A85 Method Development for the Rapid Separation and Detection of Organic Gunshot Residue by UPLC/MS

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After attending this presentation, attendees will become familiar with the key principals of ultra-performance liquid chromatography and the advantages of using this newer technique for analyzing gunshot residue.

This presentation will impact the forensic science community by providing new methods to law enforcement personnel for determining whether or not an individual has fired a weapon, which can link the individual to a crime scene, victim, or gun.

Upon firing a gun, a mixture of vapors and particulates are ejected from the weapon and deposited onto the shooter's hands and clothing. These particulates are referred to as gunshot residue (GSR) and the detection of this residue may assist law enforcement personnel in determining whether or not an individual has fired a weapon.

GSR is composed of inorganic and/or organic constituents that arise from the primer, propellant, bullet, and other sources within the gun. For the purpose of this research, we are primarily focusing on the analysis of organic GSR (O-GSR) resulting from smokeless powder by ultra high pressure liquid chromatography (UPLC). UPLC is a newer analytical technique which provides increased resolution and separation speed when compared to traditional HPLC. The advances are due to the smaller particle columns which help to minimize band spreading and the pumping system's ability to accommodate higher backpressures. For detection, a tandem MS was utilized for its sensitivity, selectivity, and fast acquisition speeds. With the tandem MS, both parent and daughter ions can be monitored for more accurate identification of the individual components.

The overall purpose of this project was to develop and optimize methods for the UPLC/MS analysis of organic gunshot residue. In this project, a total of 20 different smokeless powder additives were analyzed. These included diphenylamine, N-nitrosodiphenylamine, 4- nitrosodiphenylamine, 2-nitrodiphenylamine, 4-nitrodiphenylamine, 2,4'-dinitrodiphenylamine, 4,4'-dinitrodiphenylamine, methyl centralite, ethyl centralite, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, nitroglycerin, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 2,3- dinitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, and 3,4- dinitrotoluene. These additives may act as a propellant, stabilizer, plasticizer, flash inhibitor, or as a combination of several of these functions.

The sample preparation process involved first preparing stock solutions of each explosive in organic solvent at 1mg/mL and then combining each one to form a mixture. Working solutions were prepared by diluting aliquots of the solution mixture to the appropriate concentrations using a 50:50 mixture of acetonitrile and water with 2mM ammonium acetate added to promote efficient electrospray ionization. A C8 reverse phase column (100mm length, 2.1µm i.d.) was evaluated for its ability to separate the mixture of 20 standards. In order to optimize the separation, the mobile phase, gradient, and flow rate were examined at various combinations. Simultaneous positive and negative ESI was used along with APCI to detect all relevant compounds. Optimized analysis times were under 12 minutes with a gradient of 10%-80% organic at a flow rate of 0.500mL/min.

A variety of extraction techniques were then examined to permit optimum recovery of real and simulated GSR from several different types of handguns. The resultant method permits simultaneous and sensitive determination of a wide variety of organic compounds present in gunshot residue.

Organic GSR, UPLC, MS

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