparation of culture – bottles

Jars with soil and water have been prepared to place the impregnated test-blocks together with a piece of fungi into it to let it grow out. The decay of test – blocks being measured after 3 months.

Evaluation of soil / water content

Three soil / water mixes in 16 oz. jars were prepared with each 50-gram soil and added amount of water:

- 110 ml
- **140 ml**
- 155 ml

Jars put inside autoclave for 15 minutes 250° F (121° C) plus 10 minutes' downtime.

The decision was made to take the jar with the filling of **140 ml** as there was no pooling water seen and the soil showing a wet glance all – around the jar. This was the aim to have and gain a proper condition as base for the fungi.

In each jar, there are to place:

- One wooden strip, same species as the wooden blocks and a piece of fungi on top of the strip
- Three impregnated blocks same wood species as the strip and same concentration of creosol impregnation

Actual Preparation of jars for fungi decay – test:

- 54 pcs. of 16 oz. jars
- 50 g of soil each jar plus 140 ml water
- wooden – strip of (27 pcs.) gum and (27 pcs.) pine
- Jars put inside autoclave for 15 minutes 250° F (121° C) plus 10 minutes' downtime.

Small block degradation-test

As the properties of recovered creosote are not yet known to be used again as a proper wood – preservative this test should help to gain missing data. To achieve this the fungi – degradation test has been prepared oriented by AWPA (American wood protection association) Standard E10 (Standard method of testing wood preservatives by laboratory soil – block cultures).
Inside the prepared jars, a small stripe of pine or gum has been placed and put into autoclave. After the jars cooled down a small piece of fungi been placed on the stripe and the jars put into an incubator. After around 10 days the fungi showed enough signs of growth for the impregnated test – blocks to be placed inside the jars. Three blocks per jar.

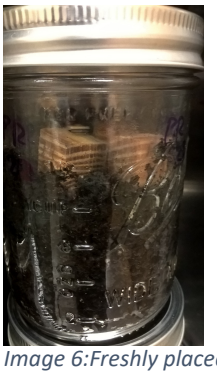


Image 6:Freshly placed test blocks inside jar, pic.: Stelzer R.

After around a week there could have been seen different growth on fungi inside different jars.

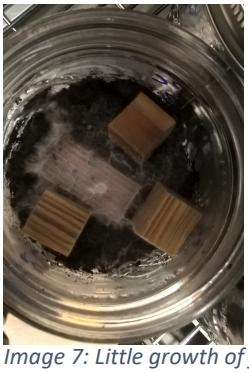


Image 7: Little growth of fungi after a week of application of pine test-blocks, pic.: Stelzer R.

It could have been observed, jars holding test – blocks with lower concentrations of commercial or recovered creosote, showing a stronger growth of fungi (Image 7). Those containing blocks with higher concentration showing a smaller growth of fungi (Image 8).

Image 8: Intensive growths of fungi after a week of application of pine test blocks, pic.: Stelzer R.

Results for degradation – test

Following chapters are showing results for degradation – test on pine and gum samples with recovered and commercial creosote.

Postia placenta with pine – test blocks

Record for fungi – decay – test on pine (*Pinus* spp.) with *Postia placenta* on small blocks treated with different solutions of commercial and recovered creosote like shown in Table 2. More than half of the test – blocks could reach an actual retention of 80 % + (46 blocks) towards the calculated target retention.

After around three months the test – blocks been taken out of the jars. There was shown different appearance for the growth of fungi inside the jar.

Appearance indicating a healthy condition for fungi:

- Lots of growth
- Some growth
- Minimal growth

Appearance not indicating a healthy condition for fungi:

- Some growth, possible contamination, green & white in color
- Some growth, white & slightly yellow in color
- Some growth, possible contamination, green in color
- Lots of growth, white & light brown in color

Due to a possible contamination, some jars didn´t provide a fully healthy condition for the fungi to spread. Most of fungi showed minimal to lots of growth.

Sample#	Creosote	Target retention	Act. retention	Dry Block	After	Mass	Mass loss	
	Concentr.	in Kg/m³	in %	in g	test in g	loss in g	in %	Appearance Inside Jar
PN-1	0,00%	*0,0000*	0,00%	3,2265	2,2700	0,9384	29,25%	Lots of growth
PN-2	0,00%	*0,0000*	0,00%	3,3299	1,5100	1,7879	54,21%	Lots of growth
PN-3	0,00%	*0,0000*	0,00%	3,0644	1,7100	1,3269	43,69%	Lots of growth
PN-4	0,00%	*0,0000*	0,00%	2,6672	2,3300	0,3126	11,83%	Some growth, possible contamination, green & white in color
PN-5	0,00%	*0,0000*	0,00%	3,3738	3,0400	0,3017	9,03%	Some growth, possible contamination, green & white in color
PN-6	0,00%	*0,0000*	0,00%	2,7169	2,5100	0,1683	6,28%	Some growth, possible contamination, green & white in color

Table 4 Control sheet for pine-samples – control blocks

The control samples help to detect efficiency of the treated test – blocks in comparison to untreated test – blocks. Those control – samples have been treated with 100 % toluene.

The two jars holding each 3 samples indicating two different appearance for growth of fungi. For the jar showing “lots of growth” for fungi samples indicating mass loss between 30 to 54 %. The jar holding fungi with possible contamination, mass loss is between 6 to 12 %.

Sample#	Creosote	Target retention	Act. retention	Dry Block	After	Mass	Mass loss	
	Concentr.	in Kg/m³	in %	in g	test in g	loss in g	in %	Appearance Inside Jar
PC-1	0,66%	2,4030	97,26%	2,7430	2,0700	0,6552	24,04%	Some growth
PC-2	0,66%	2,4030	100,97%	2,3860	1,1600	1,2042	50,93%	Some growth
PC-3	0,66%	2,4030	61,37%	3,2274	2,9800	0,1968	6,19%	Some growth
PC-4	0,66%	2,4030	59,39%	3,2363	2,9700	0,2395	7,46%	Minimal growth, possible contamination, green in color
PC-5	0,66%	2,4030	94,82%	2,6496	2,4200	0,2057	7,83%	Minimal growth, possible contamination, green in color
PC-6	0,66%	2,4030	59,51%	3,1038	2,8400	0,2264	7,38%	Minimal growth, possible contamination, green in color
PC-7	1,32%	4,8060	98,93%	2,7504	2,5300	0,1700	6,30%	Minimal growth, possible contamination, green in color
PC-8	1,32%	4,8060	61,66%	3,2667	2,9600	0,2678	8,30%	Minimal growth, possible contamination, green in color
PC-9	1,32%	4,8060	98,07%	2,5753	2,4000	0,1464	5,75%	Minimal growth, possible contamination, green in color
PC-10	1,32%	4,8060	105,66%	2,0403	1,6500	0,3548	17,70%	Lots of growth
PC-11	1,32%	4,8060	70,54%	2,9347	1,5900	1,3010	45,00%	Lots of growth
PC-12	1,32%	4,8060	81,18%	3,1725	2,5200	0,6251	19,88%	Lots of growth
PC-13	2,47%	7,2090	101,17%	2,7436	2,4000	0,3165	11,65%	Lots of growth, white & light brown in color
PC-14	2,47%	7,2090	108,86%	2,6144	1,6200	0,9546	37,08%	Lots of growth, white & light brown in color
PC-15	2,47%	7,2090	72,02%	3,1858	1,2800	1,8648	59,30%	Lots of growth, white & light brown in color
PC-16	2,47%	7,2090	72,69%	3,3141	2,2100	1,0608	32,43%	Some growth
PC-17	2,47%	7,2090	107,41%	3,2480	2,9900	0,1875	5,90%	Some growth
PC-18	2,47%	7,2090	73,62%	2,9948	1,6600	1,2950	43,82%	Some growth
PC-19	3,29%	9,6120	147,65%	2,4822	2,3000	0,1362	5,59%	Minimal growth
PC-20	3,29%	9,6120	78,18%	3,3509	3,0100	0,2605	7,97%	Minimal growth
PC-21	3,29%	9,6120	149,56%	2,7590	2,5500	0,1878	6,86%	Minimal growth
PC-22	3,29%	9,6120	76,07%	3,1399	2,6300	0,4370	14,25%	Some growth
PC-23	3,29%	9,6120	80,51%	3,1655	2,7300	0,3937	12,60%	Some growth
PC-24	3,29%	9,6120	82,01%	3,3325	2,9500	0,3005	9,24%	Some growth
PC-25	4,94%	14,4180	141,57%	2,5793	2,2900	0,2510	9,88%	Some growth
PC-26	4,94%	14,4180	115,79%	2,7236	2,5000	0,1630	6,12%	Some growth
PC-27	4,94%	14,4180	99,04%	2,6695	2,4700	0,1390	5,33%	Some growth
PC-28	4,94%	14,4180	86,61%	3,3663	3,1200	0,1970	5,94%	Minimal growth
PC-29	4,94%	14,4180	128,24%	2,1225	1,9700	0,0972	4,70%	Minimal growth
PC-30	4,94%	14,4180	66,01%	3,2701	3,0200	0,1997	6,20%	Minimal growth
PC-31	5,27%	19,2240	110,74%	2,6999	2,5000	0,1163	4,45%	Some growth
PC-32	5,27%	19,2240	139,40%	2,3754	2,1500	0,1568	6,80%	Some growth
PC-33	5,27%	19,2240	92,36%	2,6872	2,2100	0,4195	15,95%	Some growth
PC-34	5,27%	19,2240	99,49%	2,7447	2,5600	0,1152	4,31%	Minimal growth
PC-35	5,27%	19,2240	114,74%	2,5306	2,3400	0,1168	4,75%	Minimal growth
PC-36	5,27%	19,2240	119,11%	2,5060	2,2900	0,1680	6,83%	Minimal growth

Table 5: Control sheet for pine-samples with commercial creosote

There could been observed a different appearance for growth of fungi inside jars containing test – blocks treated with commercial creosote concentrations. There have been three jars indicating possible contamination.

Samples PC – 1 to 6 treated with lowest concentration 0.66 % (2.4030 kg/m³ target Retention). Mass loss for all 6 samples have been between 6.19 % to 50.93 %. Sample PC – 2 has been only one reaching an actual retention of 100 % but indicated highest mass loss with 50.93 %.

Between all samples treated with commercial creosote, PC – 21 (creosote concentration 3.29 %) reached highest actual retention with 149.00 %, a mass loss of 6.86 % with “minimal growth” of fungi. Sample PC – 3 (creosote concentration 0.66 %) reached lowest actual retention with 61.37 % but a low mass loss with 6.19 %, showing “some growth” for fungi.

For samples PC – 31 to 36 been treated with highest concentration of 5.27 % commercial creosote appearance in jar showed “some and minimal growth”. 5 out of 6 samples reached an actual retention of 100 % with a mass loss between 4.31 – 6.83 %. Those samples are the ones with highest numbers of blocks reaching an actual retention of + 100 %. Sample PC – 33 reached lowest actual retention of 92.36 % and highest mass loss for this group of 15.95 %.

Sample#	Creosote Concentr.	Target retention in Kg/m³	Act. retention in %	Dry Block in g	After test in g	Mass loss in g	Mass loss in %	Appearance Inside Jar
PR-1	0,66%	2,4030	50,34%	3,4580	1,5600	1,8728	54,56%	Lots of growth
PR-2	0,66%	2,4030	57,93%	2,9976	2,5600	0,4050	13,66%	Lots of growth
PR-3	0,66%	2,4030	89,24%	2,4746	2,2200	0,2226	9,11%	Lots of growth
PR-4	0,66%	2,4030	92,78%	2,6572	2,4700	0,1684	6,38%	Lots of growth
PR-5	0,66%	2,4030	87,26%	2,6788	1,1200	1,5428	57,94%	Lots of growth
PR-6	0,66%	2,4030	83,53%	2,8154	2,2400	0,5526	19,79%	Lots of growth
PR-7	1,32%	4,8060	122,06%	2,4686	2,2600	0,1800	7,38%	Some growth
PR-8	1,32%	4,8060	65,34%	3,1859	2,3700	0,7870	24,93%	Some growth
PR-9	1,32%	4,8060	114,14%	2,3918	2,2400	0,1360	5,72%	Some growth
PR-10	1,32%	4,8060	110,23%	2,4686	2,2800	0,1830	7,43%	Minimal growth
PR-11	1,32%	4,8060	115,64%	2,3830	2,2000	0,1217	5,24%	Minimal growth
PR-12	1,32%	4,8060	84,64%	3,1561	2,9100	0,2321	7,39%	Minimal growth
PR-13	2,47%	7,2090	79,66%	3,3351	2,1000	1,2010	36,38%	Some growth, white & slightly yellow in color
PR-14	2,47%	7,2090	74,26%	3,3910	2,9000	0,4713	13,98%	Some growth, white & slightly yellow in color
PR-15	2,47%	7,2090	77,91%	3,1785	2,9200	0,2332	7,40%	Some growth, white & slightly yellow in color
PR-16	2,47%	7,2090	147,77%	2,5489	1,3500	1,1710	46,45%	Some growth
PR-17	2,47%	7,2090	101,47%	2,7483	2,5600	0,1607	5,91%	Some growth
PR-18	2,47%	7,2090	77,33%	3,1560	2,9400	0,1915	6,12%	Some growth
PR-19	3,29%	9,6120	91,27%	2,9619	2,7500	0,1606	5,52%	Minimal growth
PR-20	3,29%	9,6120	71,58%	3,5362	3,2900	0,2100	6,00%	Minimal growth
PR-21	3,29%	9,6120	145,86%	2,1646	2,4200	0,1387	5,42%	Minimal growth
PR-22	3,29%	9,6120	77,16%	3,4144	3,1700	0,1780	5,32%	Minimal growth
PR-23	3,29%	9,6120	81,90%	3,2412	2,9900	0,1958	6,15%	Minimal growth
PR-24	3,29%	9,6120	104,92%	3,0928	2,8700	0,1730	5,69%	Minimal growth
PR-25	4,94%	14,4180	102,74%	2,7204	2,5400	0,1334	4,99%	Minimal growth
PR-26	4,94%	14,4180	116,10%	2,6759	2,4600	0,1441	5,53%	Minimal growth
PR-27	4,94%	14,4180	155,56%	2,5271	2,3300	0,1438	5,81%	Minimal growth
PR-28	4,94%	14,4180	123,71%	2,7265	2,5500	0,1307	4,88%	Minimal growth
PR-29	4,94%	14,4180	78,96%	3,2352	3,0000	0,1809	5,69%	Minimal growth
PR-30	4,94%	14,4180	63,22%	3,5454	3,2600	0,2225	6,39%	Minimal growth
PR-31	5,27%	19,2240	102,14%	2,4690	2,2900	0,1175	4,88%	Minimal growth
PR-32	5,27%	19,2240	130,53%	2,3013	2,1200	0,1266	5,64%	Minimal growth
PR-33	5,27%	19,2240	61,41%	3,2962	3,0300	0,1978	6,13%	Minimal growth
PR-34	5,27%	19,2240	95,10%	2,8000	2,5500	0,1764	6,47%	Some growth
PR-35	5,27%	19,2240	55,67%	3,1971	2,9400	0,2079	6,60%	Some growth
PR-36	5,27%	19,2240	59,17%	3,2352	2,9900	0,1957	6,14%	Some growth

Table 6: Control sheet for pine-samples with recovered creosote

There could been observed a different appearance for growth of fungi inside jars containing test – blocks treated with recovered creosote concentrations. There has been one jar indicating possible contamination. Every other jar showed “minimal to lots of growth”.

The two jars containing test - blocks (PC – 1 to 6) with lowest concentration, 0.66 %, reached an actual retention between 50 – 93 % with the appearance for fungi “lots of growth”. The mass loss is between 6.38 % - 54.56 %. Sample PR – 4 reached highest act. retention with 92.78% and lowest mass – loss with 6.38 % in this group.

For samples PR – 31 to 36 been treated with highest concentration of 5.27 % of recovered creosote appearance in jar showed “minimal to some growth”. 2 out of 6 samples reached an actual retention of + 100 % with a mass loss of 4.88 % and 5.64 %. Sample PR – 36 reached lowest actual retention of 55.67 % and highest mass loss for this group of 6.60 %.

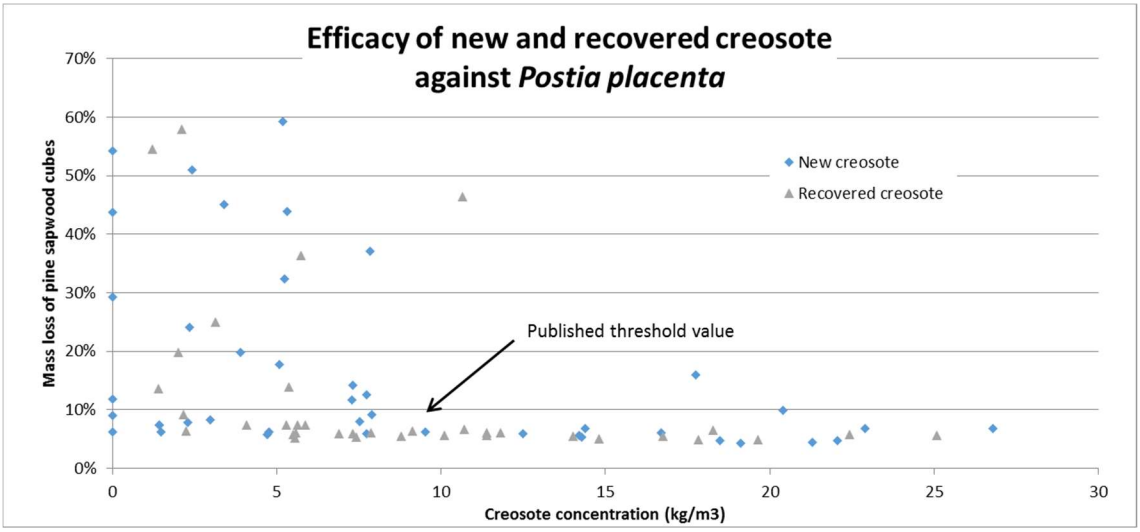


Figure 2: Efficacy of new and recovered creosote against Postia placenta

Figure 2 shows efficacy of new and recovered creosote against *Postia placenta*. The two sets of data look same in terms of mass loss / concentrations. There is no categorical distribution to determine differences as they all show more less same properties. From the point of "published threshold value"[3] mass loss mainly kept under 10 %.

Trametes versicolor on gum test-blocks

The fungi-decay – test with Trametes versicolor on small gum test – blocks treated with different solutions of commercial and recovered creosote is still running and to the time of the writing of this report, there have not yet been any results for mass loss / concentration for this wood species / fungi.

[3] Freeman M. et Al. (2013): PXTS; A metal free oligomer wood preserving system; AWPA

Conclusion

Samples#	Means	Samples#	Means
Concentration	Com. Creosote	Concentration	Rec. Creosote
PC-1 to 6 0.66 %	Act. Retention:	PR-1 to 6 0.66 %	Act. Retention:
	78,89%		76,85%
	Mass loss in %:		Mass loss in %:
	17,31%		26,91%
PC-7 to 12 1.32 %	Act. Retention:	PR-7 to 12 1.32 %	Act. Retention:
	86,01%		102,01%
	Mass loss in %:		Mass loss in %:
	17,15%		9,68%
PC-13 to 18 2.47 %	Act. Retention:	PR-13 to 18 2.47 %	Act. Retention:
	89,30%		93,07%
	Mass loss in %:		Mass loss in %:
	31,70%		19,37%
PC-19 to 24 3.29 %	Act. Retention:	PR-19 to 24 3.29 %	Act. Retention:
	102,33%		95,45%
	Mass loss in %:		Mass loss in %:
	9,42%		5,68%
PC-25 to 30 4.94 %	Act. Retention:	PR-25 to 30 4.94 %	Act. Retention:
	106,21%		106,72%
	Mass loss in %:		Mass loss in %:
	6,36%		5,55%
PC-31 to 36 5.27 %	Act. Retention:	PR-31 to 36 5.27 %	Act. Retention:
	112,64%		84,00%
	Mass loss in %:		Mass loss in %:
	7,18%		5,98%

Table 7: Comparison of means

Table 7 shows mean for actual retention and mass loss in % for 6 blocks treated with same concentration of commercial or recovered creosote. Data of performance are close to each other.

Generally Looking on Figure 2 and Table 7 it can be seen equivalent performance of new and recovered creosote – for one test organism. The two sets of data – recovered and commercial – look the same in terms of mass loss / concentration. There can be named an influence from uneven uptake of creosote. This could be different for another test fungi.

Therefore, I suppose to try another test fungi and / or do field test and maybe leaching tests.

After these fungi – decay test it can be inferred, that recovered creosote gained at the bench scale fixed bed reactor at 280° C still shows protective performances as wood – treating chemical after the recovering process.

Main Part 2: Use of small volume cups in XRF – Analyses

On March 10. 2016 Lebow et. Al. published a pre-proposal about "*Reduced volume wood sampling method to enable uncertainty estimation in retention measurements for treated wood*" suggest to split standard cup size, holding 20 core sets of treated wood powder samples into a lower number of 4 to 5 samples being measured in a cup with reduced volume on an analytical tool (X – Ray fluorescence – XRF) which would lead into "an accurate reading"[4].

The proposed concept of "using a reduced volume cup to enable smaller wood samples to be used in XRF measurement"[4] has been performed within this research to confirm its efficiency.

Hypothesis of using smaller cups for XRF – Analyses

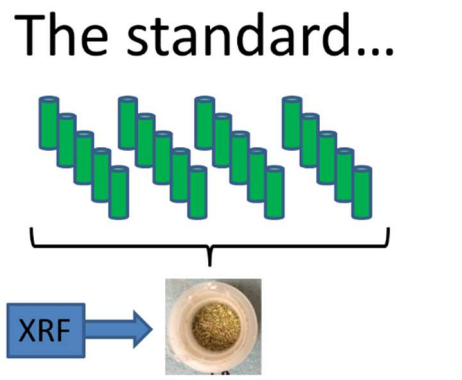


Figure 3: Standard process for XRF – Analyses

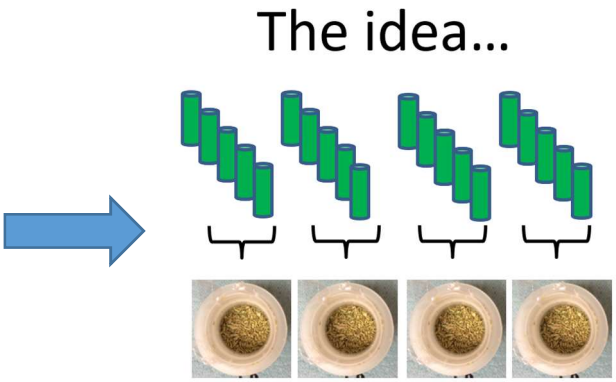


Figure 4: New schematic for use of smaller cup sizes

The standard requires a number of 20 cores to be taken from the treated lumbers, milled and analyzed. The cores been all measured together in one cup. This method also allows samples from low treated lumbers to be mixed with those being treated well. According to the standard commodity specification (AWPA T1 -section), at least 85% of the entire samples are required to pass the test. It was stated that a 15 % range for low treated lumber would be too low for a safe and constant product quality. Those lumbers having a low retention of wood-treated preservatives could be possible to pass the test if the results of all 20 cores mixed together are within the standards. But those with a low treatment are possible to be affected and showing poor performance.

To assure a more defined result in XRF – Analyzing the idea has been created by Professor Adam Taylor to take less cores for each measurement to increase the possibility to find low treated wood. Smaller cups with smaller diameter opening been used to hold the smaller amount of core samples. This research was about to compare the 4 smaller cups (diameter 20 mm, 15 mm, 10 mm and 6 mm) (Image 9) with the standard cup size (29 mm for Oxford / 24 mm for Asoma)

Image 9: Commercially available cups

The standard for machines like Asoma Ametek 200 Benchtop Analyzer requires samples to be compressed before analyzing. For Oxford Benchtop XRF Analyzer – Lab – X 3500 standard cup with a diameter of 29 mm is been at least filled with material ≥ 1,30 g or "cup half full".

[4] Lebow et al (2016): Reudced volume wood sampling method, Forest Products Journal

Example of XRF – Analyses at a wood-treating mill

Companies who do pressure-treatment of wood with wood-preservatives have to make analyses for quality assurance. These been done with XRF – Analyzers like Oxford Benchtop XRF – Analyzer X 3500 or Asoma Ametek 200 Benchtop Analyzer to assure the concentration of wood treating chemicals in their product. After pressure-treatment core borings been randomly taken from treated lumber.
Following Images show by example the process to gain sample material for XRF – Analyses (Images by David Juriga and René Stelzer taken at Langdale Forest Products Company of Sweetwater, Tennessee):

Image 10: Treated lumber pressure cylinder

Image 11: Cylinder for pressure treatment

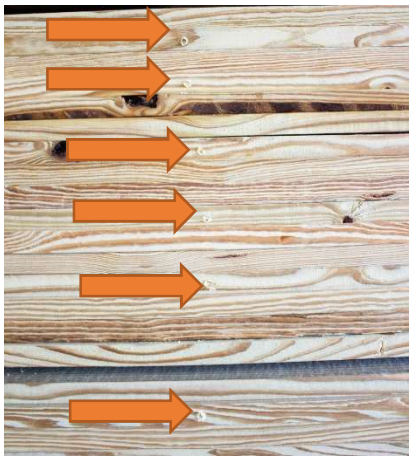


Image 12: Core borings from treated lumber

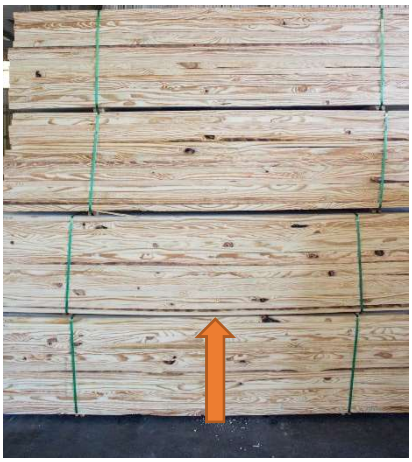


Image 13: Sample boring location

Image 14: Drill for core sample borings

Image 15: 20 Core samples taken from treated lumber

After core-samples been taken heartwood is been identified by an indicator spray using O – anisidine hydrochloride or 10 percent sodium nitride solutions (according to AWPA M 2 – 4.3.1.1) and turning the heartwood in a red color. These parts been cut off and another indicator spray, a mixture of chrome

azurol S and sodium acetate applied (IMAGE 10) (AWPA A 3 – 2.) identifying the treated parts by turning into dark color.

Image 16: Cutting and removing of heartwood

Image 17: Apply indicator spray for copper on core samples

The test reveals the sufficiency of preservative as can be seen by a color change and insufficient indication is showing poor penetration by the preservative. This indicates a poor quality. Requirements ask for at least 85% of all samples to pass the test. After cutting the cores to a length of 0.6 inches (15.24 mm) (Image 18) (length requirement by AWPA T 1 11) they have been transferred to a microwave or oven to reach a moisture content of kiln dry or at least dry (at least 0.0 % moisture content by AWPA A 9, 5.1.5 / 8.1.1.1).

Image 18: Samples cut to size of 0.6 inches

Image 19: Grinding dried cores for XRF – measurement

The dried samples are being grinded (Image 19) to a size of 20 mesh (0.0331 inch /0.841 mm) (A 9, 8.1.1.2). The grinded material is being placed in cup and softly compressed (Image 20)
Each sample is required to be labelled with exact identification. The concentration for wood-preservatives (given in %) was evaluated in lb/ft³ (pounds per cubic foot, pcf) from following equations taken from standard AWPA A 9, 12.2.

$$(\%\ of\ preservative\ in\ Sample)\ x\ \frac{(A12\ Density\ of\ wood)}{100} = Total\ pcf$$

Equation 1; Compressed wood method (AWPA A9 12.2.2.2)

$$(\%\ of\ preservative\ in\ Sample)\ x\ \frac{Sample\ Density}{100} = Total\ pcf$$

Equation 2: Compressed wood method (AWPA A9 12.2.3)

$$Sample\ Density = W\ x\ F$$

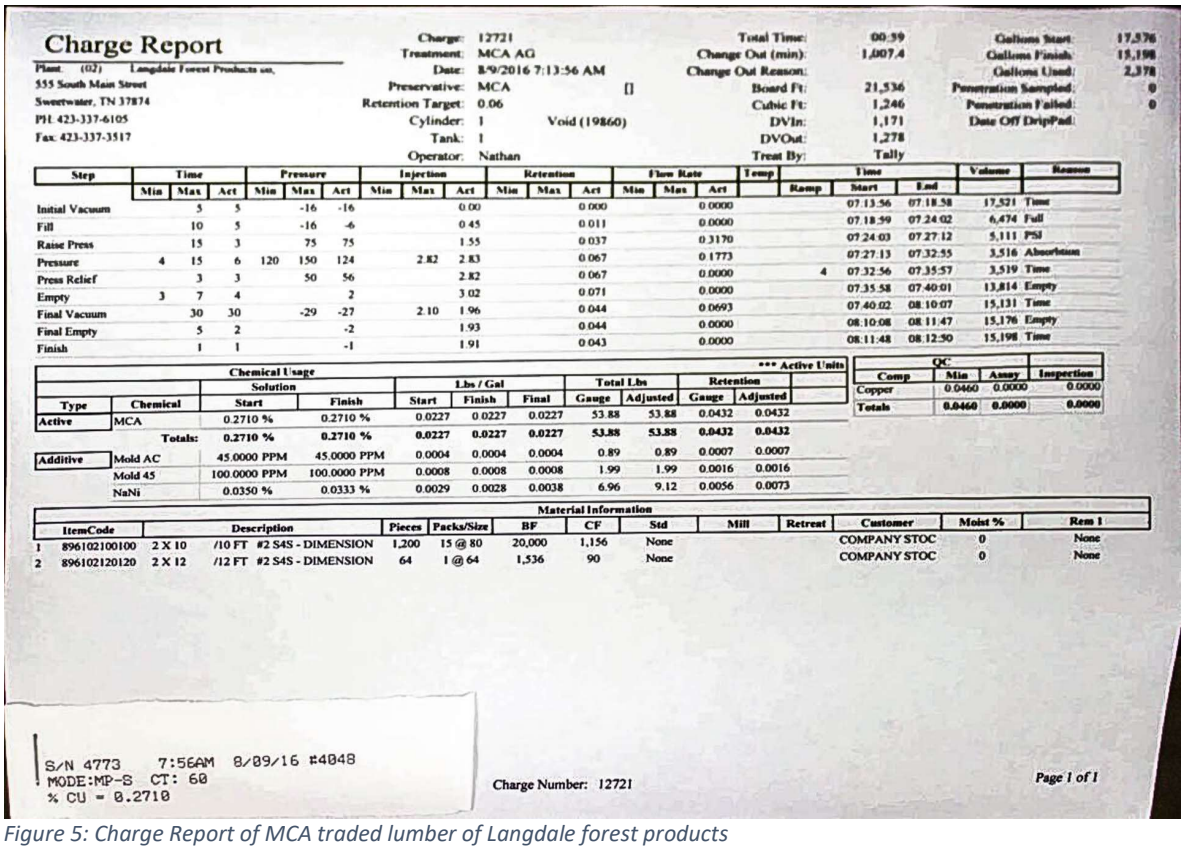
Equation 3: Sample density (AWPA A9 12.2.3.1)

W Sample Weight
D Bit Diameter
L Core Length
N Number of Cores

Image 20 Compressing sample,

Image 21: Sample ready for XRF – measurement

The Preservative levels been compared with retention values given in the AWPA standards U 1, section 6, commodity specification A and for MCA in the ESR 1721 (Table 8). Penetration values and retention have to be reported after every analyzing. Figure 5 showing charge report from Langdale Forest Products Company of Sweetwater, Tennessee. Samples can be retested 3 times if the batch fails retention test. The batch will be retreated after 3 failing tests (procedure of Langdale Forest Products Company).



Charge Report

Plant (02) Langdale Forest Products co,
555 South Main Street
Sweetwater, TN 37874
PH: 423-337-6105
Fax: 423-337-3517

Charge: 12721
Treatment: MCA AG
Date: 8/9/2016 7:13:56 AM
Preservative: MCA []
Retention Target: 0.06
Cylinder: 1 Void (19860)
Tank: 1
Operator: Nathan

Total Time: 00:39
Charge Out (min): 1,007.4
Charge Out Reason:
Board Ft: 21,536
Cubic Ft: 1,246
DVIn: 1,171
DVOut: 1,278
Treat By: Tally

Gallons Start: 17,376
Gallons Finish: 15,198
Gallons Used: 2,378
Penetration Sampled: 0
Penetration Failed: 0
Date Off DripPad:

Step	Time Min	Time Max	Time Act	Pressure Min	Pressure Max	Pressure Act	Injection Min	Injection Max	Injection Act	Retention Min	Retention Max	Retention Act	Flow Rate Min	Flow Rate Max	Flow Rate Act	Temp	Time Ramp	Time Start	Time End	Volume	Reason
Initial Vacuum		5	5		-16	-16			0.00			0.000			0.0000			07:13:56	07:18:58	17,521	Time
Fill		10	5		-16	-6			0.45			0.011			0.0000			07:18:59	07:24:02	6,474	Full
Raise Press		15	3		75	75			1.55			0.037			0.3170			07:24:03	07:27:12	5,111	PSI
Pressure	4	15	6	120	150	124		2.82	2.83			0.067			0.1773			07:27:13	07:32:55	3,516	Absorbtion
Press Relief		3	3		50	56			2.82			0.067			0.0000		4	07:32:56	07:35:57	3,519	Time
Empty	3	7	4			2			3.02			0.071			0.0000			07:35:58	07:40:01	13,814	Empty
Final Vacuum		30	30		-29	-27		2.10	1.96			0.044			0.0693			07:40:02	08:10:07	15,131	Time
Final Empty		5	2			-2			1.93			0.044			0.0000			08:10:08	08:11:47	15,176	Empty
Finish		1	1			-1			1.91			0.043			0.0000			08:11:48	08:12:50	15,198	Time

Chemical Usage (*** Active Units)

Type	Chemical	Solution Start	Solution Finish	Lbs / Gal Start	Lbs / Gal Finish	Lbs / Gal Final	Total Lbs Gauge	Total Lbs Adjusted	Retention Gauge	Retention Adjusted
Active	MCA	0.2710 %	0.2710 %	0.0227	0.0227	0.0227	53.88	53.88	0.0432	0.0432
	Totals:	0.2710 %	0.2710 %	0.0227	0.0227	0.0227	53.88	53.88	0.0432	0.0432
Additive	Mold AC	45.0000 PPM	45.0000 PPM	0.0004	0.0004	0.0004	0.89	0.89	0.0007	0.0007
	Mold 45	100.0000 PPM	100.0000 PPM	0.0008	0.0008	0.0008	1.99	1.99	0.0016	0.0016
	NaNi	0.0350 %	0.0333 %	0.0029	0.0028	0.0038	6.96	9.12	0.0056	0.0073

QC

Comp	Min	Assay	Inspection
Copper	0.0460	0.0000	0.0000
Totals	0.0460	0.0000	0.0000

Material Information

	ItemCode		Description	Pieces	Packs/Size	BF	CF	Std	Mill	Retreat	Customer	Moist %	Rem 1
1	896102100100	2 X 10	/10 FT #2 S4S - DIMENSION	1,200	15 @ 80	20,000	1,156	None			COMPANY STOC	0	None
2	896102120120	2 X 12	/12 FT #2 S4S - DIMENSION	64	1 @ 64	1,536	90	None			COMPANY STOC	0	None

S/N 4773 7:56AM 8/09/16 #4048
MODE:MP-S CT: 60
% CU = 0.2710

Charge Number: 12721

Page 1 of 1

Figure 5: Charge Report of MCA traded lumber of Langdale forest products

End Use	Minimum Actives Retention lb/ft³ (kg/m³)			
	CA-B	CA-C	µCA-B (MCA-B)	µCA-C (MCA-C)
Above ground – general use	0.10 (1.7)	0.06 (1.0)	0.06 (1.0)	0.05 (0.8)
Above ground – decking & specialties use				
- Species listed in Section 3.3 (primarily sapwood)	0.08 (1.4)	0.06 (1.0)	0.06 (1.0)	0.05 (0.8)
- Species listed in Section 3.3 (primarily heartwood)	0.21 (3.3)	0.15 (2.4)	0.15 (2.4)	0.14 (2.2)
Ground contact – general use	0.21 (3.3)	0.15 (2.4)	0.15 (2.4)	0.14 (2.2)
Ground contact – heavy duty	0.31 (5.0)	0.25 (4.0)	0.23 (3.7)	0.23 (3.7)
Ground contact – wood fountain systems	0.31 (5.0)	0.25 (4.0)	0.23 (3.7)	0.23 (3.7)
Ground contact – extreme duty	0.41 (6.6)	0.35 (5.7)	0.33 (5.3)	0.33 (5.3)

Table 8: Minimum preservative retention requirements (ICC_ES Report – ESR 1721)

Terms and explanations

Next chapters giving explanations about terms or methods used within this research.

XRF – Analyzers

There have been two different XRF – Analyzers been used in this research:

- Asoma Ametek 200 Benchtop Analyzer
- Oxford Benchtop XRF Analyzer – Lab-X 3500

These machines are widely used in industry or laboratories to analyze samples of wood-preservative-treated wood. They are both working with X-Ray-source detecting a wide range of elements. It´s possible to analyze concentrations down to parts per million and up to high percentage of samples being solid, liquid or powder. The Analyzer has to be adjusted for each material which is been tested.

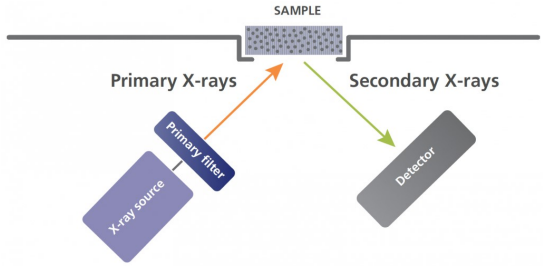


Figure 6: Function of X-Ray[5]

XRF – Analyzers made with two main components: The X – Ray source and the detector. The X – Rays, generated by X – Ray source, been directed to the samples and "reacting by generating secondary X –

[5] http://www.the-experts.com/x-ray-fluorescence-xrf-explained (12.02.2016)

Rays that are collected and processed by a detector"[4]. Those emitted X – Rays collected by the detector been processed in an analyzer which is giving the elements amount and its concentration in %.

CPS – Counts Per Second

The analyzers are calculating the amount of the tested element and printing out its concentration within the sample in %. Every generated X – Ray (secondary X – Rays) can also be counted. The amount of reflected X – Rays per second from a specific element can, shown as CPS (Counts per Second) can be compared and put in relation to each other.

Coefficient of determination

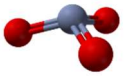
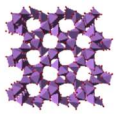
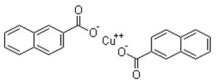
Coefficient of determination, stated R^2, is a quality measure in the statistics, which indicates how much of the variation (variance) in the data can be explained by a present regression model. The statistic measure R^2 is the fraction of the variation of the dependent variable y (or the variance of y, as given *Variation (y) = n * Var (y)),* by the linear regression, and therefore is between:

0 (or 0 %): no linear coherence

1 (or 100 %): perfect linear coherence

Wood Preservatives

Lumbers been treated with:

- Chromated Copper Arsenate – CCA Wood
  - Chromium trioxide CrO_3  6
  - Copper oxide CuO  7
  - Arsenic pentoxide As_2O_5  8
- Copper Naphthenate – treated wood  9
- Pentachlorophenol – treated wood  10

[6] https://en.wikipedia.org/wiki/Chromium_trioxide (12.02.2016)
[7] https://en.wikipedia.org/wiki/Copper%28II%29_oxide (12.02.2016)
[8] https://en.wikipedia.org/wiki/Arsenic_pentoxide (12.02.2016)
[9] http://www.chemblink.com/products/1338-02-9.htm (12.02.2016)
[10] https://pediaview.com/openpedia/Pentachlorophenol (12.02.2016)

Method

For the measurements, the cups have been filled around half size and measured with a replication of 5 times each cup size / wood preservative. This method has been used every time with a different preparation of samples to see the effects. Standards require oven-dried samples for Oxford XRF – Analyzer X 3500 (Image 23)and Asoma Ametek 200 XRF – Analyzer (Image 24). Samples also should be compressed for Asoma XRF – Analyzer. For comparison, samples have been measured with air – died material (with moisture content) and not compressed at the Asoma to gain an understanding about the reliability of measuring under different conditions and to understand how to possibly change the whole analyzing-process.

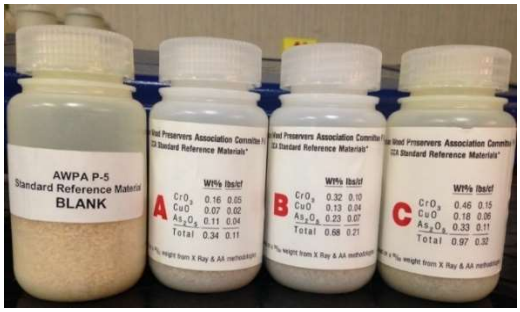


Image 22: CCA – standard reference materials, pic.: Stelzer R.

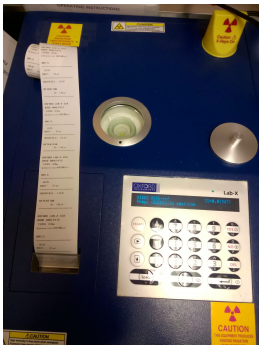


Image 23: Oxford XRF – Analyzer X 3500, pic.: Stelzer R.

Image 24: Asoma Ametek 200 XRF – Analyzer, pic.: Stelzer R.

Results

After collecting data from XRF – Measurements on Oxford X 3500 and Asoma Ametek 200 Benchtop Analyzers with different treated wood-powder samples with different preparations.

CCA – treated wood on Oxford X 3500

Following 3 Figures showing results for XRF – measurements on an Oxford X 3500 Analyzer. CCA – treated contains the elements Chromium, Copper and Arsenic, which have been measured separately. The samples have been oven dried (around 90° C / 175° F) for preparation. The following concentrations have been analyzed:

For Chromium CrO^3:

- 0,00 % / 0,16 % / 0,32 % / 0,46 % / 0,62 % / 0,86 % / 1,12 %

For Copper CuO:

- 0,00 % / 0,07 % / 0,13 % / 0,18 % / 0,24 % / 0,32 % / 0,41 %

For Arsenic As^2O^5:

- 0,00 % / 0,11 % / 0,23 % / 0,33 % / 0,43 % / 0,58 % / 0,77 %

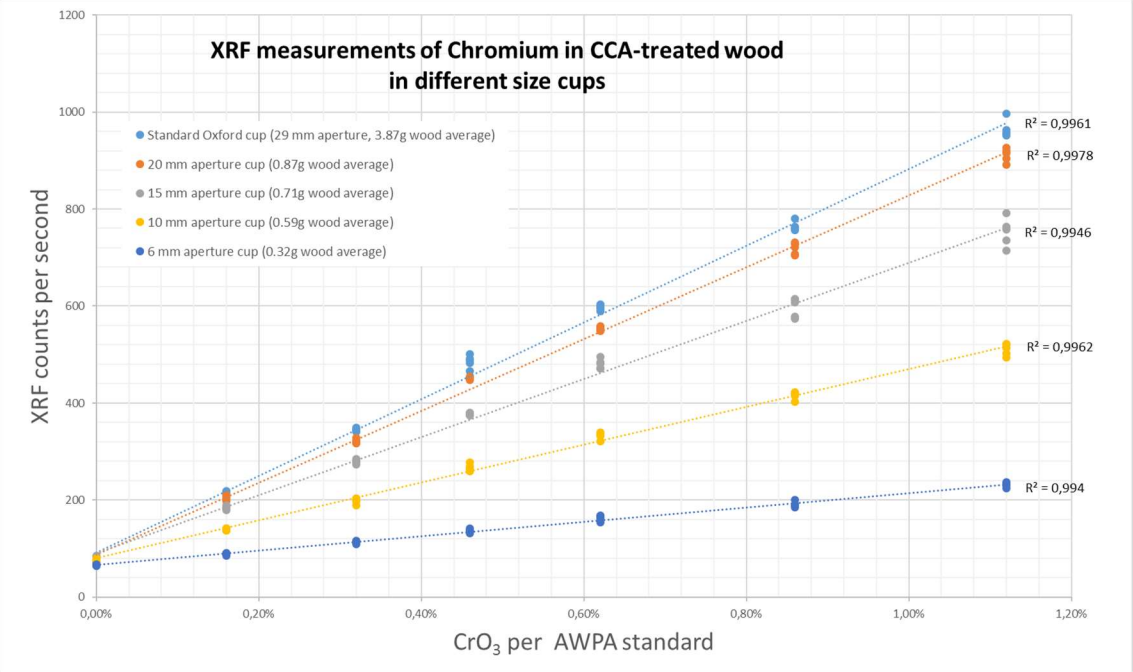


Figure 7: XRF – measurements of Chromium in CCA – treated – wood on Oxford XRF – Analyzer

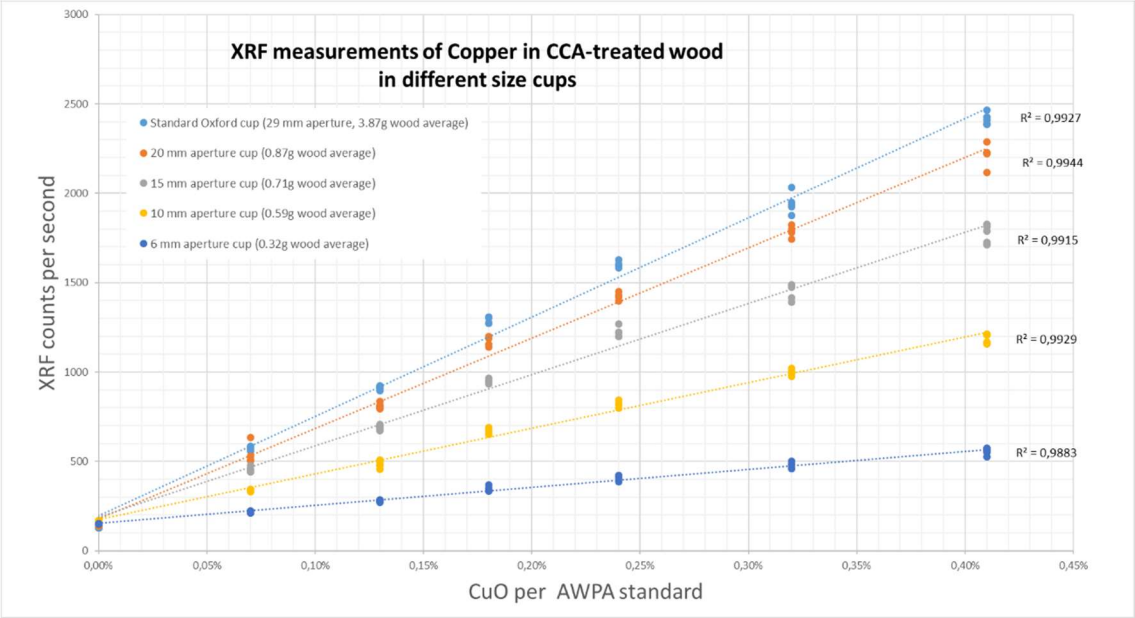


Figure 8 XRF – measurements of Copper in CCA – treated on Oxford XRF – Analyzer

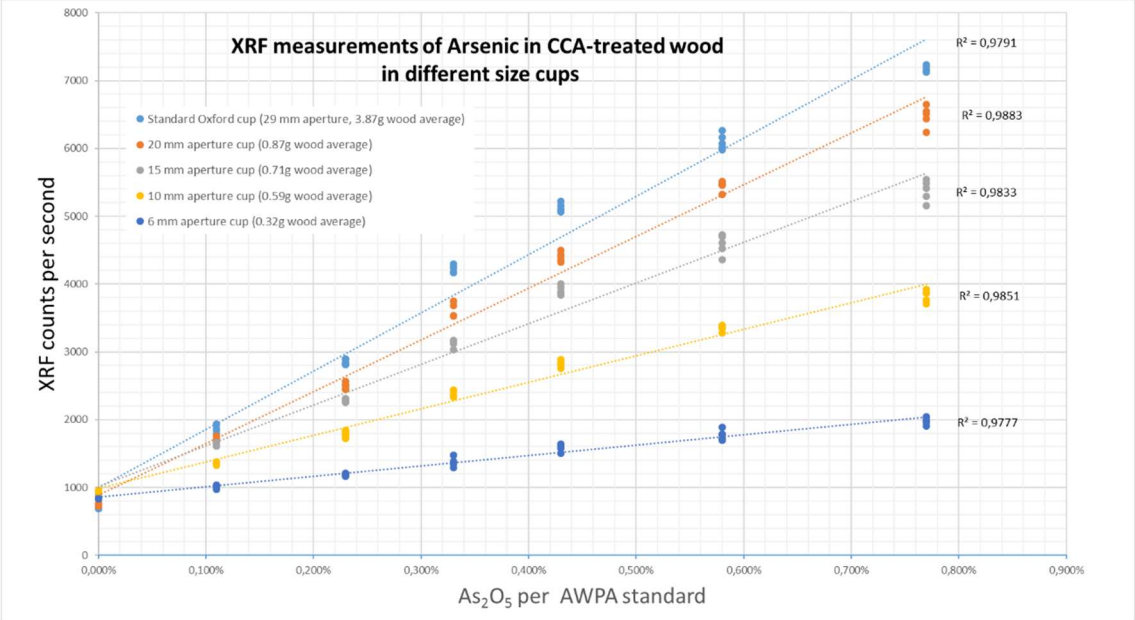


Figure 9: XRF – measurements of Chromium in CCA – treated on Oxford XRF – Analyzer

It can be determined, that all results have a reliability for coefficient of determination R^2 close to 1.0 (100 %) for each cup size and chemicals tested.

CCA – treated wood on Asoma

The usual standard with measuring CCA – treated wood on an Asoma is compressing the sample inside the cup with a compressing-tool with around 29 newtons as can be seen in Image 25.

Image 25: Tool for compressing samples

CCA – treated contains the elements Chromium, Copper and Arsenic, which have been measured separately. The next three figures showing the results with effect of samples being not compressed but oven-dried. The following concentrations have been analyzed:

For Chromium CrO^3:

- 0.00 % / 0.16 % / 0.32 % / 0.62 % / 1.12 %
  For Copper CuO:
- 0.00 % / 0.07 % / 0.13 % / 0.24 % / 0.41 %
  For Arsenic As^2O^5:
- 0.00 % / 0.11 % / 0.23 % / 0.43 % / 0.77 %

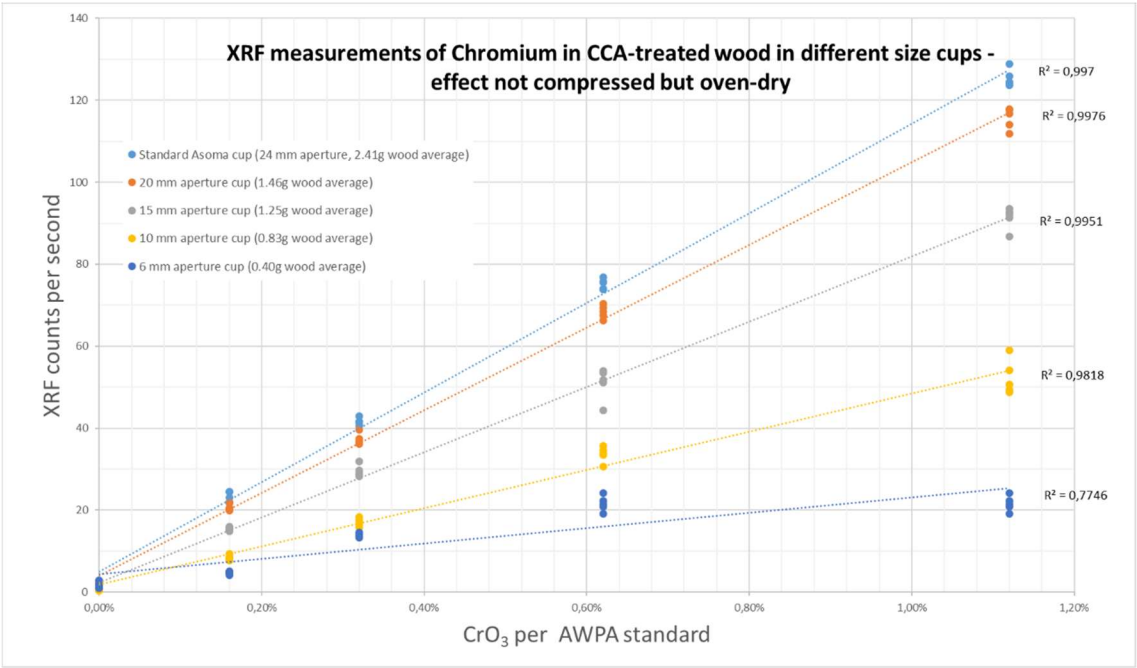


Figure 10: XRF – measurements of Chromium in CCA – treated wood – effect not compressed but oven dry

The results for coefficient of determination R^2 for “Standard Asoma cup”, “20 mm”, “15 mm” and “10 mm” cup size in Figure 10 showing a high reliability for all the measurements. The smallest cup size with 6mm opening shows a lower R^2 with 0.7746.

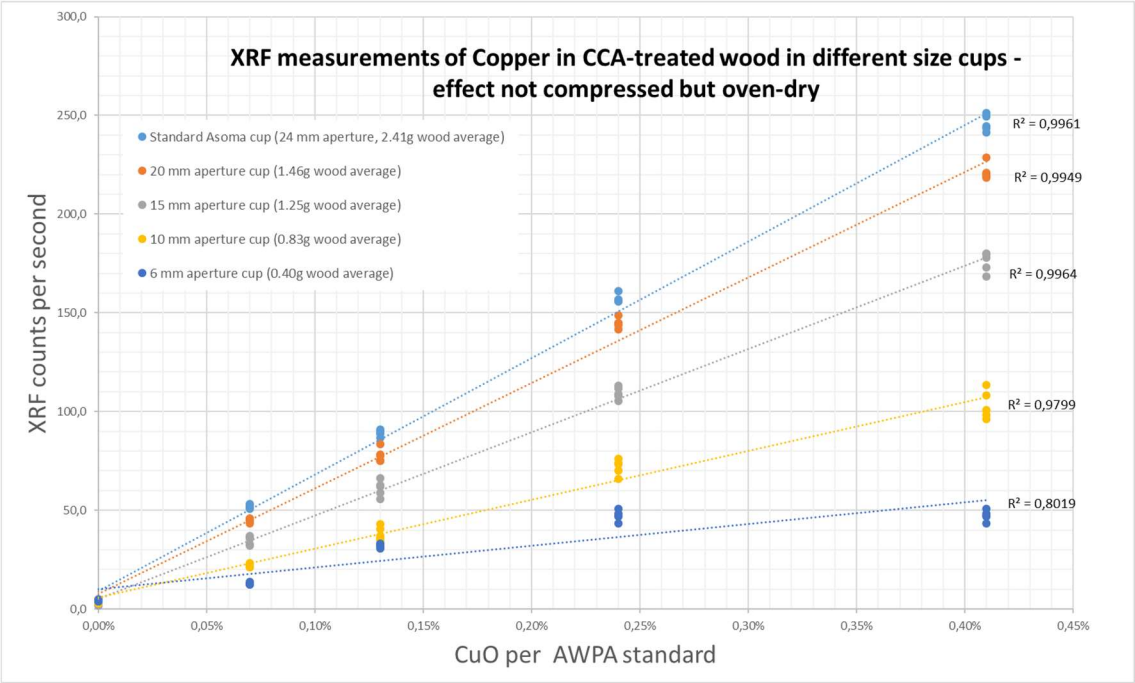


Figure 11: XRF – measurements of Copper in CCA – treated wood – effect not compressed but oven dry

In Figure 11 Standard Asoma cup to 10 mm cup size showing again high reliability for coefficient of determination R^2 close to 1.0 (100 %). Results for aperture cup = 6 mm is almost 10 % lower with R^2 = 0.8019.

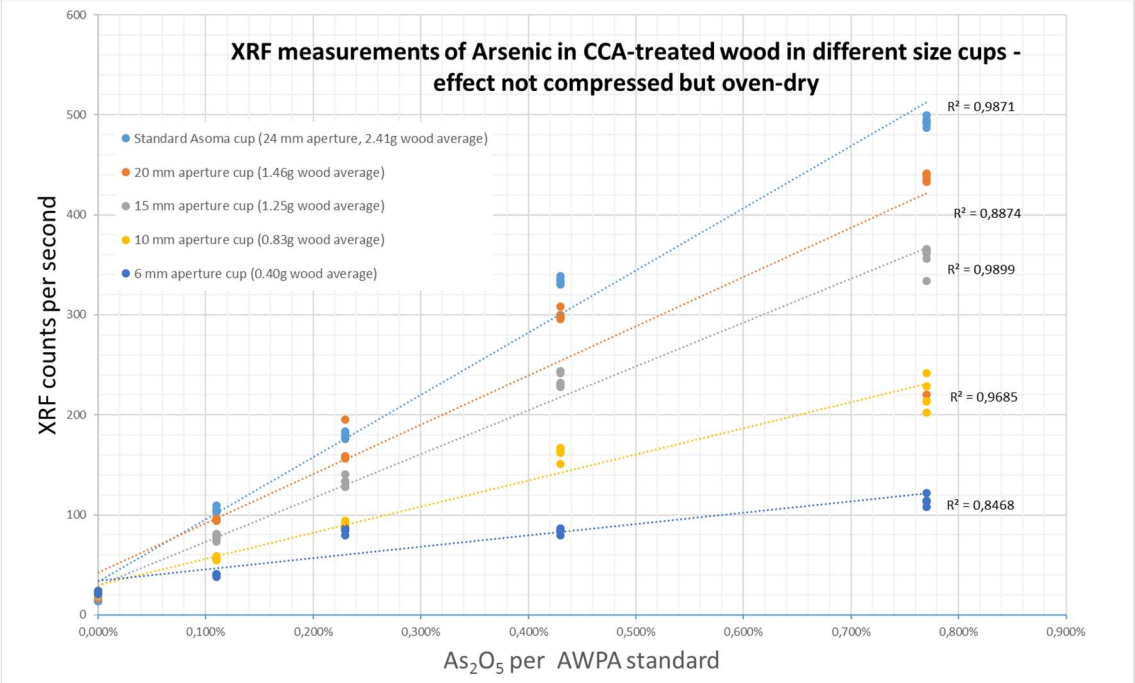


Figure 12: XRF – measurements of Arsenic in CCA – treated wood – effect not compressed but oven dry

Figure 12 for Arsenic is a little more unregular with 20 mm and 6 mm showing lower results with coefficient of determination R^2 = [6 mm = 0.8468; 20 mm = 0.8874], while all others have reliability close to R^2 = 1.0.

Effect of compression and moisture content on Asoma Analyzer

The next three figures showing measurements of CCA – treated wood with the effect of samples being compressed and air – dried on an Asoma Ametek Analyzer. It was to find out how much influence is to see for the effect of compressing and oven – dry samples in comparison to samples being not compressing and air – dried. The hypothesis was to see a higher difference. In Figure 13, Figure 14 and Figure 15 results for all three preparations of samples show high reliability for each setting of samples with minor differences in the coefficient of determination R^2.

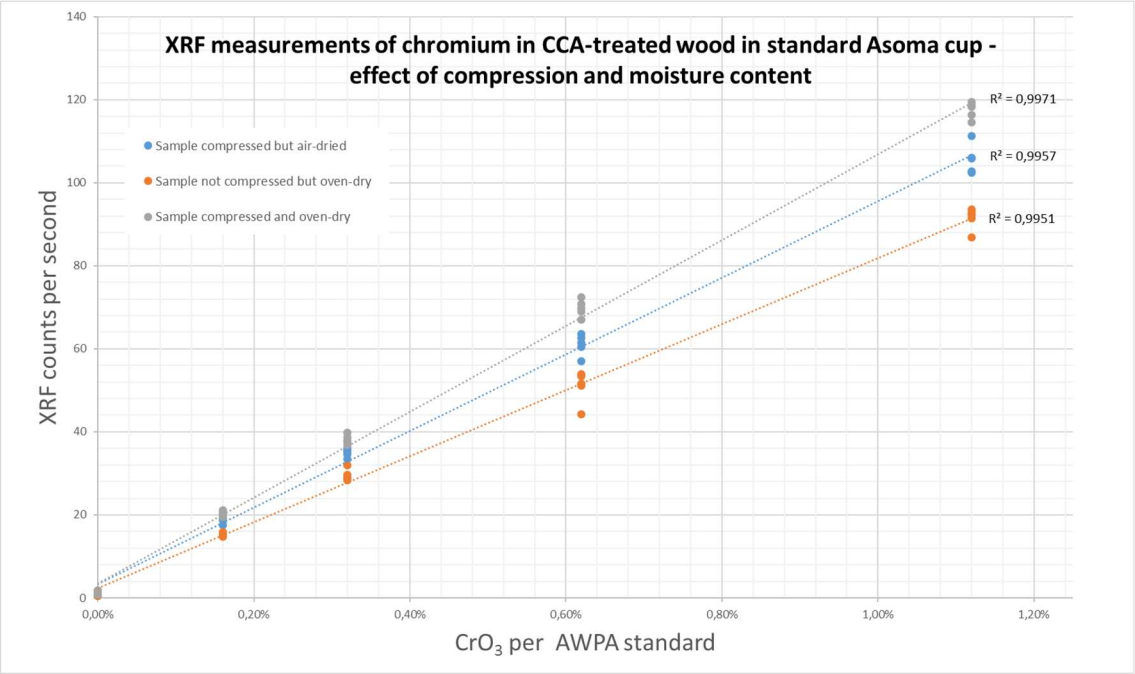


Figure 13: XRF – measurements of Chromium in CCA – treated wood – effect compression and air – dried

With all numbers being close to 1.0 for R^2, results for Chromium and Copper show high reliability.

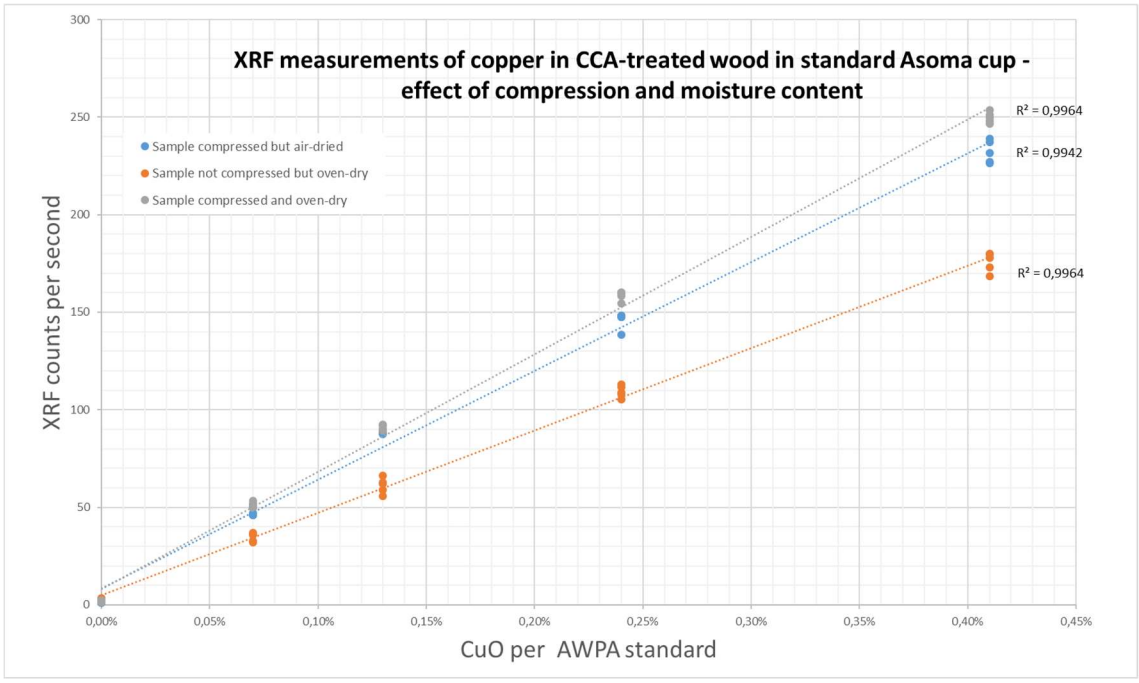


Figure 14: XRF – measurements of Copper in CCA – treated wood – effect compression and air – dried

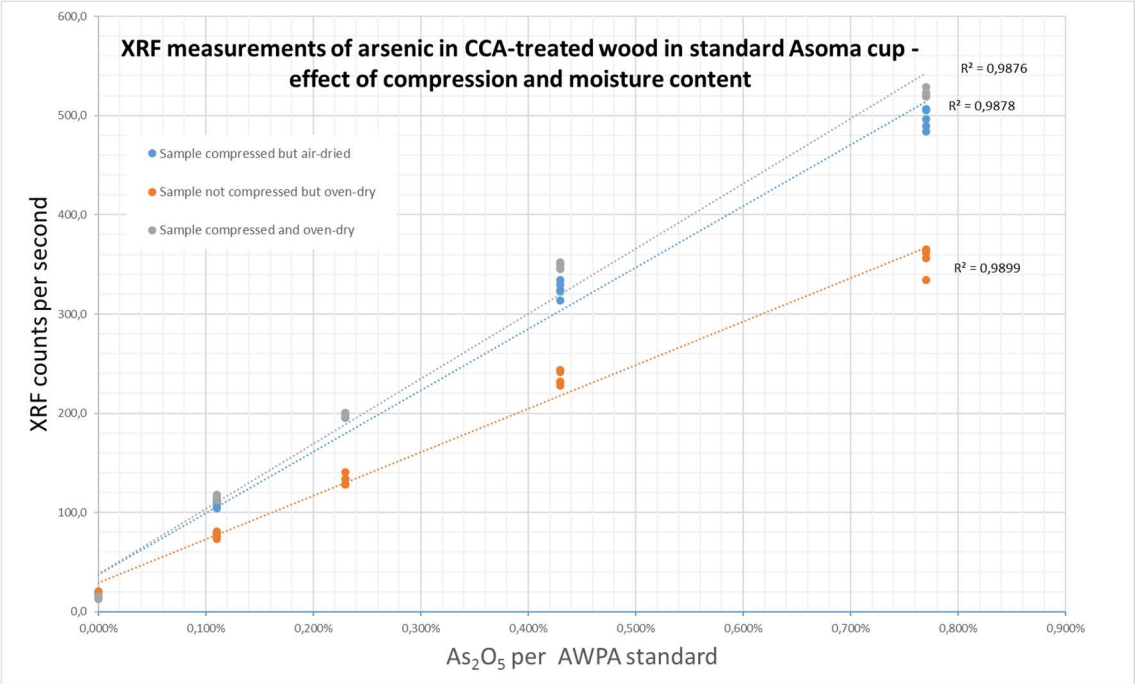


Figure 15: XRF – measurements of Arsenic in CCA – treated wood – effect compression and air dried

Arsenic shows a minor variance to Chromium and Copper, still with high reliability for R^2 with 0.98 for all three preparations of samples.

Pentachlorophenol on Oxford X 3500

Next two figures showing XRF – measurements of Chlorine in Pentachlorophenol-treated wood on an Oxford X 3500 Analyzer. The samples have been analyzed air – dried and oven – dried.
The following concentrations have been analyzed:

- 0.05 % / 0.633 % / 0.98 1% / 1.18 % / 1.40 % / 1.78 %

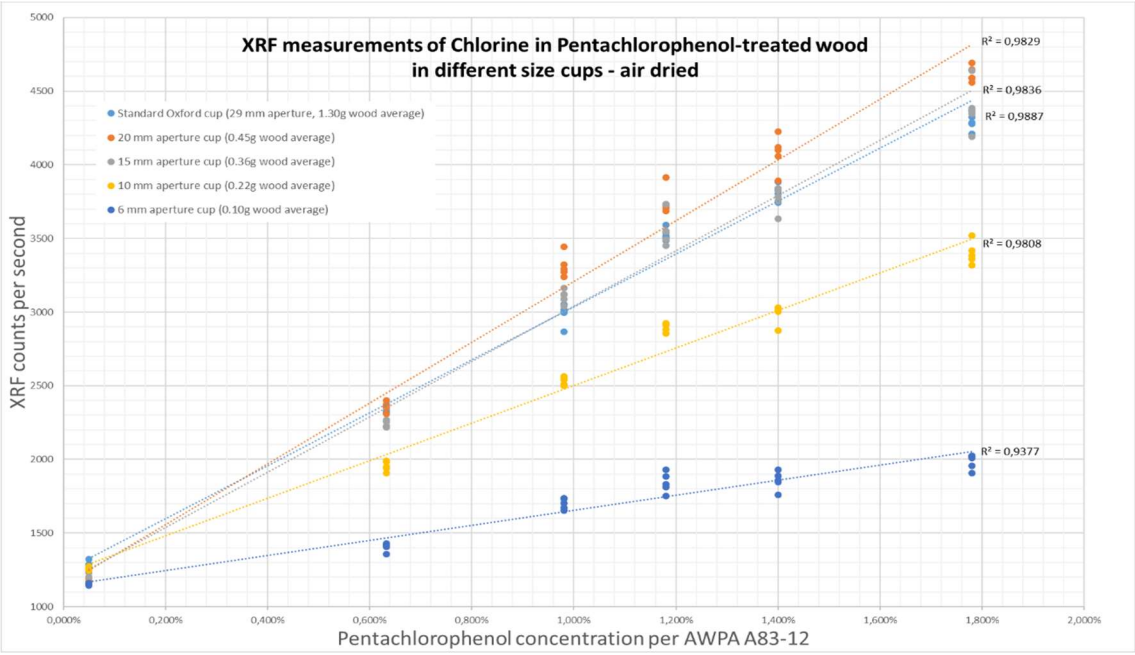


Figure 16: XRF – measurements of Chlorine in Pentachlorophenol – treated wood – samples air – dried

Results for air dried samples showing reliable data with coefficient of determination R^2 between 0.9808 and 0.9887 for each cup size. Smallest cup with a diameter of 6 mm showing a quite smaller result with $R^2 = 0.9377$.

Figure 17: XRF – measurements of Chlorine in Pentachlorophenol – treated wood – samples oven – dry

Results for samples being oven – dried, which goes by the standard shows a higher deviation. The standard cup size shows results with high reliability with coefficient of determination $R^2 = 0.9547$. All other smaller cup sizes show lower reliability: $R^2 = 0.8495 – 0.8729$. Also, the propensity for the graphs of smaller cup sizes in comparison with standard cup size show deviations in the results. There is a difference for Pentachlorophenol-treated wood to be measured air – dried or oven – dried in different cup sizes.

Copper naphthenate on Oxford X 3500

Another wood preservative used is Copper naphthenate. Analyzed on an Oxford X 3500 Analyzer with samples prepared air – dried and oven – dried.
The following concentrations have been analyzed:

- 0.059 % / 0.139 % / 0.277 % / 0.196 % / 0.277 % / 0.362 % / 0.516 %

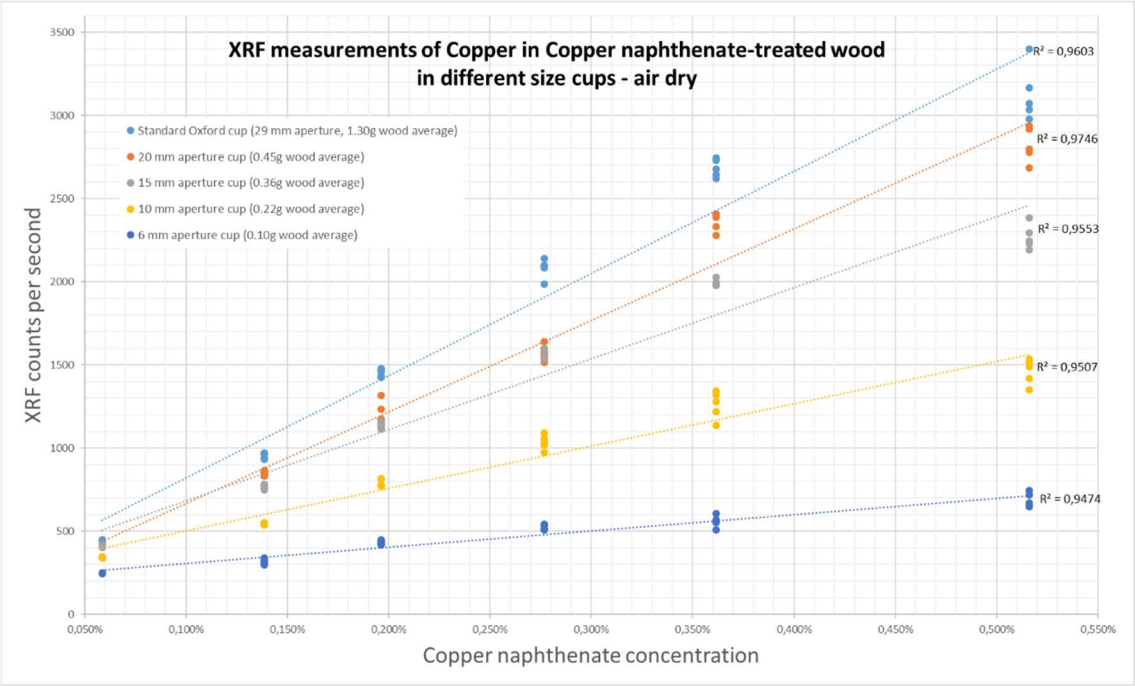


Figure 18: XRF – measurements of Copper in Copper naphthenate – treated wood – samples air – dry

Samples been tested in “20 mm aperture cup” show highest value for coefficient of determination R^2 = 0.9746.

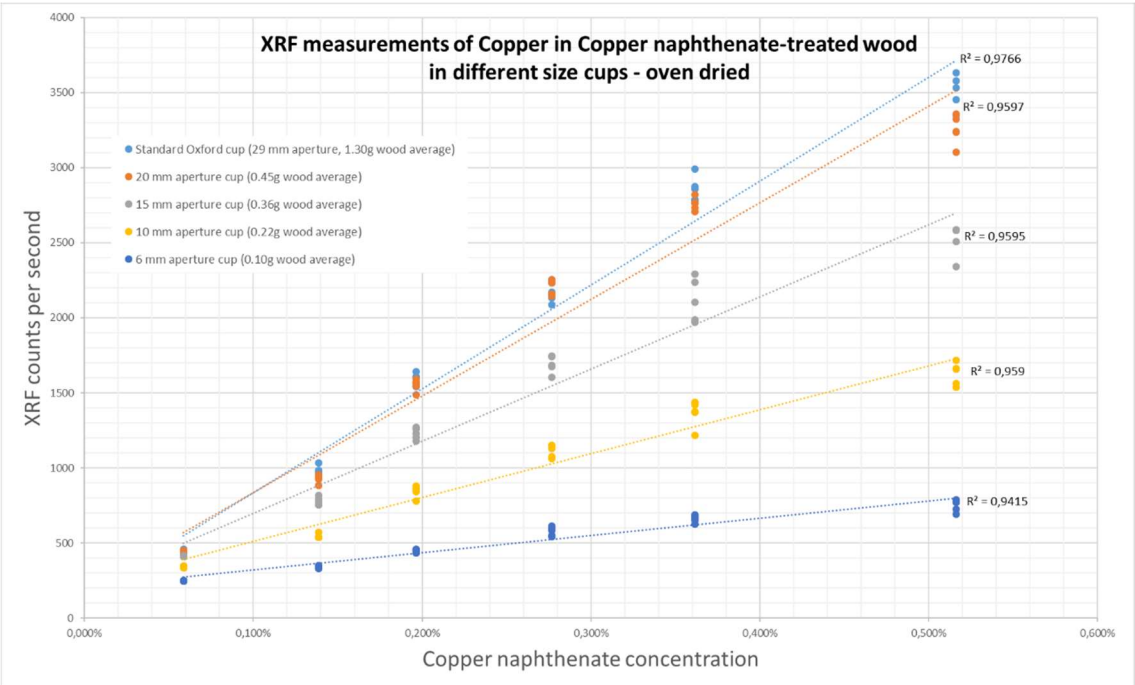


Figure 19: XRF – measurements of Copper in Copper naphthenate – treated wood – samples oven – dried

Conclusion

The measurements prove the possibility for reduced volume wood sampling method to gain reliable results. It is to be required to recalibrate Oxford X 3500 and Asoma Ametek Analyzers for the use of smaller volume cups. The permitted tolerance for 85 % cores to pass test is too low to assure a safe product. In terms of increasing product quality, the use of reduced wood samplings to enable uncertainty estimation in measurements for treated wood it is to be suggested to change standards for XRF-Analyzing. While breaking standard core set of 20 into 4 to 5 cores per small volume cup resulting in more precise results helping to increase product quality it also infers to have more steps for testing wood with a higher effort to gain results. But the effect of getting greater and more precise results helps to prevent low treated-lumber to get onto market and helps to increase permitted tolerance within standards.

It could also have been shown that it is not obligatory to have oven – dried samples.

CCA – treated wood works on an Oxford unit for all cup sizes tested and would require recalibration for each cup size. CCA – treated wood on an Asoma Ametek isotope unit works except for smallest cup tested. Would require recalibration for each cup size.

Pentachlorophenol – treated wood on an Oxford unit works for all cup sizes tested. Would require recalibration for each cup size.

The effect of air – dried versus oven – dried for Cupper naphthenate – treated wood on an Oxford X 3500 shows drying makes a difference (~ 5 %) but could be calibrated either way.

Effect of air-dried versus oven – dried and sample compression CCA – treated wood on ASOMA Ametek shows compression (~ 30 %) and drying (~5 – 10 %) both make a difference but could either be omitted if calibrated under those conditions.

The effect of compressing samples for Asoma Ametek Analyzer can also be suggested to be left out in sample testing as results for not compressed and air – dried samples showed reliable data.

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