B15 Differentiation of Commercial Ammunition Sources of Unburned and Corresponding Burned Smokeless Powders Based on Chemical Composition Using Mass Spectrometry (MS) and Principal Component Analysis (PCA)

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After attending this presentation, attendees will understand the chemical composition differences between unburned and corresponding burned smokeless powders. Attendees will learn how PCA can distinguish commercial ammunitions based on chemical composition.

This presentation will impact the forensic science community by demonstrating the effects of burning on the chemical composition of smokeless powders and the potential of PCA for associating and differentiating powders based on differences in chemical composition.

Smokeless powders are the propellant in firearms. Different organic additives are added to explosive materials to enhance powder performance. Examples are stabilizers including Diphenylamine (DPA) and Ethyl Centralite (EC) and plasticizers including Dibutyl Phthalate (DBP) and Dinitrotoluene (DNT). These organic additives can be analyzed by gas or liquid chromatography coupled to MS. Previous research has shown that differences in abundances of organic additives can distinguish ammunition brands. Masses of fragment ions aid in constituent identification, but targeted Tandem Mass Spectrometry (MS/MS) methods are usually limited by user-defined precursor ions which may preclude detection of novel or unanticipated compounds.

Previous studies investigated changes in powder composition before and after firing. Quantities of Volatile Organic Compounds (VOCs) were analyzed from spent cartridges using headspace extraction methods. Samples were collected at various post-firing time intervals, and VOCs were identified or quantified. No correlation was observed between the quantities of unburned organic additives and VOCs. PCA was only performed on VOCs from fired cartridges, not on corresponding unburned organic compounds. The uncombusted residue within cartridges provides a potential source of organics. As typical collection materials, including swabs, present matrix interferences, a direct solvent extraction from cartridges was reported; however, no comparison to the unburned counterpart was described.

The objectives in this research were two-fold: (1) to investigate differences in organic additives present in a variety of powders, including those more than 15 years old; and, (2) to investigate the composition changes that occur post-firing. A variety of ammunition types and calibers were collected. Five cartridges from each box were selected and unburned powders removed from each. Acetone and dichloromethane were used to extract the organic additives for analysis. Five cartridges from each ammunition type were also fired and collected. A direct solvent extraction was used to recover the burned residue from each cartridge.

All extracts were analyzed by liquid chromatography-high resolution MS. Separated compounds were ionized using Atmospheric Chemical Ionization (APCI) in positive and negative mode with multiplexed non-mass selective Collision-Induced Dissociation (multiplexed-CID) coupled with a time-of-flight mass analyzer for accurate mass data. CID was performed at five collision energies, ranging from 10eV to 80eV, applied between the mass spectrometer ion source and mass analyzer. At each collision energy, fragmentation occurs to different extents. Molecular ions at low collision voltages provide information about the molecular mass of the intact compound. Fragment ions, increasingly prominent at higher collision energies, provide structural information. Structural determination was supported by comparison to relevant standards or published spectra, when available. This non-targeted, comprehensive approach has potential for structural determination of unknown compounds with no available standards.

Chromatograms of each extract were pretreated via background subtraction, retention time alignment, normalization, and scaling. Pretreatment was necessary to minimize contributions of non-sample signals on subsequent data analysis. Using PCA, successful association and discrimination of unburned powders according to the original ammunition was achieved. Notably, powders from different commercial ammunitions contained similar chemical compositions, suggesting the same origin. The first two Principal Components (PC1 and PC2, respectively) accounted for 50% of the data set variance in the data set. Powders from the same ammunition closely clustered, while powders from different ammunition separated in the scores plots. PC1 and PC2 differentiated powders based on differences in abundances of EC and akardite II, respectively. Further differentiation was possible with subsequent PCs influenced by DBP, DPA, and nitroso-DPA.

Chromatograms of burned and unburned powder extracts were compared to assess chemical composition differences. The organic additives in burned powders had reduced abundance, with a depletion of DPA greater than the other additives present. The first three PCs accounted for 47% of the variance, with EC, DPA, and akardite II being most influential. Powders from the same ammunition did not associate as closely due to irreproducibility in the burning process. Powders with considerable chemical differences could be sufficiently discriminated.

Smokeless Powders, LC/MS, PCA