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# Use of small volume cups in XRF analysis of treated wood retention

René Stelzer[1], Adam Taylor[2], Patricia Lebow[3]

[1] MSc. Candidate, University of Applied Sciences, Kuchl Campus, Salzburg, Austria.
rstelzer.htw-m2015@fh-salzburg.ac.at

[2] Professor, University of Tennessee, Knoxville TN, USA. AdamTaylor@utk.edu

[3] Mathematical Statistician, US Forest Products Laboratory, Madison WI, USA. plebow@fs.fed.us

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**IRG SECRETARIAT**
**Box 5609**
**SE-114 86 Stockholm**
**Sweden**
**www.irg-wp.com**

# Use of small volume cups in XRF analysis of treated wood retention

René Stelzer[1], Adam Taylor[2], Patricia Lebow[3]

[1] MSc. Candidate, University of Applied Sciences/Kuchl Campus, Salzburg, Austria. rstelzer.htw-m2015@fh-salzburg.ac.at

[2] Professor, University of Tennessee, Knoxville TN, USA. AdamTaylor@utk.edu

[3] Research Mathematical Statistician, US Forest Products Laboratory, Madison WI, USA. plebow@fs.fed.us

## ABSTRACT

Efforts are underway in the United States to improve the conformance of commercially-treated wood with the applicable retention standards. As part of an effort to devise a practical method for on-site assessment of within-charge retention variation, we investigated whether small-volume x-ray florescence (XRF) sample cups could be used with treated wood. A range of cup sizes, preservative types, retention levels and other variables were considered. In general, small volume cups appear to be suitable for use with common industrial XRF machinery. This finding is being applied to a proposed modification to the American Wood Protection Association (AWPA) standard.

**Keywords:** retention, variation, sampling

## 1. INTRODUCTION

There is a concern in the United States that some charges of preservative treated lumber are failing retention specifications when inspected by third party agencies, despite initially having passed evaluation at the treatment facility (AWPA 2015a). One possible explanation for this discrepancy between mill and inspection agency retention values is the inherent variability in retention within and between the many pieces of lumber within a charge. Wood itself is inherently variable in its material properties and characteristics, such as specific gravity, pore size distribution, and others, as well the treatment process can induce effects on preservative uptake (Taylor and Morrell, 2014). Retention values above and below an average value are a reasonable expectation due to chance when sampling repeatedly from the same batch of treated wood. If the average value is close to the standard's specification, then 'failures' detected by the third party agency are likewise a reasonable probability.

The standard methods for treated wood preservative retention assessment in the United States involve extracting a number of cores (usually 20) from the assay zone of various pieces of lumber within a charge (see for example T1 standards (AWPA 2016)). The cores are analyzed individually for preservative penetration (visually) but are combined for retention analysis. The retention measurement is normally done using x-ray florescence (XRF) to quantify certain elements within the treated wood. This provides a single, average value for the cores collected but does not provide any information about the variability among the individual cores or within the charge that could help to establish the charge's likelihood of passing inspection.

A recent paper proposed a statistical method to generate within charge variability estimates, using the same 20 cores, by sorting them into a few groups of subsamples that are analyzed separately (e.g. 5 groups of 4 cores each) (Lebow, et al. 2015). The data generated from these multiple, separate XRF values can be averaged to provide a single average value as is currently

reported, and in addition it provides intervals that contain a future sample's mean retention value with certain levels of confidence.

The practice of combining the cores in to a single sample exists in order to provide enough sample for analysis. So, separating the 20-core set into groups of fewer cores may not provide enough material for a reliable XRF analysis. The purpose of this study was to assess whether smaller-volume, commercially-available sample cups could be used successfully for XRF analysis of treated wood.

## 2. METHODS

Treated wood standards were analyzed on commercial XRF units that are used routinely to analyze treated wood samples, without changing any of the instrument parameters. Counts per second were recorded. Variables included:

- *XRF units* included Asoma Ametek 200 Benchtop Analyzer and Oxford Benchtop XRF - Analyzer – Lab – X 3500
- *Cup sizes* were measured by their apertures and included the 29mm and 24mm of the cups supplied with the Oxford and ASOMA units, respectively. In addition, 20mm, 15mm, 10mm and 6mm aperture cups (Chemplex Industries) that fit in the sample holders for the Oxford and Asoma units were tested (Figure 1).
- *Preservative standards* included CCA and Pentachlorophenol (supplied by the American Wood Protection Association) and copper naphthenate (supplied by Nisus Corporation). A range of retentions relevant to each preservative was tested. Copper ethanolamine-treated samples were also used for an analysis of the effect of grind size.

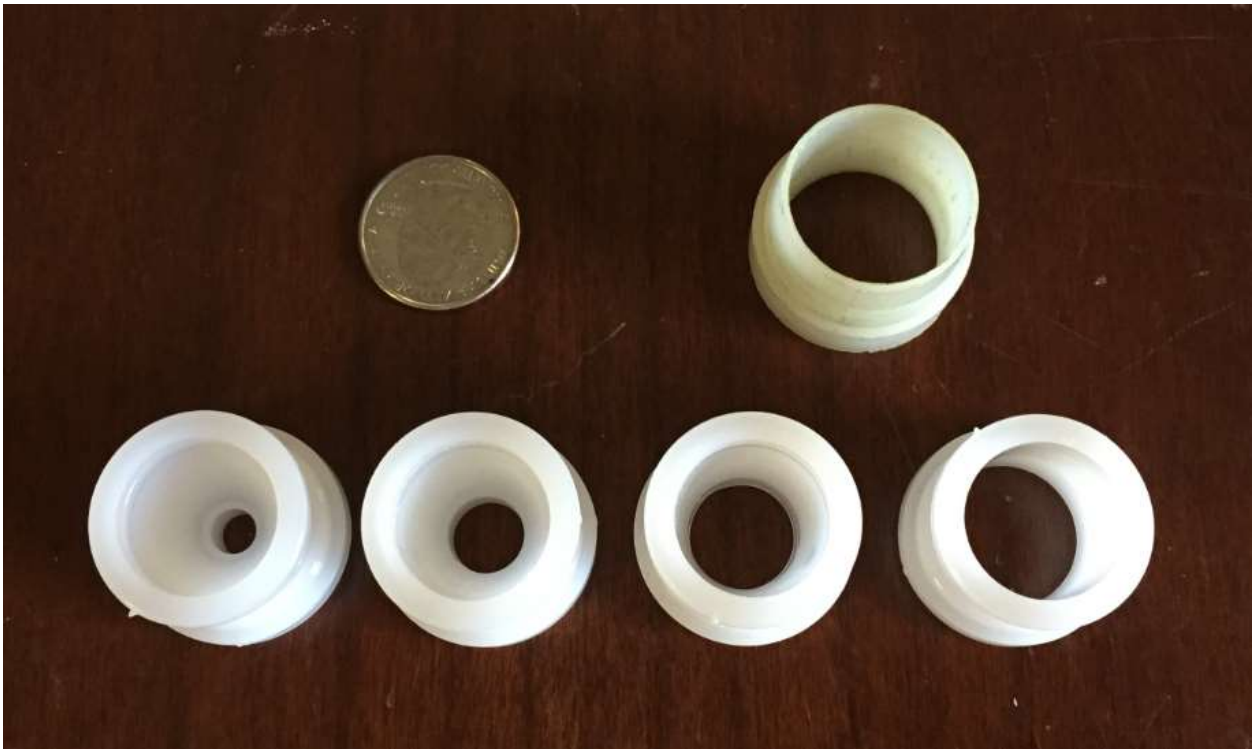

*Figure 1. Alternative sample cups for XRF analysis. From left on bottom row: 6mm, 10mm, 15mm and 20mm aperture. Top row shows American quarter and standard (24mm) Asoma cup.*

In addition, the effects of sample compression (as recommended for the ASOMA unit), moisture content and grind size were evaluated separately.

Variable combinations were analyzed separately five times at each standard retention level, using a dump and re-pour method. The cups were filled roughly half-full with the treated wood powder. The data were modelled using simple linear regression (without forcing through the origin) and the suitability of the model was evaluated using the coefficient of determination ($R^2$), while also visually checking for linearity, homogeneity of residuals, and normality. There appear to be some minor deviations from linearity in the residuals, but for comparison purposes of these assessments, the patterns appear common across cup sizes. Also, there appear to be some increases in the variance of residuals for the larger cup sizes as concentration increases, but improvements to modeling to accommodate this were not attempted (e.g., weighted least squares). Note that the width of prediction intervals based on classical calibrations (i.e., inverse predictions) for a fixed set of standard values and sample size are a function of the standard error of the regression divided by the slope estimate (which can be shown to be a function of $R^2$). See Parker, et al. (2010) or Kutner et al. (2004) for formulas for the intervals.

## 3. RESULTS AND DISCUSSION

Smaller aperture cups, which provide less surface area of sample exposure, reduced XRF signal response; however, the (reduced) responses were consistently and linearly related to the samples' preservative retentions. Figure 2 shows typical results.

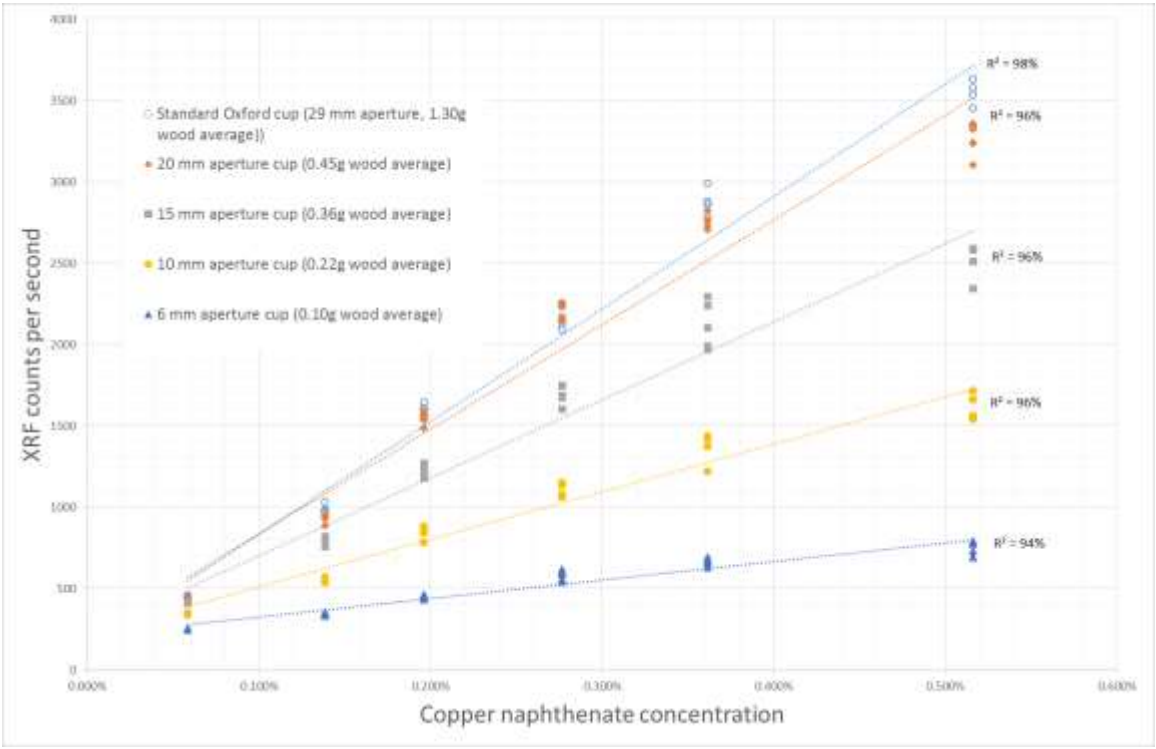


*Figure 2 Copper naphthenate standards tested in various cup sizes on an Oxford XRF unit. Associated calibrations are given by the linear regression lines.*

The various cup sizes provided excellent results in almost all cases (Table 1), as judged by $R^2$ values mostly over 95%. This suggests that smaller aperture cups, loaded with smaller wood volumes, could be used for determining treated wood retentions, when fewer cores per analysis

were desired. Because the cup sizes (and other variables) affect the XRF signals (fewer counts per second – CPS), calibration of the machine would be required for each cup size used.

*Table 1. Summary of XRF trials using different cup sizes with various preservatives and equipment and their associated calibration regression coefficient of determination.*

| Preservative | XRF machine | Standards' retention levels [%] | Cup aperture [mm] | Coefficient of determination [$R^2$ - %] |
|---|---|---|---|---|
| CCA | Asoma | Total: 0, 0.34, 0.68, 0.97, 1.29 | 24 (standard) | 96 |
| | | | 20 | 96 |
| | | | 15 | 95 |
| | | | 10 | 96 |
| | | | 6 | 96 |
| CCA | Oxford | Total: 0, 0.34, 0.68, 0.97, 1.29, 1.76, 2.30 | 29 (standard) | 98 |
| | | | 20 | 99 |
| | | | 15 | 99 |
| | | | 10 | 99 |
| | | | 6 | 98 |
| Pentachlorophenol (samples equilibrated to lab conditions, not oven dried) | Oxford | Chlorine: 0.050, 0.633, 0.981, 1.18, 1.40, 1.78 | 29 (standard) | 98 |
| | | | 20 | 98 |
| | | | 15 | 99 |
| | | | 10 | 98 |
| | | | 6 | 94 |
| Copper Naphthenate | Oxford | Copper: 0.059, 0.139, 0.196, 0.277, 0.362, 0.516 | 29 (standard) | 98 |
| | | | 20 | 96 |
| | | | 15 | 96 |
| | | | 10 | 96 |
| | | | 6 | 94 |

*3.1 Influence of grind size*. Standard practice is to grind the sample cores to pass a 20 mesh screen; however, some operators use a coffee grinder or other screen sizes, and prior to 2016 AWPA Standard A9 specified a 30 mesh screen (AWPA, 2015b). A trial was conducted using the Oxford machine, the standard-sized cup, and wood samples that were ground either in a coffee grinder (30 seconds) or with a Wiley mill to pass a 20 or 30 mesh screen. The preservative treatment in this trial was a copper-ethanolamine preservative that is commonly used for treatment of dimension lumber. The coffee grinder samples were slightly coarser (not measured) and this reduced the XRF signal slightly but in all three cases, the coefficient of determination was high (>98%; Figure 3).

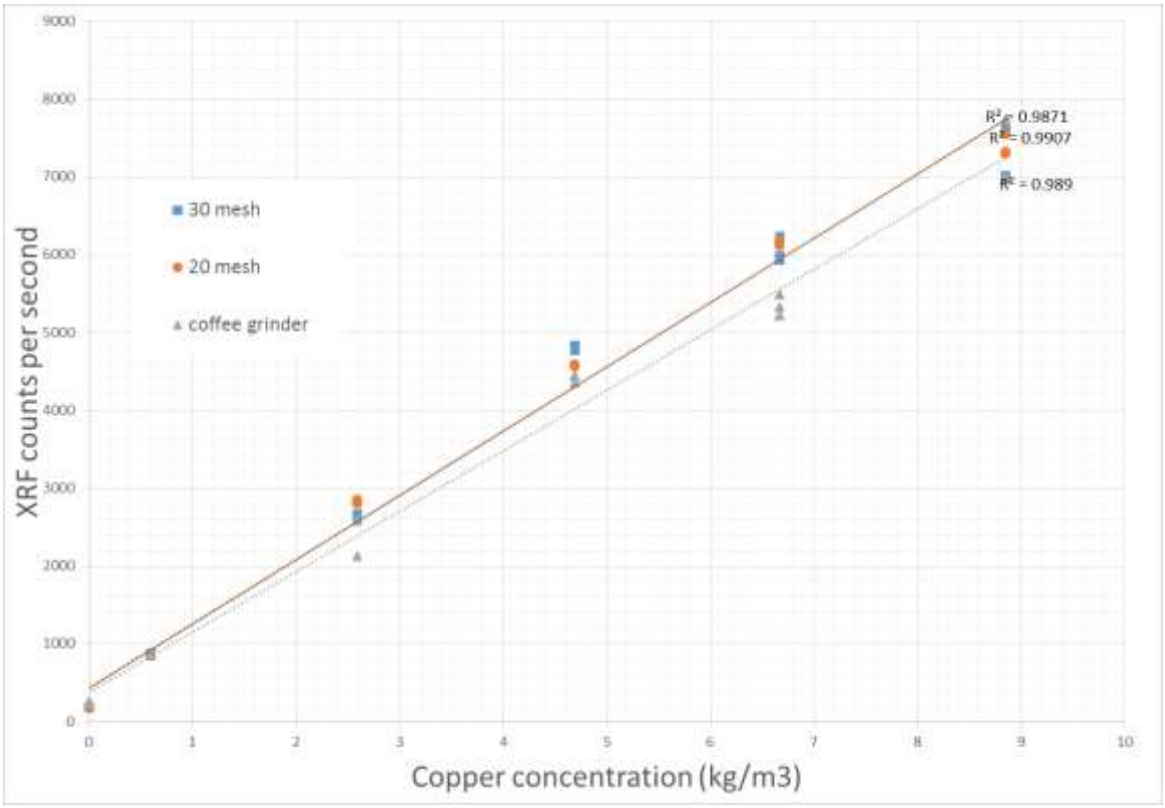


*Figure 3. XRF measurements of copper in copper ethanolamine-treated wood ground to various particle sizes and their associated linear regressions.*

*3.2 Influence of moisture content*. Standard practice is to oven dry the core samples prior to XRF analysis; however, some operators use a microwave oven for this purpose. Previous research indicates good agreement in XRF analysis between microwaved and conventionally dried wood (Gallacher, et al., 1995), but the true moisture content of the cores dried this way is uncertain. A trial was conducted using the Oxford machine, the standard-sized cup, and copper naphthenate-treated wood samples that had been conditioned over saturated salt solutions that provided relative humidity conditions of 75%, 85% and 95%. Oven-dry samples (equilibrated in an oven set to 103 degrees Celsius) and samples equilibrated to ambient lab conditions were also tested. Increasing moisture content in the samples reduced the XRF signal but, for all the sample sets, the coefficient of determination was high (>96%; Figure 4).

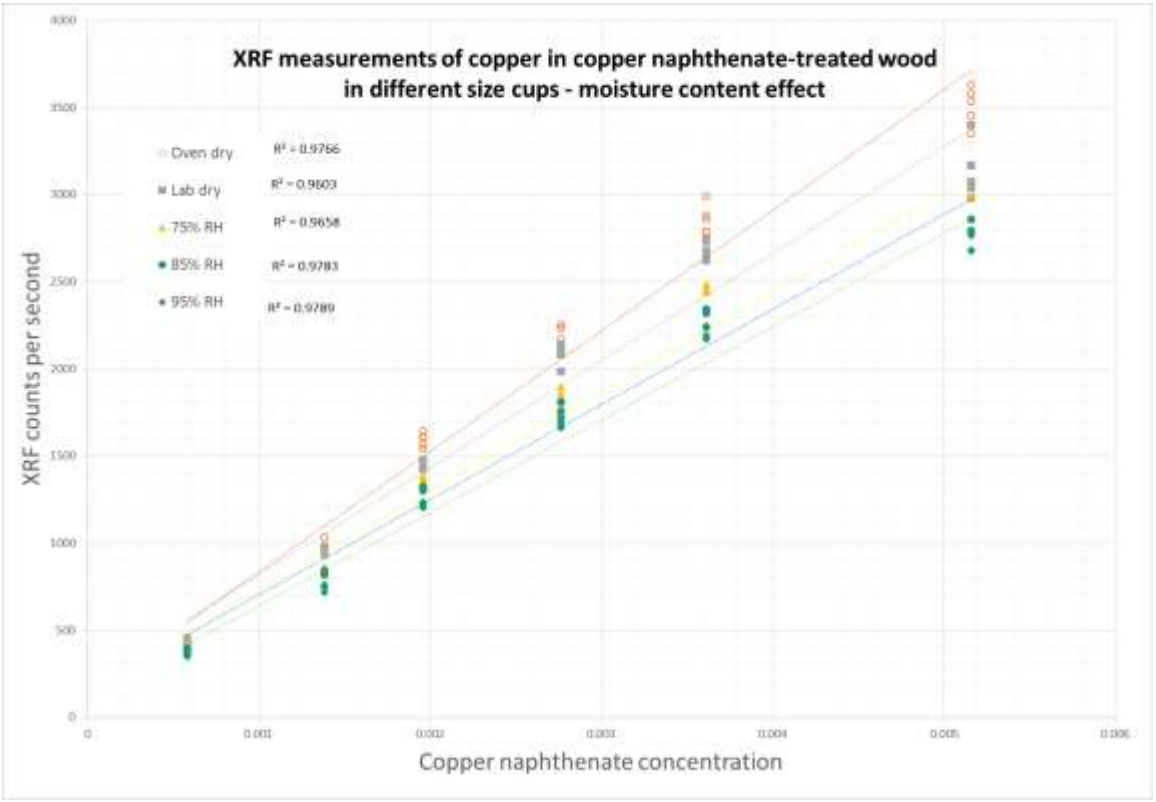


*Figure 4. XRF measurements of copper in copper naphthenate-treated wood for different drying conditions and sample moisture content levels. Their associated calibrations are given by the linear regression lines.*

*3.3 Effect of compression.* The Asoma XRF unit used in this study requires that the wood flour samples be compressed in the cup prior to analysis; however, some operators fail to follow this recommendation. As part of the CCA analysis using the Asoma equipment, samples that were not compressed were also analyzed and compared with those that had been compressed as recommended (to 150 psi or 1 MPa) (standard 24 mm aperture cup only). Compression did affect (increased) the XRF response but even uncompressed samples provided a linear XRF response over the range of retention tested (Figure 5).

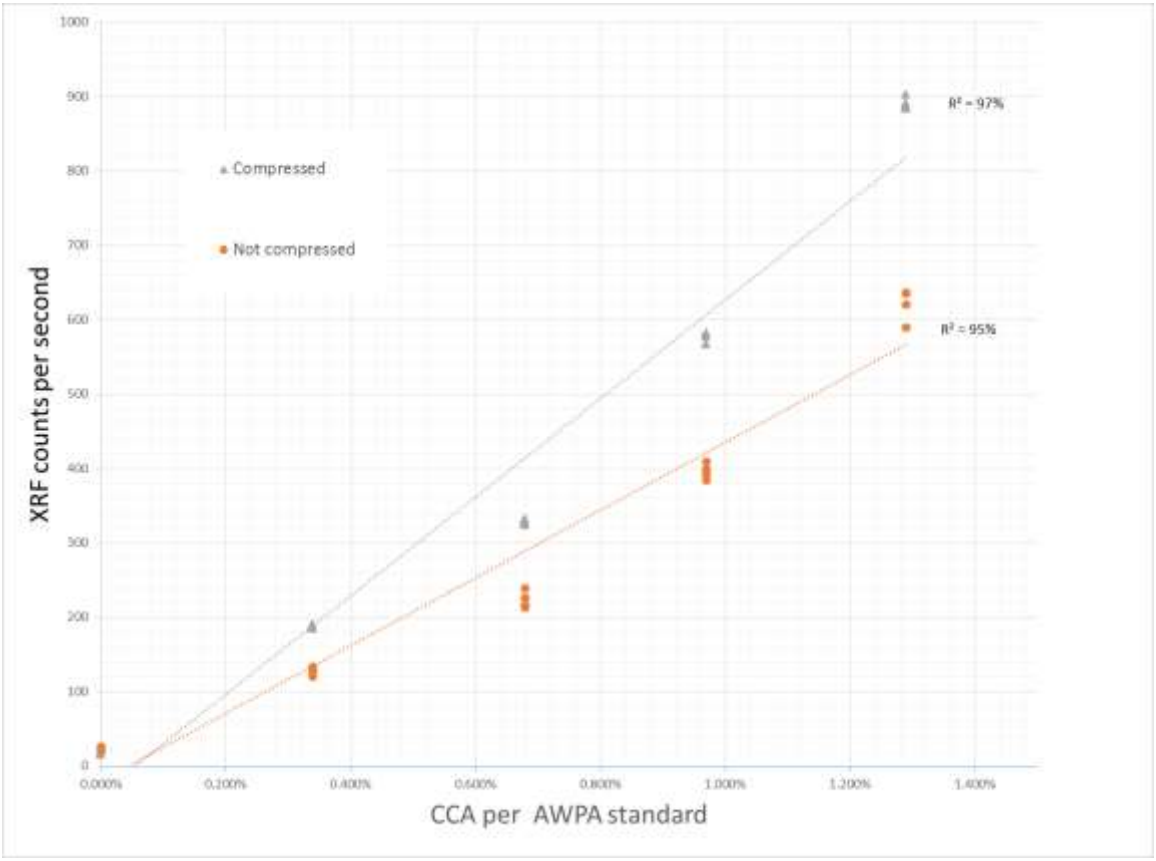


*Figure 5. Effect of sample compression on XRF response - ASOMA unit. The associated calibrations are given by the linear regression lines.*

*3.4 Standards and Practice.* Other potential variables exist that were not examined here, including other preservative systems, wood species and XRF equipment. Likely these variables will affect the results; this reinforces the need to develop separate calibrations for each set of variables, and to control those variables consistently with the conditions of the calibration when analyzing unknowns. Currently the AWPA standard describing XRF analysis of treated wood (AWPA A9-16) does not specify a cup size, or criteria for the successful calibration of XRF equipment. To provide more direction, the following draft proposal for an amendment to this standard has been prepared and will be submitted to AWPA:

> *"Sample cups with small apertures are commercially available and can be used to enable the analysis of smaller wood volumes if desired. If cup sizes used deviates from those supplied as original equipment of the XRF manufacturer, specific calibrations with reference wood materials of known preservative concentration will be required for each cup size used. Other variables that can affect the signal include moisture content of the wood (see 8.1.1.3), the mass of wood placed in the cup, sample compression, grind size and preservative mixture; calibrations and analyses of unknown sample should be conducted under consistent conditions for these variables. Calibrations should include the use of reference materials with at least five different retention levels, with at least one above and one below the expected range of values but not more than 50% above or below highest or lowest expected value, respectively. Each reference material should be analyzed a minimum of three times, using a 'dump and re-pour' method to incorporate within-reference variability. A linear calibration based on the individual measurements should have a coefficient of determination ($R^2$) of 95%*

*or more; if this is not achieved, recalibration using a narrower range and/or altering one or more of the variables listed above may improve performance.*

## 4. CONCLUSION

These data demonstrate that cup size and other variables affect the signal from XRF machinery. Thus, variables such as cup aperture, particle size, moisture content and sample compression should all be controlled and consistent for calibration and analysis of unknowns.

The potential for accurate and precise results from small-aperture cups shown here suggests that the method for measuring within-charge variation described by Lebow et al. (2015) could be applied with minimal extra work (no additional cores required).

## 5. ACKNOWLEDGEMENTS

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