B153 An Elemental Characterization of Firearms Discharge Residue Using Complexing Agents and Triple Quadrupole Mass Spectrometry (QQQ MS)

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After attending this presentation, attendees will better understand a new analytical approach to detecting metal cations from firearms discharge residue using an instrument found in many forensic toxicology laboratories

This presentation will impact the forensic science community by offering attendees a new method to screen for and identify elements associated with Gunshot Residue (GSR).

Several methods have been published reporting on the analysis of organics found in Firearms Discharge Residue (FDR) using Liquid Chromatography/Mass Spectrometry (LC/MS). The mass spectrometers used include Time-Of-Flight (TOF), quadrupole Time-Of-Flight (qTOF), and Triple quadrupole (QqQ) designs. For LC/MS analysis, a substrate such as a hand swab is typically extracted, concentrated, and introduced into the chromatographic system and analytes such as Diphenylamine (DPA), ethyl and methyl centralites, dinitrotoluenes, and other diphenylamines are detected. This capability has the potential to increase the utility of FDR analysis in that current methods using Scanning Electron Microscopy/Energy-Dispersive X-Ray Spectroscopy (SEM/EDS) target the inorganic particulate residues from the primer. Even better would be a procedure that allows for detection of the inorganic and organic constituents of FDR from a single sample. The goal of this project was to demonstrate a novel method of detecting the key elemental constituents of FDR using complexing agents and direct infusion sample introduction using a QqQ instrument. This successful demonstration opens the doors to further development of method in which the organic and inorganic constituents of FDR can be characterized from a single sample.

Crown ethers are macrocyclic complexing agents that bind with +1 and +2 cations. For this project, 15:5 crown ether was chosen because its cavity size is amenable for binding known GSR metals (Pb, Ba, Sb, Cu). These crown ether metal complexes were created independently in methanolic solution and were analyzed using Electrospray Ionization (ESI) -QqQ via direct infusion, positive mode. The parent ions in all cases were in the form of M-L-NO3 (cation-ligand (15-crown-5)) and nitrate ion. Detection limits were established (ppm range in solution corresponding to ~ µg total solid) and Multiple Reaction Monitoring (MRM) transitions optimized such that the parent ion yielded the corresponded element as the transition product. This allows for detection of isotopes of the elements that occur at a natural abundance of ~ 5% or more via M-L-NO3 à M. For example, the metal complexes in which ^{208}Pb, ^{207}Pb, ^{206}Pb, and ^{204}Pb were all observed with MRM analysis, detecting all but ^{204}Pb, which has a natural abundance of <5%. Semi-quantitative results were obtained using an internal cesium spike. This element is monoisotopic and not expected to be detected in typical GSR samples. Antimony (Sb) proved to be the most challenging to detect, either due to low concentrations in sampled residues, poor initial dissolution, poor binding efficiency, or some combination of factors. This presentation will detail experimental methods, figures of merit, and the results from authentic shooting sampling events in which lead, barium, and copper were easily and routinely detected.

Firearms Discharge Residue, Complexing Reagents, Mass Spectrometry