B95 See the Forest for the Trees: A Non-Targeted Approach to Discerning Exposure to Explosives Using Matrix-Assisted Laser Desorption/Ionization-Mass Spectrometry (MALDI-MS) and the Multivariate Statistical Model Random Forest

Cameron M. Longo, BS, State University of New York at Albany, Albany, NY 12222; Samira Beyramysoltan, PhD, State University of New York at Albany, Albany, NY 12222; Rabi A. Musah, PhD, State University of New York at Albany, Albany, NY 12222*

Learning Overview: After attending this presentation, attendees will have learned about the field of touch chemistry biometrics, how this can be applied to establishing an individual's exposure to explosive materials, some of the challenges associated with this type of analysis, and how these challenges can be overcome using a multivariate statistical analysis-facilitated approach to determine compounds that are diagnostic of exposure to explosives.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by highlighting the benefits of performing MS analysis on latent fingerprint evidence and demonstrate an approach to do so. This presentation will also acquaint attendees with using statistical analysis methods to extract pertinent information from acquired data and use it to establish exposure to a substance when diagnostic ions are not immediately apparent in the mass spectra.

Hypothesis: MALDI-MS can be used with multivariate statistical analysis to extract information about which masses detected in latent fingerprints are diagnostic of exposure to explosives.

Synopsis: Experiments aimed at detecting and imaging of explosive compounds in fingerprints for the purposes of establishing exposure is the subject of this work. This is accomplished through MALDI-MS imaging and the identification of ions that are diagnostic of a particular explosive. For example, for TNT, a prominent ion at nominal *m/z* 226 is detected, corresponding to the $(M-H)^-$ ion. However, for some explosives, intuitively obvious diagnostic ions are not as readily apparent. For example, while RDX produces diagnostic ions by Direct Analysis in Real-Time Mass Spectrometry (DART®-MS), these ions are not observed by MALDI-MS.[1] This could be due to interference from the matrix required to ionize the sample or the differences in ionization mechanisms between the two techniques. Nevertheless, exposure to RDX can still be revealed using statistical analysis of the mass spectral data. By using the entire body of information collected from an MS experiment, instead of simply selecting one or two diagnostic ions, a discrimination model that enables identification of indicative fragment ions can be created. The work presented here will demonstrate that MALDI-MS analysis of latent fingermarks, combined with multivariate statistics, can be used to confirm an individual's exposure to explosives such as RDX.

Methods and Results: Briefly, five volunteers donated fingerprints for MALDI-MS analysis. Control fingerprints were taken prior to exposure, and RDX-laden fingerprints were taken after donors rubbed their forefingers through ~50µL of dilute RDX that had been dried to a residue on a watch glass. The matrix 9-aminoacridine was then applied to the fingerprints, after which they were analyzed by MALDI-MS. A total of 500 spectra were collected from RDX-laden fingerprints. These spectra were used as the basis for training a Random Forest (RF) model using MATLAB®. The RF was performed with two classes: (1) RDX-laden fingerprints; and (2) control prints and background. One-third of the data collected were used for validation of the model. Permutation-based importance of predictive variables was used to extract information about which *m/z* values were important in enabling accurate classification of samples. This model was used to successfully discriminate RDX-laden prints from others, with an accuracy rate of 100%. Additionally, the masses predicted as important for discrimination include nominal *m/z* 102 and 129, which are known RDX fragments whose formation has been studied by both tandem mass spectrometry and density functional theory.[2]

Conclusion: The chemical information stored within a fingerprint could be of great value to investigators, though it generally remains underutilized. This information can be probed with MS imaging techniques and used to provide insight about donor exposure to chemicals of forensic relevance, such as explosives. In cases where diagnostic ions are not known or apparent, multivariate statistics can be used with the MS data acquired to reveal which ions are indicative of exposure.

Reference(s):

1. Sisco E., Dake J., Bridge C. Screening for trace explosives by AccuTOF™-DART®: An in-depth validation study. *Forensic Science International.* 2013;232(1):160-168.
2. Jeilani Y.A., Duncan K.A., Newallo D.S., Thompson, Jr. A.N., Bose N.K. Tandem mass spectrometry and density functional theory of RDX fragmentation pathways: Role of ion–molecule complexes in loss of NO3 and lack of molecular ion peak. *Rapid Communications in Mass Spectrometry.* 2015;29(9):802-810.

Mass Spectrometry, Statistical Analysis, Fingerprints

*Presenting Author