

## **B19** Increased Objectivity of Shooting Distance Determinations by Spectrochemical Mapping

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**Learning Overview:** The goal of this presentation is to show how the superior selectivity and sensitivity of Laser-Induced Breakdown Spectroscopy (LIBS) analysis, compared to color methods, will offer more reliable investigative information and more defensible results in court when a firearm is involved in a crime.

**Impact on the Forensic Science Community:** This presentation will impact the forensic science community using Laser-Induced Breakdown Spectroscopy (LIBS) to improve the scientific reliability of the detection and observation of gunshot residues on target materials.

In the most recent data from the Gun Violence Archive, there have been a total of 32,483 firearm related incidents in 2018, thus far. In the investigation of these crimes, the detection of gunshot residue (GSR) for firing distance estimations is crucial to support or reject the hypothesis of a suicide, a homicide, or an accidental shooting.

Currently, the most common method for estimating the muzzle-to-target distance is by colorimetric assays that react when lead (sodium rhodizonate test) or nitrites (Modified Griess test) are present. While these colorimetric tests are widely used in forensic laboratories, there have significant drawbacks like poor selectivity and limited scope. False positives can arise from common contaminants like dirt and oil, and dark colored or blood-stained clothing can significantly reduce the efficiency of these color analyses. As a result, there is a need to modernize and enhance the scientific validity of these examinations.

Laser-Induced Breakdown Spectroscopy (LIBS) is proposed as a more objective analytical tool that can generate spectrochemical images of the distribution of multiple GSR elements around the bullet hole. The central hypothesis of this research is that the use of LIBS will improve the scientific reliability of the detection and observation of gunshot residues on target materials. This assumption is based on the ability for LIBS to simultaneously detect multiple elements at low parts per million (ppm) levels and to have the potential to measure numerous emission lines per analyte of interest.

A calibration curve was created using 20 grey clothing samples (100% cotton) and 15 patterned clothing samples (100% cotton) shot with a 9 mm pistol at known distances (contact, 6 inches, 12 inches, 24 inches and 36 inches). These samples were used as a training set for statistical analysis. Additionally, 25 clothing samples, varying in color (grey, orange, maroon, navy, black, patterned), were shot at distances unknown to the analyst, thus blinding the test samples. A 100um laser beam was fired into the sample and radially moved 13 cm away from the entrance hole. The sample holder was automatically moved at a speed of 0.3 mm per second while acquiring a spectral signal in real time. Integration of the peaks was performed on elements of interest, including Sb (259.8 nm and 252.8nm), Pb (405.8 nm and 368.3nm), and Ba (493.4nm and 454.4nm). The elemental intensities of the signals and their relative spatial location allowed for the creation of 3D chemical images. Principal Component Analysis (PCA) and Leave-One-Out cross-validated Linear Discriminant Analysis (LDA) were used for prediction of unknown distances. As the LIBS method is practically non-destructive of the sample, the clothing items were then subjected to chemical color tests for comparison purposes.

While dark-colored or patterned backgrounds masked the soot pattern, making visual and color examinations challenging and some colored fabrics (black and navy) interfered with the Griess reagents and the amount of Pb deposited after firing some of the ammunition was below the sodium rhodizonate's limit of detection ( $1000 \pm 20$  ng), LIBS data offered improved selectivity, allowing the detection of multiple ionic and atomic emission lines per element with no interference from the fabric composition. LIBS limits of detection were superior to the rhodizonate test ( $20 \pm 4$ ng) with the added advantage of offering a more comprehensive identification of elements associated with GSR, both leaded and lead-free ammunition.

Color tests lead to misclassification of 3 out of 25 shooting distances (12%), while the LIBS method correctly classified the distance range of the unknown testing samples by Linear Discriminant Analysis.

This study is anticipated to aid in crime scene reconstruction when a firearm is involved in a criminal event. The superior selectivity and sensitivity of LIBS analysis in this application, compared to color methods, will offer more reliable investigative information and more defensible results in court.

## LIBS, Gunshot Residue (GSR), Distance Determination

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