B205 Direct Analysis in Real-Time Mass Spectrometry (DART®-MS) and Atmospheric Solids Analysis Probe/Mass Spectrometry (ASAP/MS) for the Detection and Analysis of Seed-Based Toxins

Edward Sisco, PhD, National Institute of Standards and Technology, Gaithersburg, MD 20899; Natalie Damaso, PhD, Oak Ridge Institute for Science and Education/FBI Laboratory, Woodbridge, VA 22191; Elizabeth Robinson, MS, National Institute of Standards and Technology, Gaithersburg, MD 20899; James M. Robertson, PhD, Reserve Support Unit, Quantico, VA 22135*

Learning Overview: After attending this presentation, attendees will have an understanding of how two ambient ionization MS systems could be used for the analysis of seed-based toxins in pure form or in the presence of the complex seed or seed mash matrices. This type of analysis could be crucial in suspected poisoning cases.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by providing the necessary methods and capabilities for the detection of seed-based toxins in suspected poisoning cases through a rapid analysis that does not require any sample preparation.

Atmospheric Ionization Mass Spectrometry (AIMS) techniques (e.g., Direct Analysis in Real Time Mass Spectroscopy [DART®-MS] and Atmospheric Solid Analysis Probe/Mass Spectrometry [ASAP/MS]) have demonstrated utility for varying applications, such as psychoactive plant drug analysis and plant seed species identifications. These methods have been shown to be significantly faster than conventional methods without the need for sample pre-processing or derivatization steps. In cases in which poisonous plant evidence is to be identified, morphological characteristics are typically used in the initial presumptive identification. However, when there are no morphological characteristics, such as the case of seed mash, techniques such as DART®-MS or ASAP/MS may be helpful to presumptively identify possible poisons associated with the evidence. The chemical information from this type of presumptive analysis would aid toxicologists in deciding which extraction protocol (e.g., organic, acidic, or alkaline) to use for the isolation of the toxin from the mash. This would streamline the process of identification of the toxin present in the evidence.

This work provides the foundation to demonstrate the use of AIMS techniques (namely DART®-MS and ASAP/MS) for chemical analysis of seed-based toxins. In this project, a total of seven different toxins from five different seed species were targeted. Development of optimized methods for analysis required the ability to detect a large range of molecular weights and volatilities, necessitating some modifications from traditional analysis, specifically for DART®-MS. The use of techniques such as Infrared Thermal Desorption (IRTD) DART®-MS were employed to heat the sample to temperatures necessary for analyte desorption. From the optimal methods, instrument limits of detection of sub-nanogram to tens of nanograms was exhibited for DART®-MS, along with single to tens of micrograms per milliliter for ASAP/MS.

Analysis of actual seeds and seed mashes highlighted the rapid and sensitive analysis of these techniques for a presumptive test such as this. Detection of the toxin or toxins in the seeds was readily achievable, in most instances. For DART®-MS, samples were able to be analyzed as either an intact seed, dry seed mash, or extracted seed mash. For ASAP/MS, both the dry seed mash and extracted seed mash were capable of being analyzed, though for both techniques, the use of the extracted mash was superior.

The chemical information produced by these techniques also may allow for species identification. The mass spectral profile produced from all seeds analyzed, which included seeds from the same genus (i.e., *D. inoxia* and *D. stramonium*) and seeds of the same type (i.e., oleander) were compared using linear discriminant analysis. Differentiation of the species based on the chemical signatures was readily achievable in this instance, highlighting the ability to provide more information than just the toxin present. Current work is focusing on additional evaluations of this capability and on the use of random forest analysis to identify the most discriminative peaks for targeting purposes.

The use of AIMS techniques in the detection of seed mashes for the presumptive identification of toxins has not been demonstrated before. However, given the successful results of this work and the increasing usage of AIMS techniques, especially DART®-MS, in forensic laboratories, this offers a unique opportunity to deliver rapid presumptive information to toxicologists and investigators. The ability to also be able to obtain species-specific information using these tools could provide crucial information in these investigations.

Toxins, Mass Spectrometry, Toxicology

*Presenting Author