B101 The Characterization and Detection of Organic and Inorganic Firearm Discharge Residue (FDR) Using High-Performance Liquid Chromatography-Triple Quadrupole (HPLC-QQQ) and Host-Guest Chemistry

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Learning Overview: After attending this presentation, attendees will better understand a novel method developed for the detection of Inorganic Gunshot Residues (IGSR) and Organic Gunshot Residues (OGSR) by LC-QQQ and how its use in forensic laboratories could enhance interpretation of GSR evidence.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by contributing toward the enhancement of the evidentiary value of FDR by providing dual detection of IGSR and OGSR, as well as assisting in the understanding of metal-ligand interactions for other types of applications (e.g., environmental extractions, drug delivery, and organometallics).

FDR or GSR contains both organic compounds (OGSR) and inorganic particulates (IGSR) originating from the powder and primer, respectively. When fired, the heat of the ignition burns the powder and propels a bullet or pellets forward. After the projectile leaves the barrel, a plume of burned and unburnt particulates and powder are spread into the surrounding environment and attach to nearby persons and objects. The current standard practice for GSR analysis relies on the identification of particle morphology and elemental composition of IGSR (American Society for Testing and Materials [ASTM] E1588-17). Nonetheless, there is still a need to complement the examination of IGSR by detecting organic residues' markers. Advances in multiple analytical techniques allow for the detection of OGSR in the ppm and ppb range and IGSR in the ppb to ppt range using Liquid Chromatography/Mass Spectrometry (LC/MS), Gas Chromatography/Mass Spectrometry (GC/MS), and Inductively Coupled Plasma/Mass Spectrometry (ICP/MS). The goal of this project was to perform a simplified confirmatory analysis of both IGSR and OGSR components using the same sample, the same column setup, on one instrument, via an HPLC-QQQ.

In this work, 11 analytes were under investigation: barium (Ba), lead (Pb), antimony (Sb), zinc (Zn), copper (Cu), N-nitrosodiphenylamine (N-NDPA), 4-nitrodiphenylamine (4-NDPA), 2-Nitrodiphenylamine (2-NDPA), Diphenylamine (DPA), Ethyl Centralite (EC), and Methyl Centralite (MC). To be analyzed by QQQ, the inorganic constituents must interact with larger, transporter molecules to traverse the columns toward the detector, whereas the organic molecules require no modification for characterization. The proposed idea includes two different types of binding agents, a cavitand (crown ether species) and a chelating agent (tartaric acid). A pre-column/column setup was used, consisting of a Polymeric Reversed-Phase (PRP) guard column with a trimethylammonium functional group for the tartaric acid and a Pentafluorophenyl (PFP) column for the separation and retention of crown ether complexes and organic constituents. Multiple Reaction Monitoring (MRM) methodology of HPLC-QQQ analytes was used for confirmation of isotope ratios and patterns for these analytes.

Furthermore, to corroborate the accuracy of the technique in characterizing and identifying Metal-Ligand (M-L) complexes, molecular modeling and High-Resolution Mass Spectrometry (HRMS) techniques such as Orbitrap™ were implemented. This work will demonstrate the extraction of multiple species from a single hand swab and address the efficiency of crown ether and tartaric acid complexation with the metals and species formed after the firing event. The validation of the proposed method includes analysis of standard solutions and a set of 50 blind samples collected from the hands of individuals who fired a gun and from those who had not handled a gun. Selectivity, sensitivity, and error rates are reported for the blind set. Limits of detection in the order of 1ppb to 10ppb and limits of quantitation between 3ppb to 30ppb were observed for all analytes of interest, with intra-day and inter-day precision better than 5% Relative Standard Deviation (RSD).

Gunshot Residue (GSR), Simultaneous Detection Technique, HPLC-QQQ