B96   Smokeless Powder Additive Profiles and Compound-Specific Stable Isotope Signatures for Potential Brand Identification and Sample Discrimination

Claire J. Page*, Pennsylvania State University, State College, PA 16801; Ryan Schonert, MPS, VUV Analytics, Cedar Park, TX 78613; Todd Sowers, Pennsylvania State University, State College, PA 16801; Wayne Moorehead, MS, forensicTRACE, Rancho Santa Margarita, CA 92688; Jack Hietpas, PhD, Pennsylvania State University, University Park, PA 16802

Learning Overview: After attending this presentation, attendees will better understand the strengths and limitations of Gas Chromatography/Mass Spectrometry (GC/MS) profiling and isotopic analysis for differentiation, comparison, and potential brand identification of commercially available smokeless powders.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by demonstrating the value of utilizing multiple techniques for the characterization and comparison of smokeless powders that can potentially be recovered from inefficient and/or undetonated Improvised Explosive Devices (IEDs).

Small Arms Propellants (SAP) are readily accessible and cost-effective materials that firearms enthusiasts can acquire for the legitimate assembly of ammunition. Unfortunately, the ease of access to and low cost of these materials is advantageous for their utilization in the construction of IEDs. Typically, the SAP charge is loaded into a metal pipe and sealed with screw-fit end caps. Two recent high-profile domestic terrorist attacks using IEDs (Boston Marathon Bombing and New York/New Jersey attempted bombings) demonstrate their continued usage. Thus, there is a need to develop robust metrics for the characterization of propellants that are used as explosives, as well as for comparisons between exemplar and recovered explosive residues.

The goals of the presented research are to investigate GC/MS additive profiles of SAP and compound-specific stable isotope signatures of SAP for potential brand identification and sample discrimination. One hundred sixty one-pound canisters of SAP were purchased from local firearms stores. The samples represent a wide selection of different distributors (*n*=8) and product brands (*n*=160). For GC/MS additive profiling, aliquots of 250mg for each sample were extracted with 5mL of 3:1 methanol:n-butanol, following the method described by Reardon and MacCrehan.[1] This method was chosen because it preferentially extracts the additives, leaving behind the bulk nitrocellulose. Samples were run using an HP6890 series gas chromatograph equipped with an Agilent® 5973 MSD and an RTX-1 column (30m x 0.25mm ID x 0.25μm). The identified additives were primarily nitroglycerin, ethyl centralite, diphenylamine, and dibutyl phthalate. Of the 110 samples analyzed by GC/MS, 83% were double-base and 17% were single-base powders with 80% of the analyzed powders containing diphenylamine, 45% of the powders containing dibutyl phthalate, and 65% of the powders containing ethyl centralite; 73% of the additive profiles analyzed by GC/MS were the same as at least one other profile. It was noted that many samples that gave the same GC/MS additive profiles could be differentiated by powder granule morphology.

Nitrogen and carbon isotope signatures were measured using isotope ratio mass spectrometry. This was accomplished by loading samples into a Costech 4010 element analyzer. The capsule containing the samples was placed into a heated zone containing chromium and cobalt catalysts along with pure oxygen to convert all of the nitrogen (N_2)and carbon to nitric acid (NO) and carbon dioxide (CO_2). The helium carrier stream carries the N_2, NO, and CO_2 to a reduced copper furnace where the NO species are reduced to N_2. The sample stream then proceeds to a GC column where the N_2 and the CO_2 are chromatographically separated. The separate N_2 and CO_2 peaks are then routed to a ConFlo III interface. The open split in the ConFlo III feeds the MAT 252 MS along with reference peaks of pure N_2 and CO_2. All peaks were integrated and the $\delta^{15}N$ and the $\delta^{13}C$ of the samples calculated relative to the reference peaks in the chromatogram.

The SAP sample isotopic compositions were examined to determine if there were recognizable geographic signatures. SAP manufactured in Canada and Belgium cluster in the most negative $\delta^{15}N$ and the $\delta^{13}C$ space. The samples from Finland tightly cluster with negative $\delta^{13}C$ and positive $\delta^{15}N$, thus allowing for discrimination of these powders. Samples from Sweden cluster in the center of the data set. Samples from the United States and Australia tend to show the least negative $\delta^{13}C$ compositions and the positive $\delta^{15}N$ signatures. This clustering is encouraging but will require a more complete dataset to draw robust conclusions.

The results from this study show there is a need for the fusion of data from different analytical methods for more robust sample differentiation and comparison.

Reference(s):

[1.]   Reardon, M.; MacCrehan, W. Developing a quantitative extraction technique for determining the organic additives in smokeless handgun powder. *J Forensic Sci* 2001:46(4):802-807.

Smokeless Powder, Improvised Explosive Device, Additive Profiling