

## A114 Elemental Analysis of Unprocessed Cotton by LIBS, LA-ICP-MS, and μ-XRF: A Comparison of Methods

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After attending this presentation, attendees will: gain an insight into the need to verify the source of cotton commodities; learn how provenancing can be accomplished using analytical tools; be shown a comparison between three different analytical methods used in this study; and, better understand the chemometrics approach used for data interpretation and validation of the methods.

This presentation will impact the forensic science community, as well as the trade and commerce community in that the work described provides a means for the elemental analysis of cotton, which can be used for provenancing in forensic and fraud detection applications. Yarn fraud

affects the multi-billion dollar cotton imports industry, resulting in serious consequences for fair competition of U.S. produced goods with fraudulent imported cotton material.

Cotton is the most abundant natural fiber in the world. Many countries are involved in the importation and exportation of this commodity. Because customs documentation can be easily falsified it is a necessity to develop an irrefutable method for corroborating the source of the cotton commodities. Elemental analysis of natural fiber evidence provides a means to increase the discrimination power beyond the physical and morphological examinations normally performed. Cotton exhibits an elemental signature that is characteristic of the attributes from the plant skeleton, nutrients absorbed in the plant, and environmental contributions that can either be absorbed through the plant system or collect on the outer fibers of the cotton boll. Previous work<sup>1</sup> has demonstrated that elemental analysis by laser ablation inductively coupled mass spectrometry (LA-ICP-MS) can provide a means for differentiating between different processed cotton samples. Also reported recently is a correlation between the composition and the geographic origin of unprocessed cotton.

This presentation will impact both the forensic science discipline and the trade and commerce community in that the work described provides a means for the elemental analysis of cotton, which can be used for provenancing in forensic and fraud detection applications. Yarn fraud affects the multi-billion dollar cotton imports industry, resulting in serious consequences for fair competition of U.S. produced goods with fraudulent imported cotton material. The goal of this work is to more thoroughly evaluate the correlation between growing region and other environmental factors to the elemental composition of the cotton using a larger sample set – incorporating samples from the U.S. and from international origins.

The analytical methods of laser-induced breakdown spectroscopy (LIBS), LA-ICP-MS and micro X-ray fluorescence ( $\mu$ -XRF) were used for comparison of the analytical figures of merit between all three techniques.

LA-ICP-MS is an accepted analytical instrument that is commonly used in forensic laboratories. However, this technique is expensive to purchase and maintain, which can be beyond the budget allotted to some laboratories. LIBS is a less expensive alternative to LA-ICP-MS that offers many advantages including simplicity of instrumentation, the quickness of acquisition, and the ability to provide the user with a spectrum rich in information with no prior knowledge of the sample matrix. In addition, many forensic laboratories are already equipped with  $\mu$ -XRF instrumentation and therefore, this method was also incorporated as a possible technique for elemental analysis of raw cotton.

LA-ICP-MS and LIBS data showed good analytical correlation suggesting that LIBS is a viable alternative for elemental analysis of cotton commodity samples. Grouping trends based on geographic regions were observed using principal component analysis (PCA) and partial least squares – discriminant analysis (PLS-DA) for the samples in this study. This study suggests that LIBS could, in the future, prove to be a beneficial tool to associate cotton evidence that has the same source of origin and in the field for prevention of cotton fraud at U.S. ports.

## Reference:

1 J.M. Gallo and J.R. Almirall, Elemental Analysis of Cotton Fiber Evidence using Solution ICP-MS and LA-ICP-MS, *Forensic Sci. Int.*, 2009, 190(1), 52-57.

Cotton, Elemental Analysis, Provenancing

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