K37 Variability in Direct Analysis in Real Time-High Resolution Mass Spectrometry (DART®-HRMS) Instrument Parameter Optimization Due to Molecular Identity

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Learning Overview: This presentation will introduce attendees to the importance of the identity of targeted molecules when optimizing DART®-HRMS instrument parameters. This presentation will show attendees that when developing protocols for DART®-HRMS targeted screening, the identity of the target molecule will drastically impact the performance of the instrument. Therefore, it is necessary to optimize DART®-HRMS parameters for specific compounds, rather than whole classes of molecules or evidence samples that other screening methods may target.

Impact on the Forensic Science Community: For DART®-HRMS instrumentation to be operationalized in a crime laboratory, instrumental methods for analysis must be optimized by the crime laboratory facility. This presentation will impact the forensic science community by emphasizing the importance of optimizing DART®-HRMS to specific compounds, which in turn improves the sensitivity of the instrument as a screening tool.

DART®-HRMS instrumentation is rising in popularity in forensic research, due to its vast applications in all forensic disciplines as a robust evidence screening tool. Recent research has shown DART®-HRMS applications in drug chemistry, toxicology, and trace evidence subdisciplines, including sexual assaults, explosives, and fire debris investigations. DART®-HRMS can be used as a faster, more specific, and more sensitive alternative to traditional forensic screening methods (i.e., Enzyme-Linked Immuno-Sorbent Assay (ELISA) and canine detection).

DART®-HRMS analysis is a highly sensitive and specific instrumental technique. Evidence samples can be introduced to the DART® ionization source in any phase of matter. Analyte molecules desorb from the surface of the sample after exposure to a heated metastable gas stream (i.e., excited-state helium). The excited metastables interact with atmospheric air molecules (i.e., water and oxygen), forming atmospheric ions. These ions cause the analyte to undergo soft ionization, resulting in the creation of molecular ions and adducts. Analyte ions are then carried through an HRMS, and the masses of the ions can be reported to four decimal places. Relative isotope abundances can then be used to preliminary identify unknown analytes.

The instrumental parameters used in DART®-HRMS can affect the sensitivity of analysis for semi-quantitative work. Variable instrument parameters include the voltage at the exit grid, desorption temperature, and width of the sample gap, among others. Such instrument parameters can affect the ionization mechanisms at the ionization source by varying the availability and thermochemical energy of both the metastable and analyte species. Molecules that ionize most readily in DART® atmospheric conditions can dominate the resulting mass spectra, reducing the sensitivity in the analysis of other molecules in mixtures.

Optimization of DART®-HRMS parameters will be necessary for any forensic lab attempting to adopt DART®-HRMS instrumentation for casework. The preliminary data in this study notably show that the instrument parameters *must* be optimized for each compound of interest in forensic screening. Five compounds of evidentiary value were analyzed at varied exit grid voltages (50–550V, in positive or negative mode as appropriate). Each compound exhibited different functional groups and thermochemical properties, but were prepared at the same concentrations (ppm). There were no definable trends in the resulting analytical sensitivity as measured by relative standard deviations of the slope of the generated calibration curve. The results lead to the recommendation that any optimization of DART®-HRMS analyses must be performed for each specific molecule of analytical interest, rather than general molecular classes utilized by alternative screening methods.

DART®-HRMS, Forensic Screening, Instrument Optimization