B55 The Fusion of Electrochemical and Spectrochemical Data for the Detection of Organic and Inorganic Gunshot Residues (GSR)

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Learning Overview: The goal of this presentation is to demonstrate the combined use of electroanalytical and spectrochemical methods for the detection of firearm discharge residues.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by offering a first-generation screening method that allows on-site analysis with fast detection and high accuracy. The data fusion of the organic (OGSR) and inorganic residues (IGSR) involves both selectivity and sensitivity of the analysis.

Current gunshot residue (GSR) confirmatory methods are either costly and time-consuming (SEM-EDS) or destructive of the sample (LC/MS). The incorporation of a fast and reliable screening test could streamline the current turnaround time in firearm investigations, but such methods are not currently available. In this study, electrochemical (Square Wave Anodic Stripping Voltammetry) and laser-based spectroscopic methods (LIBS) are proposed as screening assays that are quick, selective, and effective. These methods offer superior information by simultaneous detection of organic and inorganic gunshot residues, including a substantial number of elements used in modern ammunition. Moreover, the selected analytical scheme permits subsequent confirmatory analysis (SEM-EDS) on the same sample. LIBS is a rapid chemical analysis technique that uses a pulsed laser for direct qualitative and quantitative analysis of materials with no sample preparation and minimal destruction. LIBS allows high-speed measurements (usually 30-50 seconds for multiple shot analysis) and simultaneous multi-element detection in the low ppm range. On the other hand, electrochemical sensors use electrical stimulation to induce redox reactions of the analyte at the surface of the electrode. Inorganic species (e.g., Pb, Cu, Zn, Sb) and organic species (e.g., nitroaromatics, nitroamines) are electroactive, allowing the detection at low ppb levels. Electrochemical methods offer several advantages including rapid response, low cost, excellent sensitivity, good selectivity, and potential for miniaturization.

Optimization of the LIBS and electrochemical sensors was conducted using response surface Box Behnken experimental designs. Standards were prepared by spiking 50ng to 25 ug of Pb, Ba, Sb, Cu, Ti and Zn over a surface of approximately $1cm^2$ of SEM carbon adhesives. Moreover, in-house GSR particulate standard, characterized by SEM-EDS and ICP/MS methods, were used for the optimization process. The rapid scanning of the laser beam and the voltammetric cycling allows separation and identification of trace elements (Pb, Ba, Sb) and organic compounds (e.g., DNT, NG) in less than five minutes per sample.

From a set of 200 samples, 50 samples from shooters and 50 samples from non- shooters, for up to 4 hand specimens per individual were collected as part of the validation study. Pistols (9 mm and .22) and a revolver (.357 Magnum) were fired at indoor and outdoor shooting ranges. Metrics of performance, such as error rates (false positives and false negatives), specificity, sensitivity, and accuracy, indicate the fusion of LIBS and electrochemical data are a reliable and promising approach to advance current practice. The accuracy of classification of samples into shooter vs. non-shooters groups improved from 75% (EC), and 83% (LIBS) to 98% (EC+LIBS) when the data from both sensors was fused.

Gunshot Residues (GSR), LIBS, Electrochemistry