X-Ray Fluorescence for the Analysis of DCOI in the Industrial Market

Ryan L. Sturdivant
Viance LLC
Charlotte, NC
Vicki Luckie
Hitachi High-Tech Analytical Science America, Inc.
Westford, MA
Robert P. Bartek
Applied Rigaku Technologies, Inc.
Austin, TX

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ABSTRACT

X-Ray Fluorescence (XRF) has been used in the wood treating industry for decades as a simple, quick, non-destructive way to measure treating actives in treated wood and treating solutions. Current XRF technologies on the market can analyze many treating actives without costly configuration changes that were previously required. A method was developed and validated for the determination of DCOI in oil-borne treating solutions and treated wood. Data were developed using two different commercially available analyzers: The Hitachi Lab-X5000 and the Rigaku NEXQC. The data show that the method can be used for both treating quality control as well as determination of chemical treatment in unknown samples.

Key Words: DCOI, X-Ray fluorescence, industrial wood preservation, oil-borne, DCOI-A, HS-A

INTRODUCTION

X-Ray Fluorescence (XRF) is a relatively fast and accurate way to determine elemental composition of a sample. With minimal sample preparation, the concentration of elements of interest can be determined non-destructively in minutes. Prior to the work covered in several 1954 patents, crystals were used to reflect the radiation which was detected by a Geiger counter[2]. There were many drawbacks to these designs such as cost, high detection limits and limitations in matching crystal materials and elements of interest. The technique as it is used today comprises a source which excites electrons near the nucleus of the atoms and produces K-band X-Rays. Designs from the 1950's through the early 2000's paired a source, filter and detector that was optimized to a particular element or group of elements to be employed in a single application of interest. The radiation was directly detected using proportional counters and compared against known samples[1]. These designs were robust and provided reproducible results, however configured instruments were not adaptable to changes in actives or shifts in industry. The last decade has seen the introduction of X-Ray technology that allows for the analysis of the elements Na-U without the costly configuration changes that were previously required.

4,5-Dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI) in a waterborne carrier has been used as a primary active biocide in the US residential treated wood market since 2008. Analysis of this product has historically been completed using high-performance liquid chromatography (HPLC) (AWPA Standard A30). Recently the DCOI active was standardized for the treatment of utility poles and cross arms in an HS-A compliant oil-borne carrier. Industrial preservatives for treated wood have historically been analyzed using XRF. Using these newer instrument designs as noted above, users can seamlessly treat and analyze DCOI, PCP, CCA, and CuNap using one instrument. Two manufacturers who have tailored applications for the wood industry are Applied Rigaku Technologies and Hitachi High-Tech Analytical Science America, Inc. Data is provided in this paper that shows that DCOI in treated wood and treating solutions can be quickly and reliably analyzed using either of these XRF technologies.

The ability to analyze wood treated with unknown actives is important when determining what pole remediation procedures are best suited to increase the life expectancy in unmarked poles as well as for determining any end of life dispositions that are available. As DCOI is a candidate for end of life disposal by incineration in a co-gen facility, the operator must have assurance that it is indeed DCOI treatment that is being processed. XRF technologies allow for the rapid determination of treatment actives and differentiation. Analysis of the copper content can discern copper vs non-copper containing while analysis of the S:Cl ratio can provide differentiation between DCOI and PCP in the determination of unknown or end-of-life wood samples.

METHODS AND MATERIALS

DCOI has two elemental components, sulfur (S) and chlorine (Cl), that can be easily quantified by XRF. Quantification can be obtained by analysis of Sulfur or a total of the Sulfur and Chlorine areas of the spectra. Due to the prevalence of PCP in the marketplace, the potential for cross contamination, and the possible need to differentiate samples, the analysis within was carried out using only the S response.

Treating solutions were prepared using DCOI in an HS-A solvent, as a model carrier system for this study. These solutions were used to treat 19x19x19mm southern yellow pine (SYP) blocks. The wood and solutions were prepared following method A9-18: "Standard Method for Analysis of Treated Wood and Treating Solutions by X-Ray Spectroscopy"[3] and analyzed following AWPA methods A9-18 and A30-18: "Standard Method for the Determination of 4,5 Dichloro-2-N-octyl-4-isothiazolin-3-one (DCOI) in Wood and Solutions by High Performance Liquid Chromatography (HPLC)."[4] A Perkin Elmer Flexar HPLC equipped with UV detection was utilized for HPLC analysis. For analysis by A9-18 samples were tapped 10 times on the counter to compact the samples prior to analysis on a Rigaku NEXQC configured with an Ag-anode tube and Si PIN-diode detector (optional silicon drift detector (SDD) also available) and a Hitachi Lab-X5000 configured with a Pd tube and SDD. Data obtained from the two methods were compared for agreement. Repeatability data from the analysis were also obtained. Thin film Mylar was used throughout the work due to its current prevalence of use in the wood industry.

RESULTS AND DISCUSSION

Wood Samples

Initial calibration of the XRF for wood sample analysis was carried out using a set of (SYP) wood dust standards treated with DCOI in an HS-A solvent. These samples were analyzed by HPLC and the data were confirmed using treatment uptake calculations. The detector response was found to be linear (0.999 R^2) throughout the expected treatment range (Figure 1).

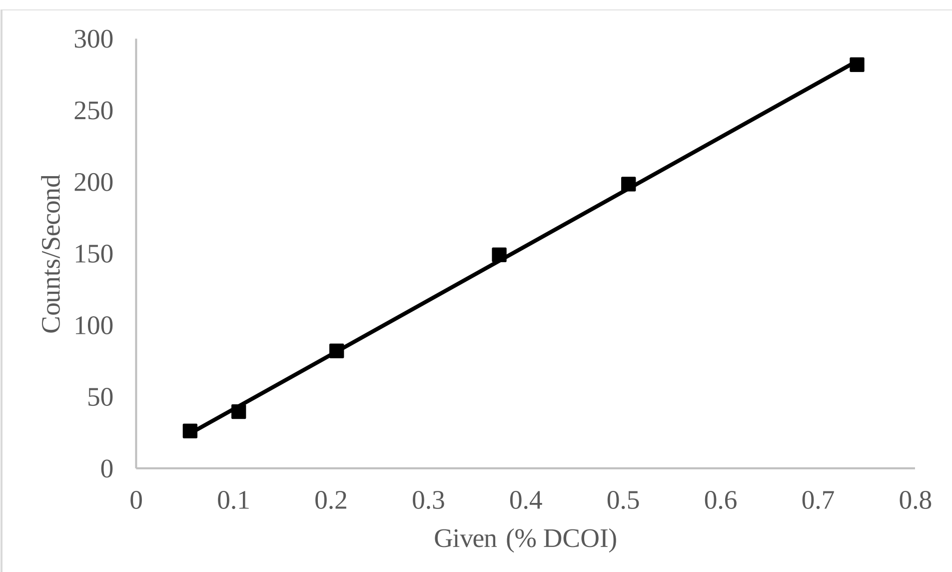

Figure 1: Detector response of standards spanning the expected treatment range vs given values.

While the detector response was higher with a summation of the S and Cl peaks, the standard error of estimate (SEE) and R^2 values of the correlation plot were essentially equivalent (Figure 2). The SEE and R^2 were found to be <0.01% DCOI and >0.999 respectively. Polypropylene film was also tested in place of the Mylar film in assembled XRF sample cups. The film allowed for slightly higher detector counts for the same configuration, but the difference was not seen to greatly impact the results. Ten replicates of 0.3% DCOI provided a precision (%RSD) using Sulfur or the sum of Sulfur and Chlorine of <2.5% and 1.0% respectively.

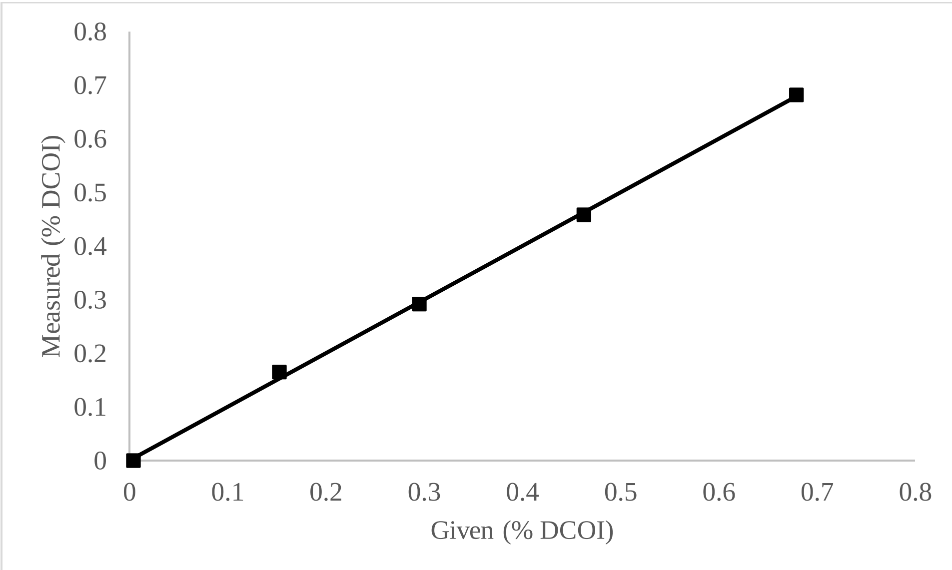

Figure 2: Wood dust standard correlation plot for DCOI-A treated wood.

An overlay of the XRF spectra of several SYP wood dust samples ranging from 0-0.75% DCOI obtained on a silicon drift detector is provided in figure 3. From the spectra, clear differentiation between concentrations can be seen for both elements of interest. This clear differentiation also allows the determination of treatment in unmarked or end of life specimens. The ratio of S to Cl in the analysis of unknown samples provides clear delineation between Penta and DCOI. Values of $\frac{\%\,Sulfur}{\%\,Chlorine}$ for Penta and DCOI were found to be <0.02 and >0.44 respectively for the samples tested.

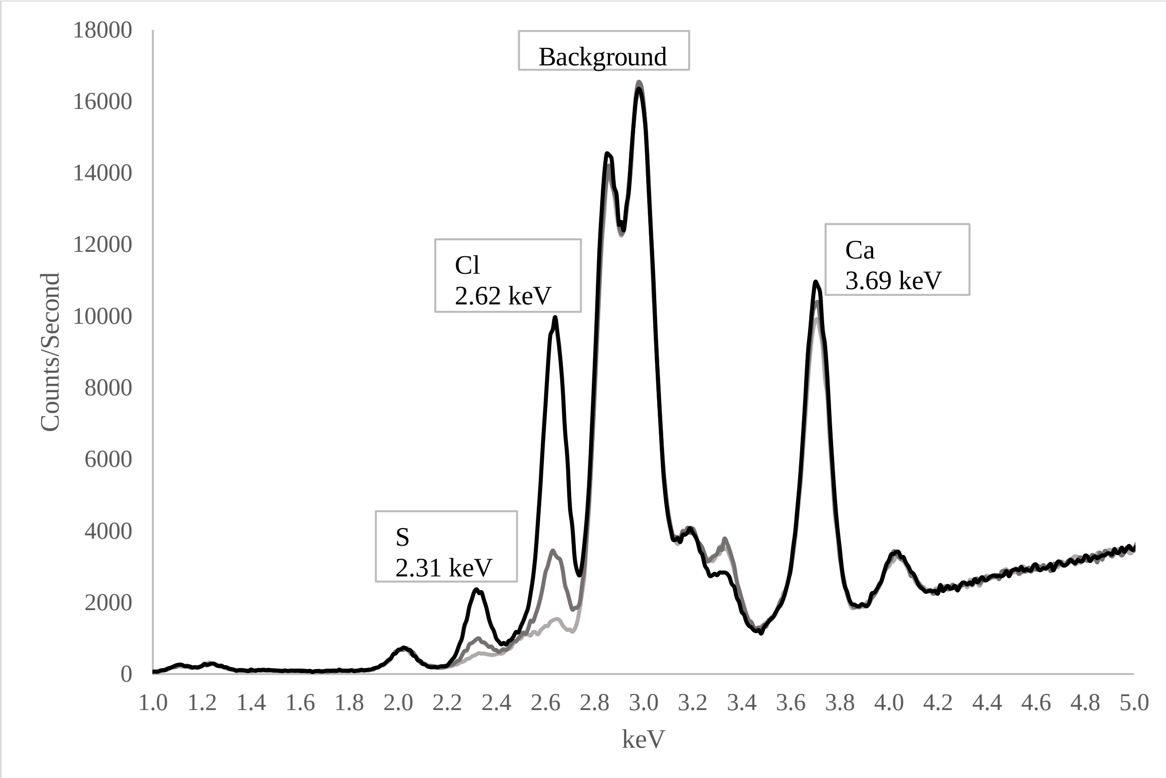

Figure 3: Overlay of spectra from a silicon drift detector for analysis of DCOI-A in wood.

Treating Solution Samples

A set of treating solutions encompassing the range of expected commercial production concentrations using DCOI in an HS-A solvent was also created. All of the standards were characterized by HPLC and confirmed using weight addition calculations. The data was found to be linear with a correlation coefficient of >0.9999 (Figure 4).

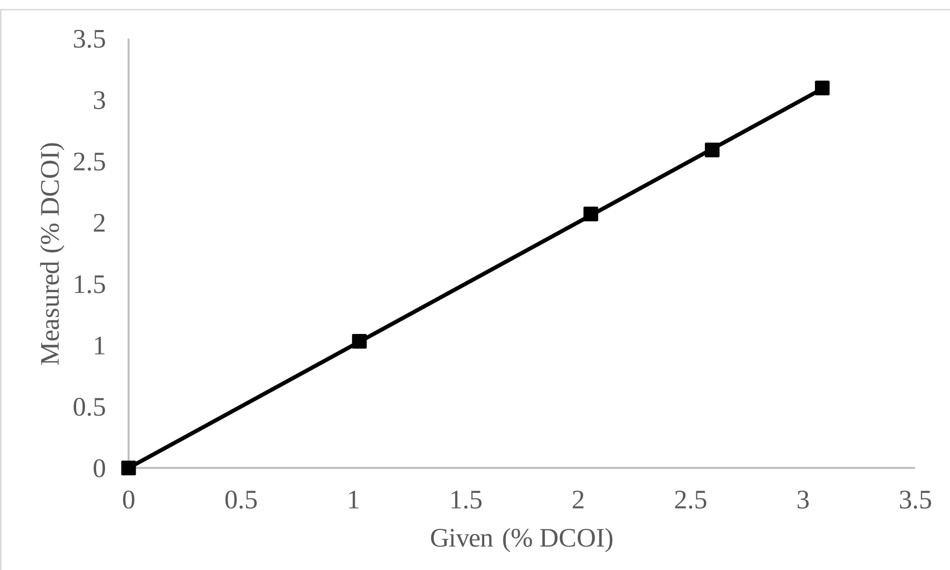

Figure 4: Solution standard correlation plot for DCOI-A treating solutions.

CONCLUSION

XRF analysis is a rapid, non-destructive way to determine the active content of industrial treated wood and oil-borne treating work solutions containing 4,5-Dichloro-2-n-octyl-4-isothiazolin-3-one. Current instrumentation is very versatile and sensitive to a wide range of elements which allows determination of DCOI using one or both of the elements Sulfur and Chlorine. Treatment in unknown or end of life samples can be readily determined using data from the individual elements of interest.

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