A104 The Application of UPLC/MS/MS to the Analysis of Smokeless Powders and Gunshot Residue Samples

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After attending this presentation, attendees will understand the fundamentals of ultra-high performance liquid chromatography coupled with tandem mass spectrometry, the advantages of these separation and detection techniques, and their forensic application to gunshot residue analysis.

This presentation will impact the forensic science community by providing an alternative method that is quick, reliable, and sensitive enough for analyzing GSR samples collected in cases involving firearms. The method can also be used as an investigative tool by law enforcement personnel when trying to identify shooting suspects, particularly in situations where inorganic primer residues are unavailable or missing.

Ultra-high performance liquid chromatography with tandem mass spectrometry (UPLC/MS/MS) is being proposed as an alternative technique for the analysis of gunshot residue (GSR) and smokeless powder samples. When a gun is fired the primer and smokeless powder in the cartridge combust forcing the bullet out of the weapon. A release of vapors and particulates are deposited onto the shooter's hands and clothing. Generally referred to as gunshot residue, these particulates contain a mixture of organic and inorganic compounds that can be collected and analyzed to determine whether or not a person has fired a weapon. However, this research focused on the detection of organic GSR and examining compositional differences between brands and lots of smokeless powder. Identifying differences between powders can be useful when trying to link a suspected shooter to a specific weapon and/or ammunition. Live-fire residue samples were also collected and analyzed to test the usefulness of the method on field samples. It is desired to have a method that is quick, reliable, and sensitive enough for analyzing GSR samples collected in cases involving firearms.

In this project, a previously developed UPLC/MS/MS method was applied to the analysis of smokeless powders and gunshot residue samples. UPLC is a newer technique that offers increased efficiency and separation speeds when compared to traditional HPLC. This is possible because the system can accommodate smaller particle columns and higher backpressures which help to minimize band spreading and decrease analysis times. The method involved the reversed-phase separation of 20 different smokeless powder additives and reaction products on a C18 column. For detection, both parent and daughter ions were monitored by tandem mass spectrometry in order to accurately identify the individual components. Simultaneously, positive and negative ESI was used along with negative APCI in the same run to detect all of the relevant compounds. Optimized analysis times were under eight minutes with a gradient of 10%-73% organic at a flow rate of 0.500mL/min. To confirm the presence of each chemical, several parameters were monitored: retention time, MS time, and specific parent-to-daughter transitions.

For smokeless powder analysis, organic additives including nitroglycerine, diphenylamine, nitrodiphenylamine, and ethyl centralite, were extracted from various smokeless powder samples using methylene chloride. An aliquot was removed from the supernatant following extraction and evaporated to dryness under a stream of nitrogen gas. This extract was then reconstituted in the HPLC eluent. For the live-fire residue samples, the swab used for collection was cut and extracted with acetone in a centrifuge tube. The extract was evaporated to dryness and reconstituted in solvent. Other procedures were also tested in order to obtain higher recoveries of the organic compounds. These results demonstrate that organic GSR can be used as an investigative tool by law enforcement personnel when trying to identify shooting suspects, particularly *in situ*ations where inorganic primer residues are unavailable or missing.

GSR Analysis, Ultra-high Performance Liquid Chromatography, Tandem Mass Spectrometry

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