

## B102 The Application of Laser-Based Methods for the Analysis of Gunshot Residue (GSR) Originating From Modern Ammunition

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Learning Overview: After attending this presentation, attendees will understand the creation and characterization of inorganic GSR standards as well as the capabilities of Laser-Induced Breakdown Spectroscopy (LIBS) and Laser Ablation-Inductively Coupled Plasma/Mass Spectrometry (LA-ICP/MS) to offer rapid and reliable screening methods for shooter and non-shooter hand samples.

**Impact on the Forensic Science Community:** This presentation will impact the forensic science community by providing attendees with two laserbased techniques that can be used for GSR hand analysis and expanded to other sample types such as facial areas, hair, vehicle interiors, clothing, and glass to enhance laboratory workflow and informative value.

GSR is a common form of trace evidence submitted to crime laboratories in firearm-related crimes that pose a risk to public safety. Even though investigation of firearm-related crimes requires fast leads, a GSR report from a crime laboratory can take weeks or months to produce, which can impede fast decision making and delay arrest of suspected individuals. Therefore, the field may benefit from the development of new methods for rapid screening of GSR evidence to provide law enforcement and the judicial system with complementary tools to improve case management.

A research group has developed laser-based methods, including LIBS and LA-ICP/MS, to address this need for rapid screening of GSR samples. The two promising methods were applied to tailor-made Inorganic GSR (IGSR) standards and to residues collected from hand samples from both non-shooters (background population) and known shooters using modern ammunition (leaded and lead-free) and different firearms. The central hypothesis of this research is that the use of LIBS and LA-ICP/MS will provide complimentary analytical techniques for detecting elemental compositions of IGSR standards, as well as rapid screening and classification of shooter samples based on the presence or absence of IGSR elemental profiles from modern ammunitions.

IGSR suspensions created using eight different primer types, four leaded (Remington<sup>®</sup>, Sellier & Bellot<sup>®</sup>, TulAmmo<sup>®</sup>, and Winchester<sup>®</sup>) and four non-leaded (CCI<sup>®</sup>, Fiocchi<sup>®</sup>, Inceptor<sup>®</sup>, and Syntech<sup>®</sup>), were analyzed by both instrumentations to establish baseline compositions. Also, 64 known-shooter samples (37 leaded and 27 non-leaded), and 60 non-shooter samples were analyzed by both LIBS and LA-ICP/MS to test the methods' abilities to correctly identify IGSR from shooter samples and evaluate the thresholds of the elemental profiles on background samples. The LIBS method completed the screening in one-and-one-half minutes per stub, while the LA-ICP/MS method was nine minutes. Therefore, LIBS was used to process all stubs collected from hands, while LA-ICP-/ was performed on shooter and non-shooter stubs previously positive by LIBS. Both methods incorporated spatial information by collecting 25 individual spectrum from a region of 100µm in diameter. For leaded ammunition, emission lines for Pb (405.8nm, 368.3nm) Ba (455.4nm, 493.4nm), and Sb (252.8nm, 259.8nm) were monitored during LIBS analysis while isotopes of lead (<sup>208</sup>Pb, <sup>206</sup>Pb) , barium (<sup>138</sup>Ba, <sup>137</sup>Ba), and antimony (<sup>121</sup>Pb, <sup>123</sup>Pb) were monitored for LA-ICP/MS. A more extensive elemental list was included for non-leaded ammunitions: Bi (293.8nm, 472.2nm), Cu (324.7nm, 327.4nm), Ti (334.9nm, 376.1nm), Zn (334.5nm, 328.2nm), K (766.4nm,769.9nm) for LIBS, and bismuth (<sup>209</sup>Bi), copper (<sup>65</sup>Cu, <sup>63</sup>Cu), titanium (<sup>48</sup>Ti, <sup>49</sup>Ti), zinc (<sup>64</sup>Zn, <sup>66</sup>Zn), and potassium (<sup>39</sup>K, <sup>41</sup>K) for LA-ICP/MS.

The methods identified the elemental composition in all IGSR suspension samples, while LA-ICP/MS provided higher sensitivity and selectivity and consistently had more positive spots in each pattern. The resulting baseline compositions were: Remington<sup>®</sup> (Pb, Ba, Sb), TulAmmo<sup>®</sup> (Pb, Sb), Sellier & Bellot<sup>®</sup> (Pb, Ba, Sb), Winchester<sup>®</sup> (Pb, Ba, Sb), Fiocchi<sup>®</sup> (Bi, Cu, K), Syntech<sup>®</sup> (Bi, Cu), Inceptor<sup>®</sup> (Cu, Ti, Zn), and CCI<sup>®</sup> (Ba). A critical threshold of the mean plus three times the standard deviation of S/N ratios in the background population was used for determining the presence or absence of elements in shooter samples. Shooter samples were broken down into three different categories of standard shooters (leaded elements), non-leaded shooters (non-leaded elements), and mixed shooters (leaded and non-leaded elements). LA-ICP/MS resulted in true positive rates of 91% for standard shooters and 78% for non-leaded and mixed shooters, while LIBS resulted in true positive rates of 78% for standard shooters and 45% for both non-leaded and mixed shooters.

Laser-based methods applied in this study demonstrate the feasibility of new techniques for the screening of GSR. LA-ICP/MS had greater sensitivity, but LIBS has the advantage of being field applicable due to its portability. Both methods improved analysis time of IGSR and could be expanded to other sample types such as facial areas, hair, vehicle interiors, clothing, and glass to enhance laboratory workflow and informative value. Continued development of rapid techniques could assist in providing fast decision making and probabilistic assessment of the evidence needed during the investigation of firearm-related crimes and interpretation of evidence in court.

## Laser Ablation, Gunshot Residues, Lead-Free Ammunition