B42 Glass Sample Discrimination by Laser Induced Breakdown Spectroscopy (LIBS)

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After attending this presentation, attendees will have learned about the discrimination capability of LIBS for glass samples.

This presentation will impact the forensic community and/or humanity by introducing a new and potentially powerful elemental analysis tool, Laser Induced Breakdown Spectroscopy.

In this presentation results will be reported of a study of Laser Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) for the discrimination of evidentiary glass samples: automobile side mirror glass, automobile headlamp glasses, and brown container glasses.

Forensic glass analysis provides direct comparison of questioned and known glass samples. This research is based on analytical methods previously used. For each glass sample studied, shards from the same glass were analyzed using both LIBS and refractive index (RI) measurements, by GRIM3. All LIBS measurements were made at the National Center for Forensic Science at UCF. All refractive index measurements were made at the South Carolina State Law Enforcement Division (SLED) Columbia, SC. Pairwise comparisons were made of the data for all samples to determine discrimination factors for each technique.

The Ocean Optics LIBS2000+ system was used for data acquisition; it utilizes a Nd-YAG laser that emits at a fundamental wavelength of 1064 nm (Big Sky, model CFR200, 98 mJ/pulse, pulse width 7 ns). For the LIBS measurements, glass samples were analyzed by comparing five spectra each comprised of an average of 10 single- shot spectra (detector delay of 2 Os) in one spot. Argon gas was constantly flowing in the LIBS sample chamber during sampling. This data was used to select emission wavelengths that were shown to have reproducible intensities for repetitive scans in each individual set of glass samples. These emission lines were in turn used to calculate intensity ratios, a method that eliminates errors in data analysis that can be caused by laser shot-to-st fluctuations and differences between the seven (7) different spectrometers. Ten intensity ratios were ultimately selected based on their ability to discriminate between glass samples.

Previous research has shown that it is possible to discriminate automobile samples based on their isotopic abundance using LA-ICP- MS plus the RI. The technique utilized in this study involved analyzing glass samples with a combination of LIBS elemental emission ratios and refractive index values. Each data set was evaluated by constructing a set of elemental emission ratios and determining the average and variance of those ratios over a set of replicate measurements. The emission ratios were evaluated by ANOVA to determine a set of ratios having significant F-statistic values to allow for discrimination between the glass samples comprising the set. The emission ratios were further analyzed by constructing a Pearson product moment correlation coefficient matrix and selecting those ratios displaying the lowest correlations, thereby maximizing the information content in the data set. The selected set of ratios were used to make pairwise comparison of the glass samples by means of a Tukey Honestly Significant Difference ANOVA post-hoc test to maintain prescribed data-wide significance levels at 0.10 and 0.01.

Glass samples incorporated in this study included sets of, fifteen (15) automobile headlamps samples (105 pair-wise comparisons), thirty-four (34) automobile side mirror glass (561 pair-wise comparisons), and fifteen (15) brown container glass (105 pair-wise comparisons). Discrimination capability was measured for both LIBS and LIBS+RI at 90% and 99% confidence intervals (CI). LIBS+RI gave greater than 90% discrimination (99% CI) in all data sets other than the side-mirror glass, and provided 100% discrimination of the automobile headlamp and brown container glasses (99% CI). The discrimination power of LIBS+RI was less for the side-mirror data set (79% discrimination at the 90% CI). LIBS discrimination of glass samples without the combined use of RI data was in the 53-100% range. Additional data analysis methodologies are being reviewed as alternative discrimination techniques.

LIBS, Trace Glass, Elemental Analysis

 ** Presenting Author*