B71 Flow Injection Analysis-Triple Quadrupole (FIA-QQQ) Characterization of Organic and Inorganic Constituents of Firearms Discharge Residue (FDR) Using a Single Injection: The Potential for Rapid Screening of FDR

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After attending this presentation, attendees will be familiar with a GSR screening method using FIA-QQQ.

This presentation will impact the forensic science community by demonstrating a novel and simple screening protocol for FDR that works on an instrument found in many, if not most, forensic laboratories.

One of the intrinsic limitations to the forensic characterization of Gunshot Residues (GSR) is the lack of a quick and reliable screening test. Color tests have been used in the past on skin swabs, but most focus on nitrites and nitrates, which are nearly ubiquitous in the environment and thus of limited value for screening. Other methods used in studies, such as distance determinations, are not amenable to skin sampling or skin swabs. An ideal method would be designed to work with skin samples collected in the same or similar manner as stubs currently collected for traditional Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (SEM/EDS) characterization using the American Society for Testing and Materials (ASTM) 1588 methodology. In addition, such a method would have to be non- or minimally destructive to insure that subsequent confirmation analysis could be conducted without limitations. This presentation will present one option that is based on stubs, skin sampling, flow injection analysis, and mass spectrometry. The methodology is capable of detecting elemental and organic constituents (diphenylamine, ethyl centralite, and 2,4-dinitrotoluene), as well as lead, barium, antimony, and copper from a single extraction and in the same injection. The method presented here utilized QQQ mass spectrometry and Electrospray Ionization (ESI), but the approach could be adapted to any ESI-MS system. With FIA, no chromatography is needed.

For this project, typical SEM collection stubs were covered with a tacky adhesive-free pad used to mount posters. In a forensic setting, this stub sample would be collected using the same dabbing method used for GSR. The GSR stub would be collected first to insure no compromise. The sticky surface of the second stub collects remaining traces of both organic and inorganic residues. The pad is transferred to a plastic tube for extraction in dilute (~ 0.4%) nitric acid/water/methanol with sonication and mild heating. An equal volume of a complexing agent (15-crown-5-ether) at 200ppm is added to complex metal cations, such as Pb^{2+} and Ba^{2+}. The solution is centrifuged before injection using FIA. The QQQ detection is based on transitions (Multiple Reaction Monitoring (MRMs)) focusing on precursor ions and collision by-products. For example, diphenylamine forms an MH+ ion with a mass of 169.9m/z; collisions result in the formation of ions with m/z values of 92.6 and 65.4. To detect metal ions, the precursor ion is a complex between the metal, the ligand (crown ether), and nitrate ion. The crown ether did not interfere with any of the organic constituents. Samples from two weapons (0.38 revolver and 9mm semiautomatic) were characterized using skin swabs collected from shooters discharging one to five rounds in controlled firing events; lead, copper, and ethyl centralite were the most common constituents detected.

This presentation will present method development and validation data in addition to the results from authentic shooting scenarios. This method shows promise for forensic applications as it uses instrumentation available in

many forensic toxicology sections but avoids the need for chromatographic analysis, reducing the barriers to routine use, given that method validation is simplified.

Firearms Discharge Residue, Flow Injection Analysis, Rapid Screening